From Defects to Devices: Design Guidelines for High-performance Diamond-based Solar Cells and Single-dopant Diodes

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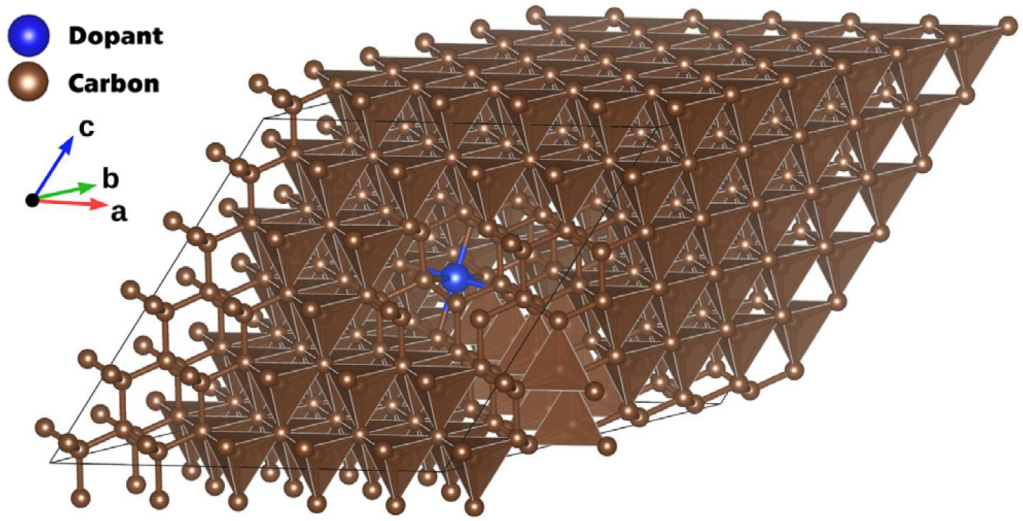






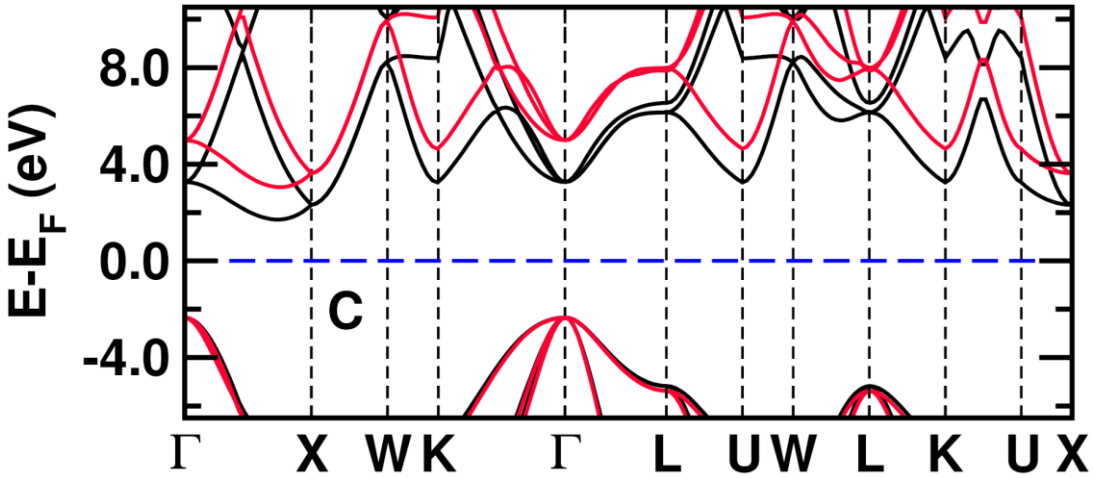
Introduction & Motivation

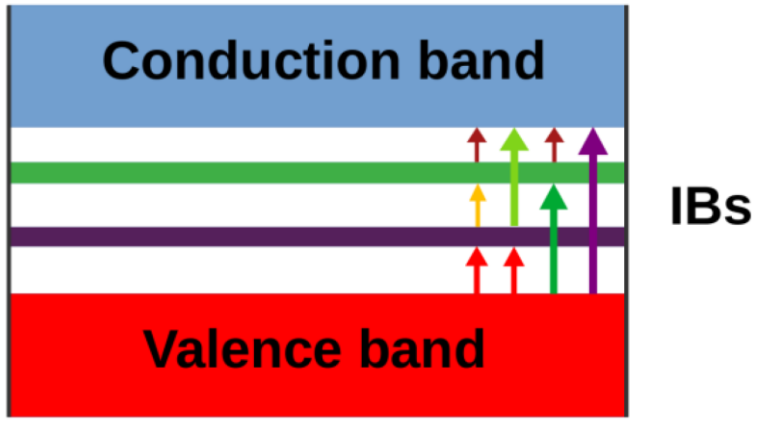
- Properties of **wide band gap semiconductors** often offer many advantages:
  - High breakdown field strength and thermal conductivity ⇒ reduced size and weight of the devices
  - Wide band gap and large carrier mobility ⇒ operation at high temperatures while maintaining low energy losses
- **Diamond**, an ideal candidate for high-power, high-frequency applications, quantum computing, magnetic sensing and many other applications
- Desired properties tailored by band gap tuning (e.g. via **doping**)
  - Adjusting valence and conduction band edges or introducing impurity bands
  - Our previous research focused on complex defects and their potential technological applications



Introduction & Motivation

- Diamond with defects = an attractive platform for energy harvesting such as intermediate-band (IB) photovoltaics:
  - Enables absorption of sub-bandgap photons (IBs as “stepping stones”) ⇒ potentially surpassing the Shockley-Queisser limit of single bandgap solar cells
  - Diamond‘s 5.47 eV band gap can host multiple IBs ⇒ numerous optical transition pathways
- phosphorus-vacancy (PV) complex shows p-type behaviour:
  - Opens pathways for single-dopant PN junctions
  - Simplification of fabrication ⇒ eliminating the need for separate p- and n-type dopants





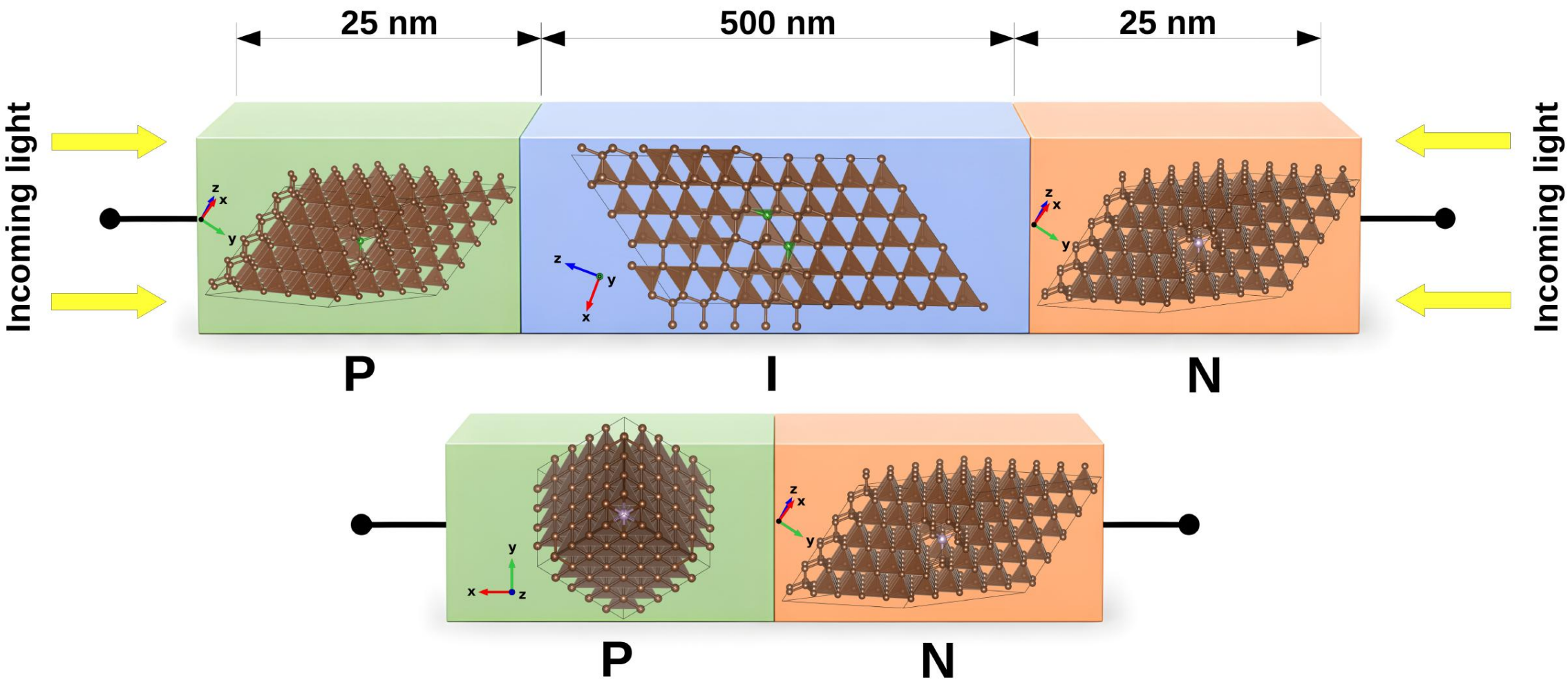
Objectives

- **Objective 1**: Evaluate the potential of deep-level impurities in diamond for IB photovoltaics
- **Objective 2**: Assess the feasibility of a PN junction based on a single dopant species

Proposed architectures: intermediate-band PIN solar cell and single-dopant PN junction

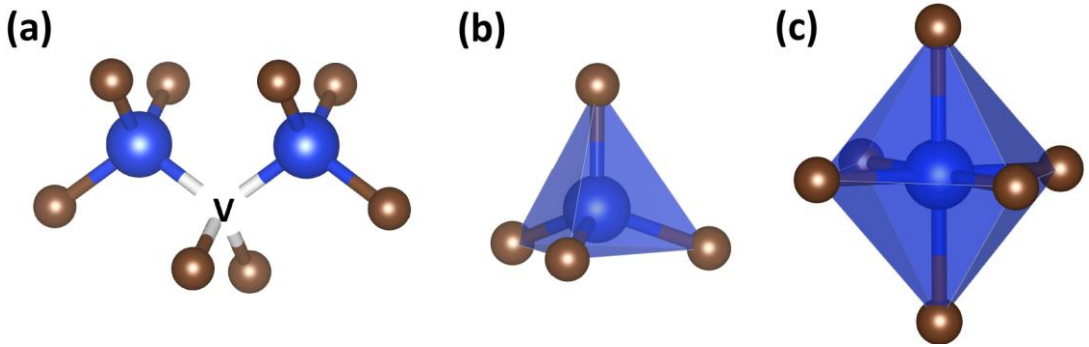
Junction		P	I	N
PIN	**Defect**	Substitutional boron (B)	Boron-vacancy-boron (BVB)	Substitutional phosphorus (P)
	Role	Contact p-type layer	IB absorber layer	Contact n-type layer
PN	**Defect**	Phosphorus-vacancy (PV)	-	Substitutional phosphorus (P)
	Role	p-type layer	-	n-type layer

Proposed Architectures



Methodology

- Ab initio simulations carried out by means of `ABINIT` software package
- Obtaining results as close to the experiments as possible
- Modelling of diamond supercells containing 0.4% defect concentrations:
  - **DFT + GW:** Electronic structure
  - **BSE/IPA:** Optical absorption
  - **Electron-phonon coupling (MRTA):** Charge transport
  - **LBTE:** Thermal transport (`phono3py`)
  - **Poisson solver:** Device electrostatics and junction design



Computational Details

- DFT-GGA, WC functional (Phys. Rev. B **73**, 235116 (2006))
- Monkhorst-Pack mesh: 3x3x3 for 5x5x5 supercells (250 atoms)
  - Denser for optical properties and electron-phonon coupling
- Plane-wave cut-off: 816 eV
- Phonons calculated via DFPT
- Third order force constants for thermal properties calculated via finite displacements
  - 6.25 % defect concentrations and results extrapolated to 0.4 % via Matthiessen‘s rule

Computational Costs

- Cost significantly affected by number of symmetries of the system
- OPEN-33-47 and OPEN-36-46 projects: 3 MCPUh

GW and BSE

- Memory intensive, `gwmem 0` helps
- Often 30-40% node CPU utilisation
- BSE = largest calculation 20 Karolina nodes for 4 days 18 hours

Phonons and E-PH Coupling

- Phonon calculation 97.5%, E-PH 2.5%
- Single core performance essential for DFPT (Barbora)

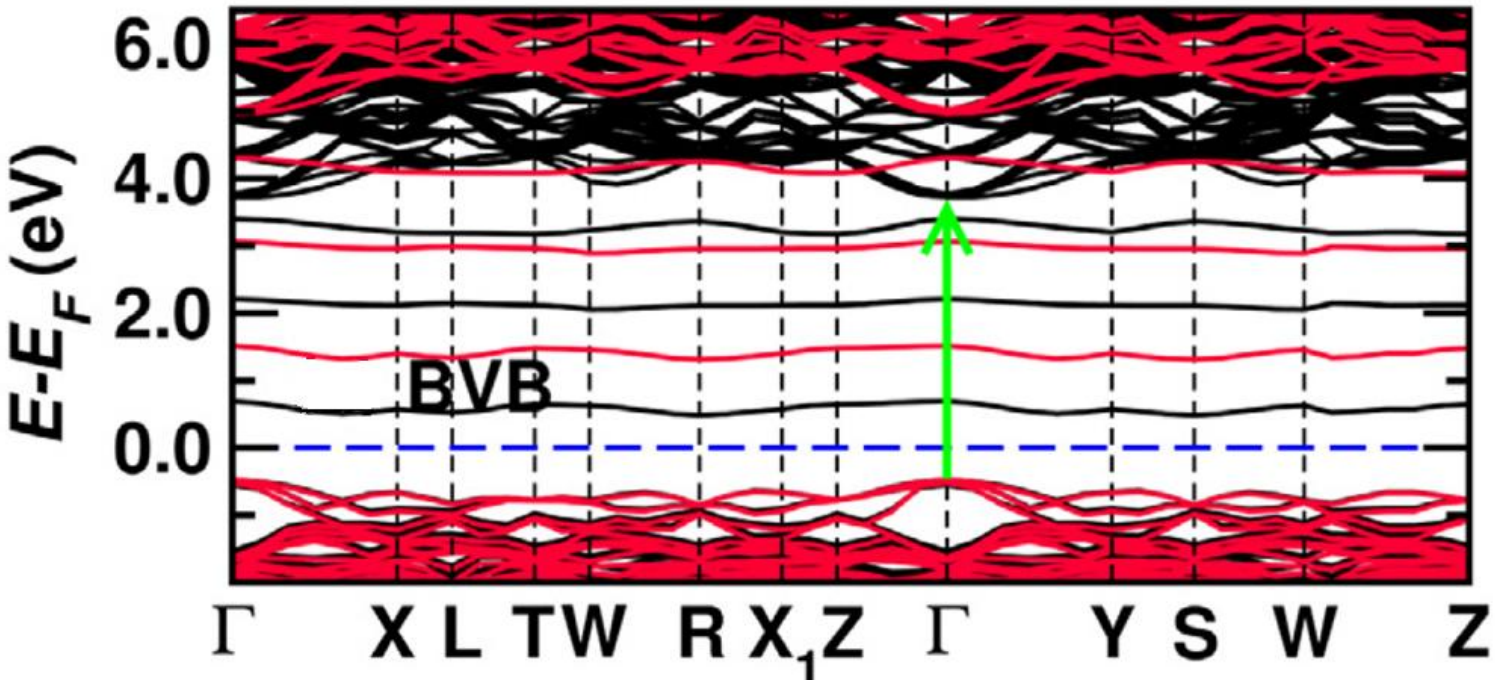
System	GW + BSE (kCPUh)	Phonons + E-PH Coupling (kCPUh)	Thermal Transport (kCPUh)
High symmetry (e.g. P)	30	84.2 + 2.5	30
Low symmetry (BVB)	291 + 298	400 + 10	161

Band Structure of BVB-doped IB Absorber

- Three IBs (IB_1-IB_3) optimally spaced within the diamond band gap

⇒ many optical transition pathways to the CB

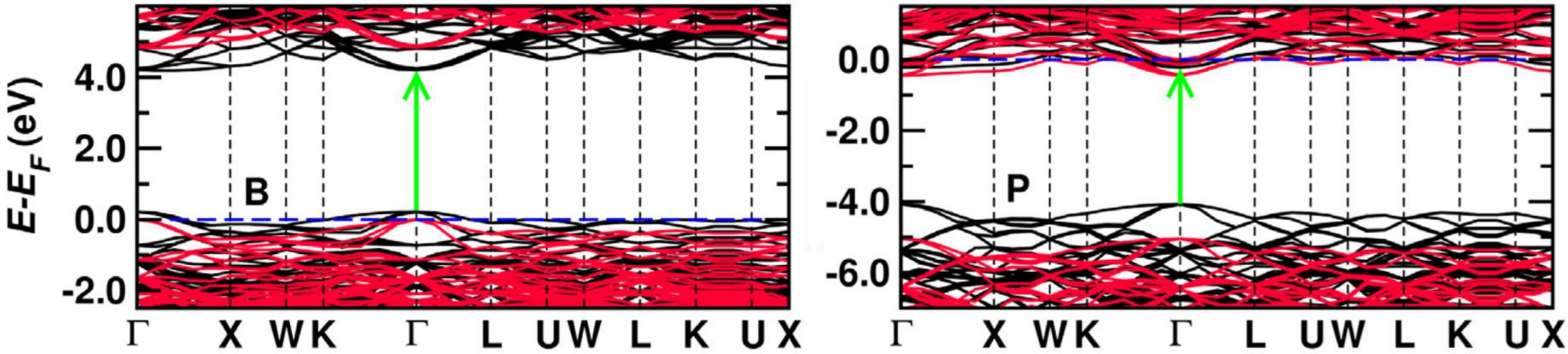
- Unoccupied IBs and Fermi level between VBM and IB_1 ⇒ slight p-type character



Band Structure of Contact Layers

- Boron-doped P-layer and phosphorus-doped N-layer
- Heavy doping yields degenerately doped p-type and n-type regions
- Fermi level shifts into the valence (B) or conduction (P) band

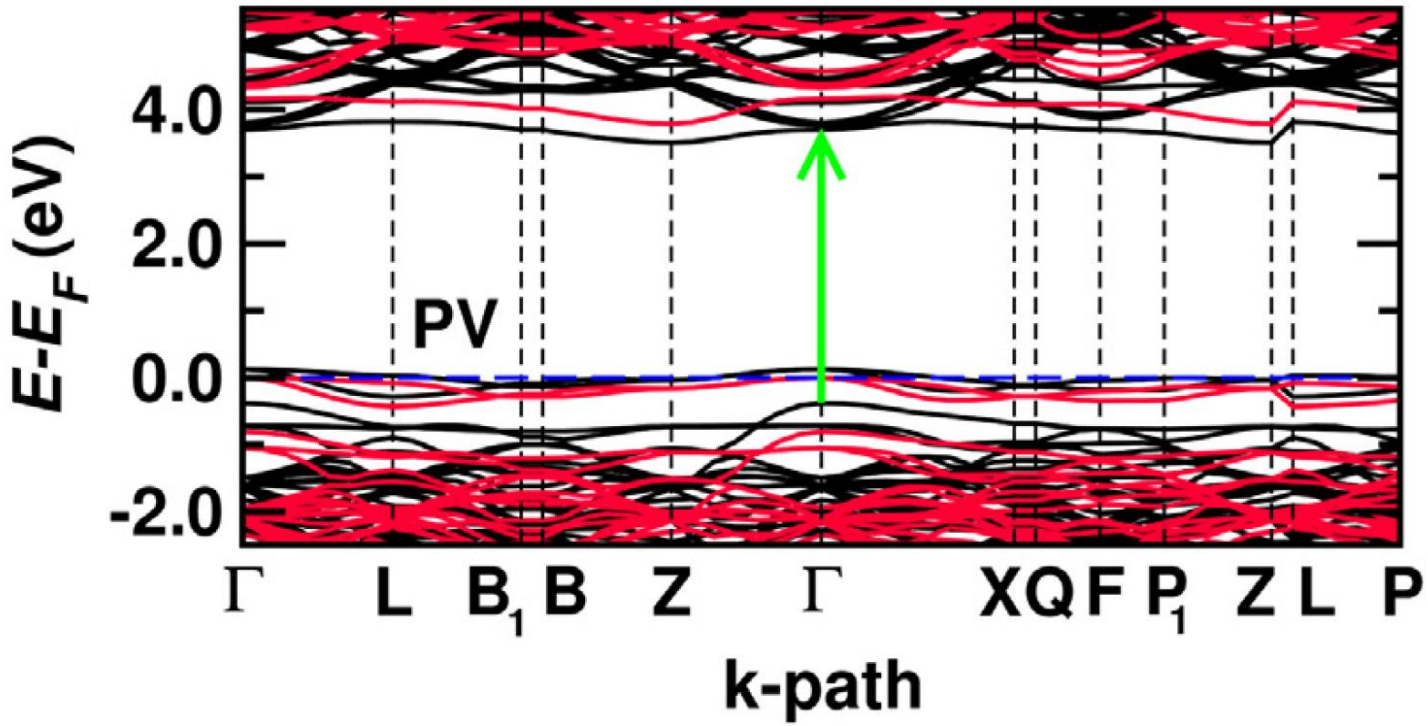
✓Enables metallic-like conductivity while retaining diamond's wide band gap



Band Structure of PV-doped P-layer

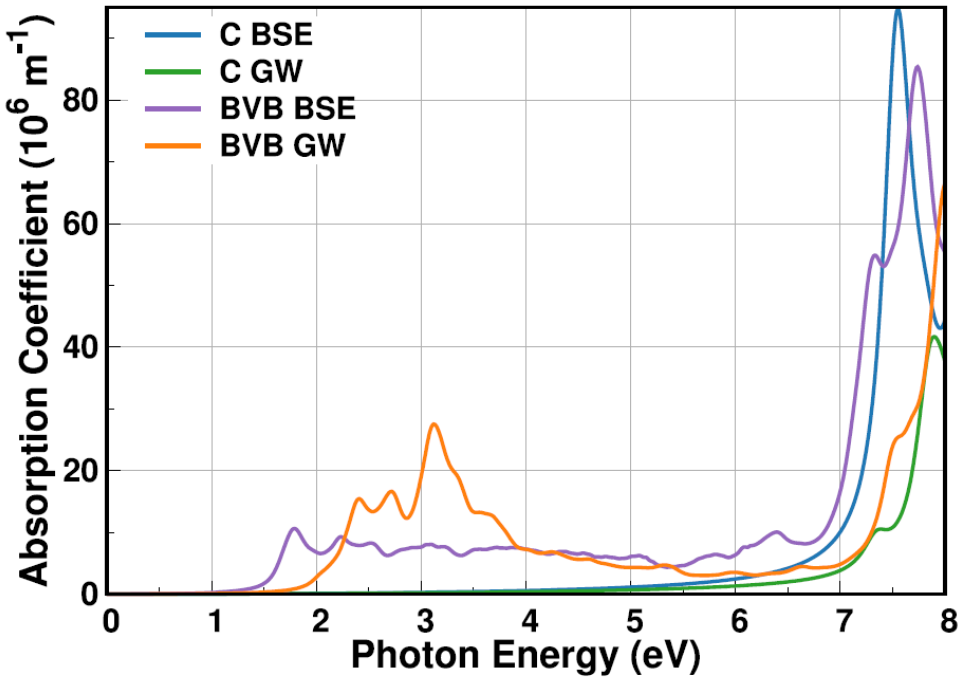
- Broad impurity band 0.37 eV above the VBM ⇒ “standard“ valence band p-type conduction very low at 300 K

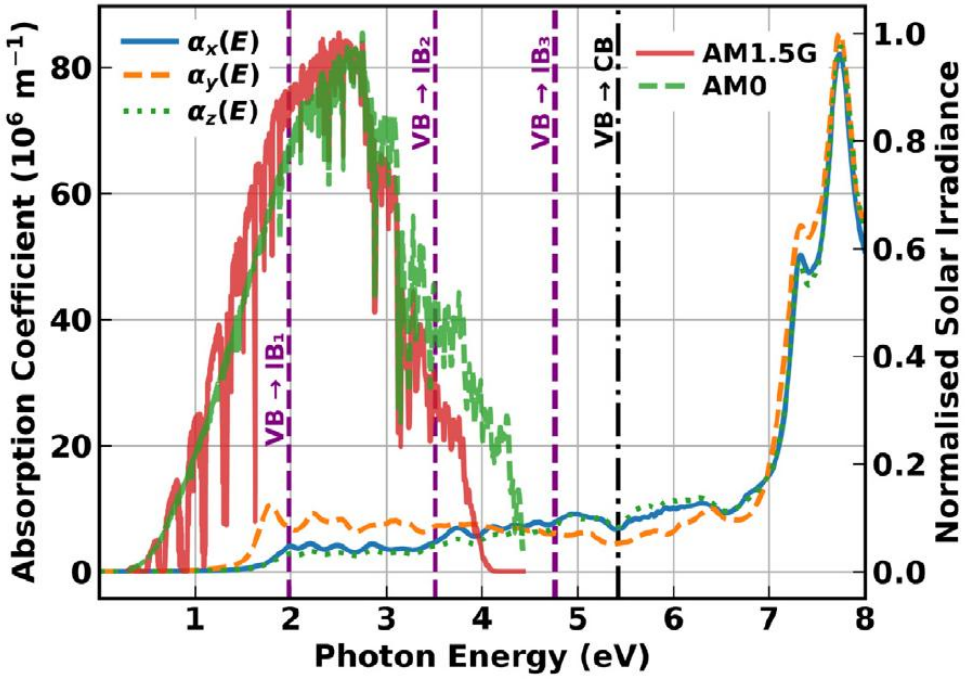
➢ Enables p-type behaviour via impurity band conduction



PIN Junction – BVB Absorption

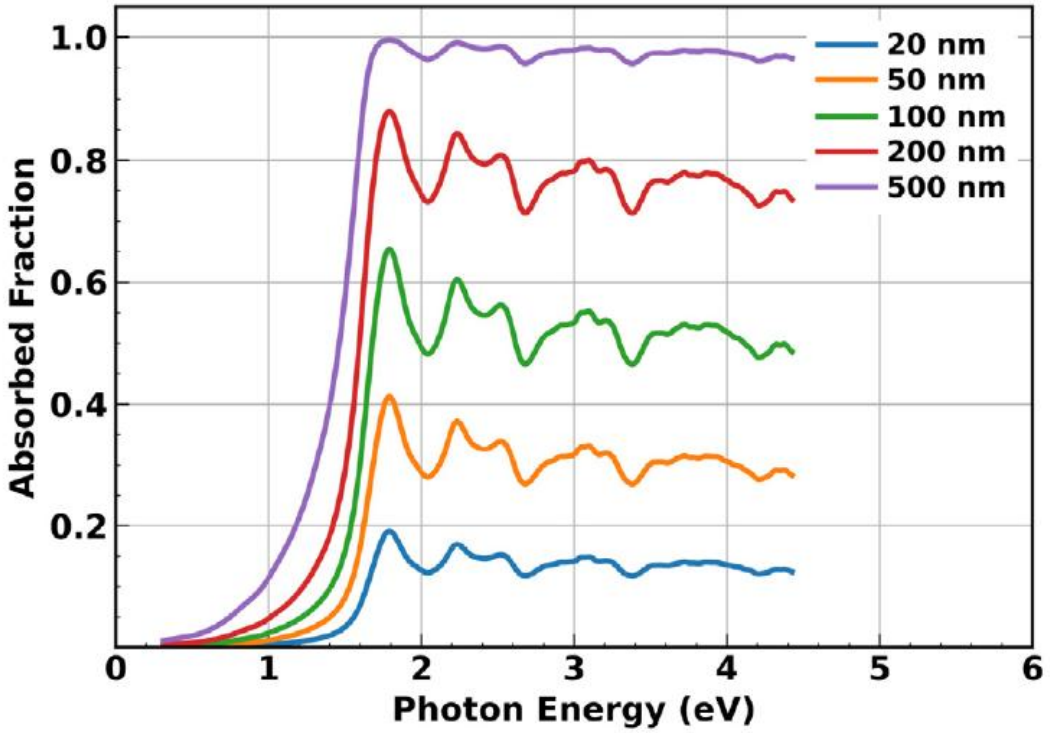
- BVB defect introduces significant sub-bandgap absorption
- Excitonic effects redshift the absorbtion to better align with solar spectrum
- **Design rule:** Orient the crystal such that light propagates in the *xz*-plane to maximise absorption

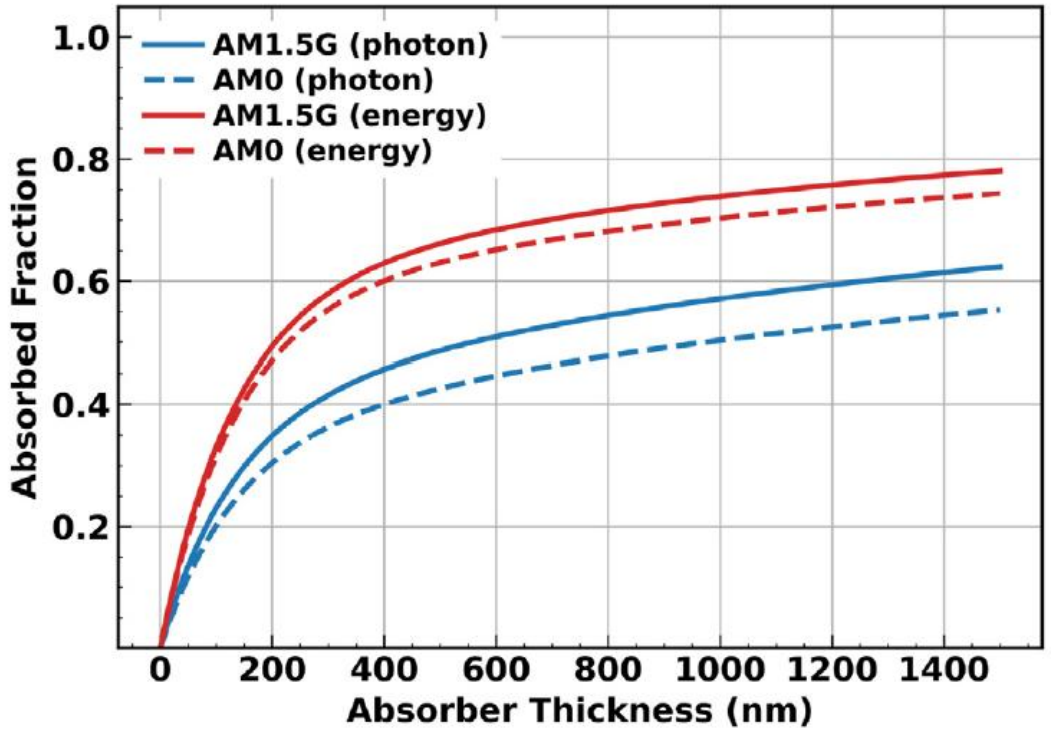




PIN Junction – BVB Absorption

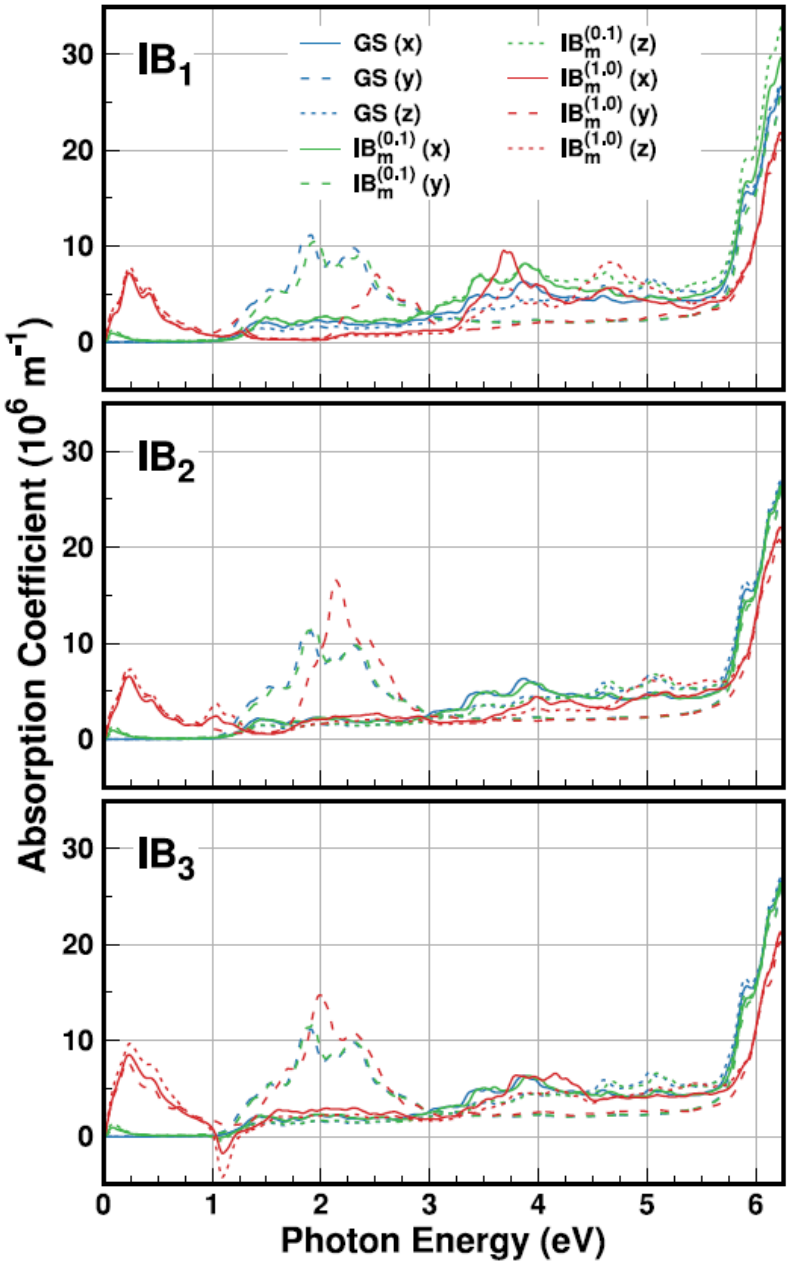
- ✓ Absorption saturates at ≈500 nm absorber thickness
- ✓ Thickness similar to thin-film solar cells (≈ 100 nm to ≈ 4 µm)





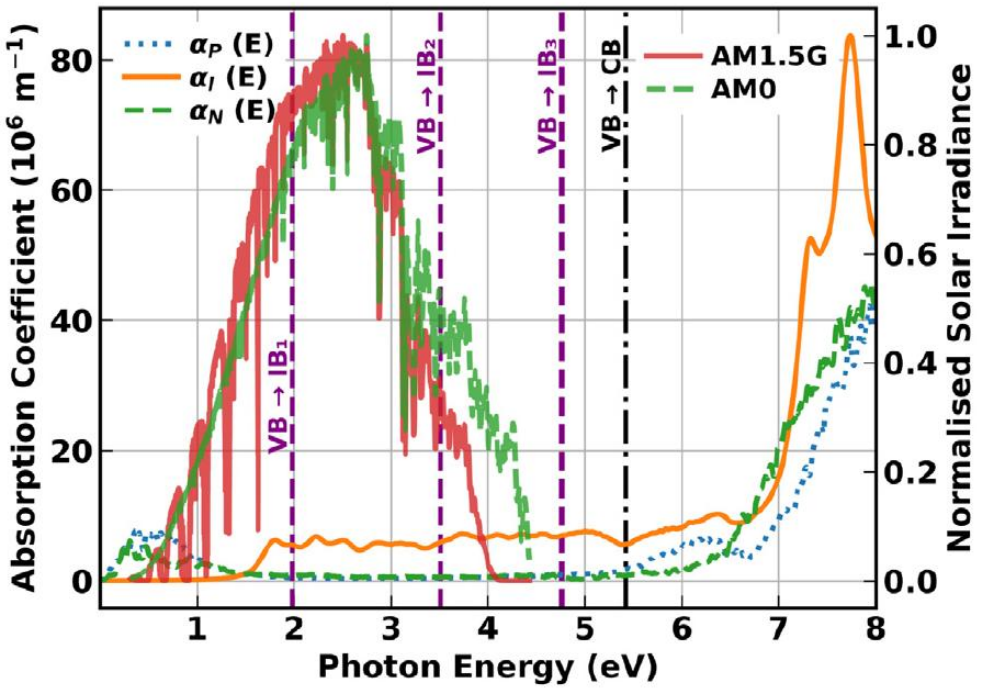
Excited State Absorption

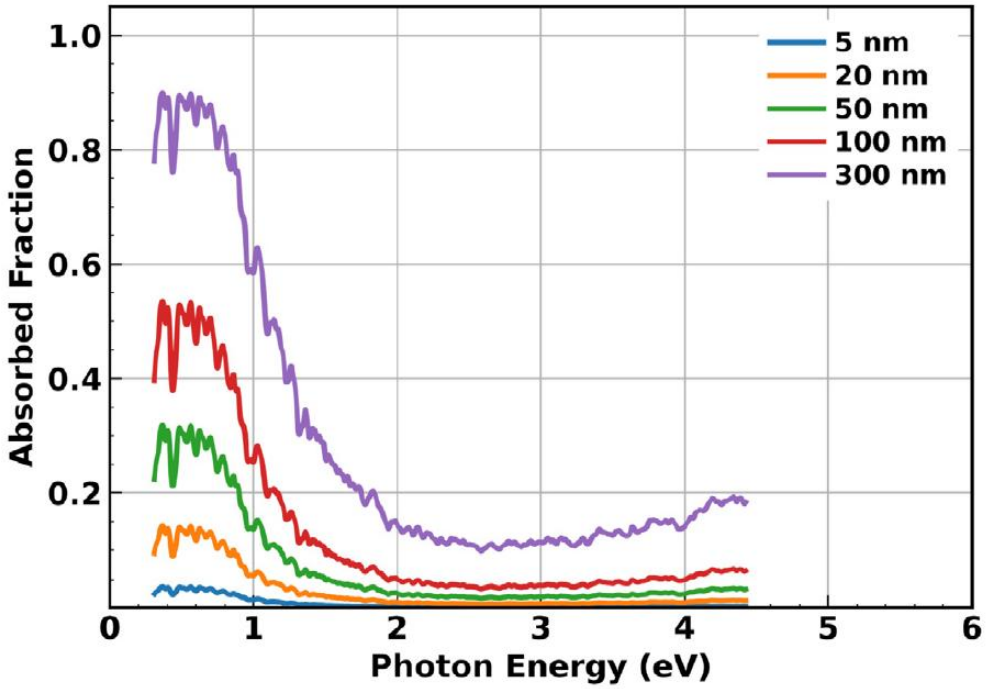
- Ground state absorption cannot capture the IB “ladder“ promotions to the CB
- Promoting 0.1 and 1 electron to IBs and calculating absorption via IPA
- ✓ Low IB occupation enhances absorption, while preserving the GS band structure
- × High occupations induce band shifts towards higher energies and merging of IB_3 with CB
- IB_3 occupation enables low energy photon absorption at 0.5–0.7 eV, but its contribution remains weak



PIN Junction – Contact Layers Absorption

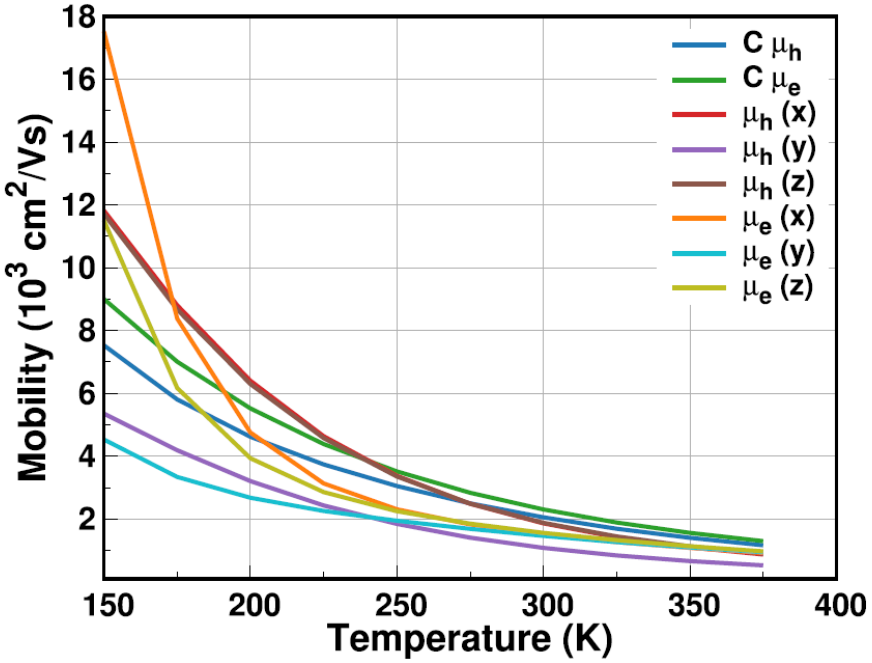
- ✓ Both contact layers are highly transparent ⇒ enable bifacial operation
- ✓ B-doped contacts exhibit the lowest optical losses in relevant energy range

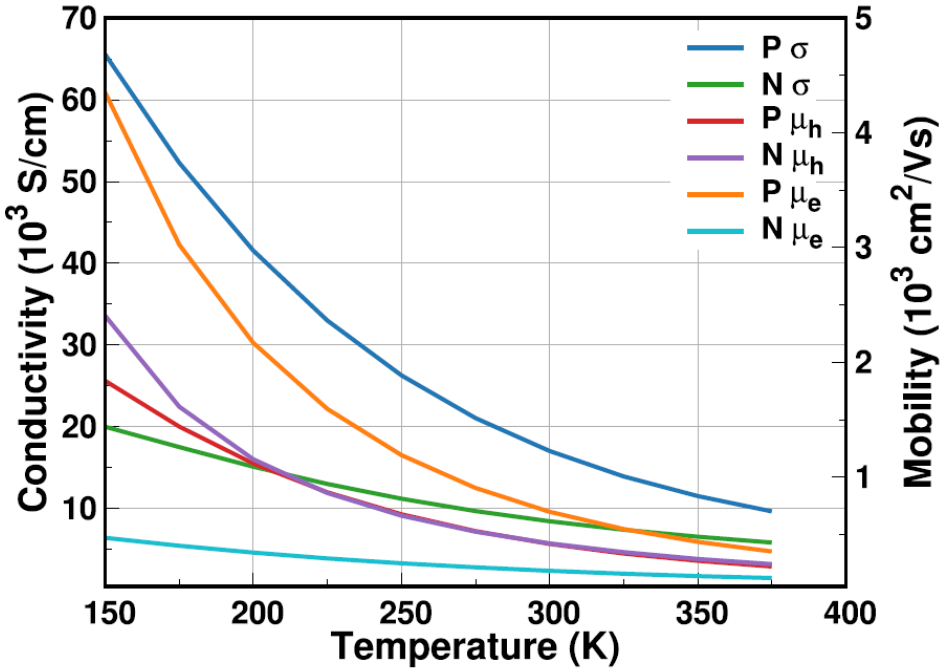




PIN Junction – Charge Transport

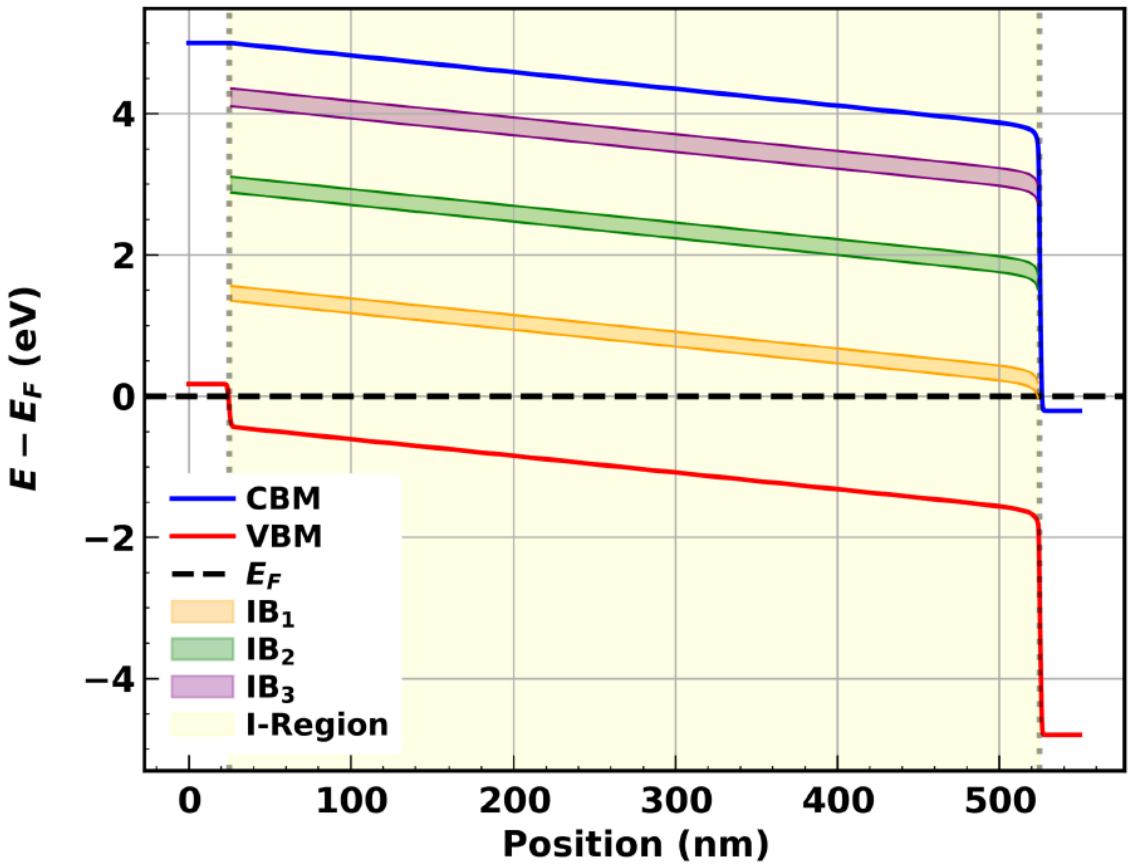
- ✓ High carrier mobility largely preserved in the BVB absorber while introducing anisotropic transport (>10^3 cm^2/Vs at 300 K)
- ✓ Degenerate P/N contacts provide high conductivity ⇒ supporting low series resistance (1.7×10^4 and 8.5×10^3 S/cm at 300 K, respectively)





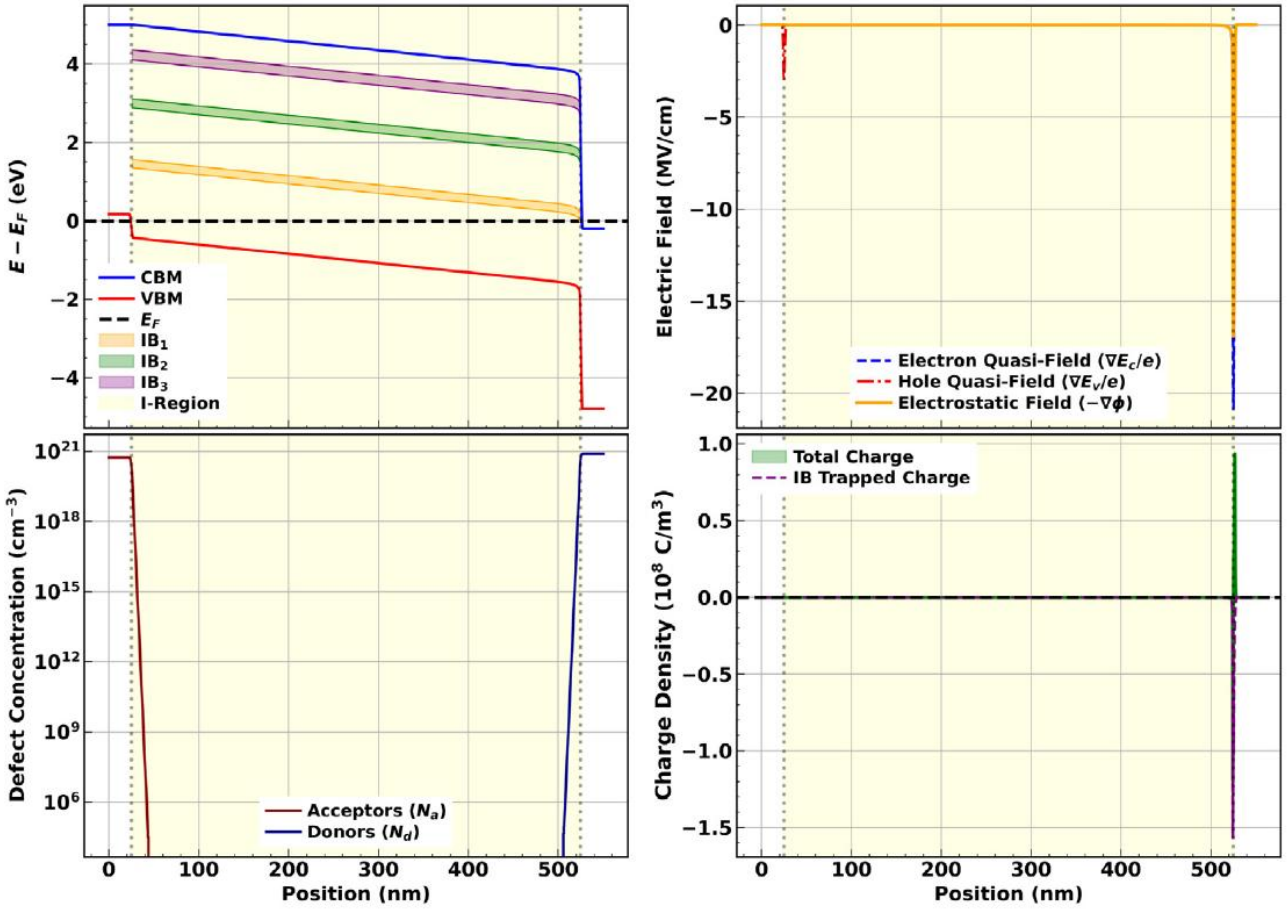
PIN Junction – Electrostatics

- Modelling of different doping profiles and I-region widths
- ✓ Intermediate bands limit the I-region electric field to ≈24 vs. ≈86 kV/cm in pristine diamond I-layer (W = 500 nm)
- ✓ The field remains sufficient for near-saturation carrier drift velocities even at W = 1000 nm
- ✓ Smoothing the doping profile suppresses interface field spikes = reduction of unwanted IB→CB tunnelling



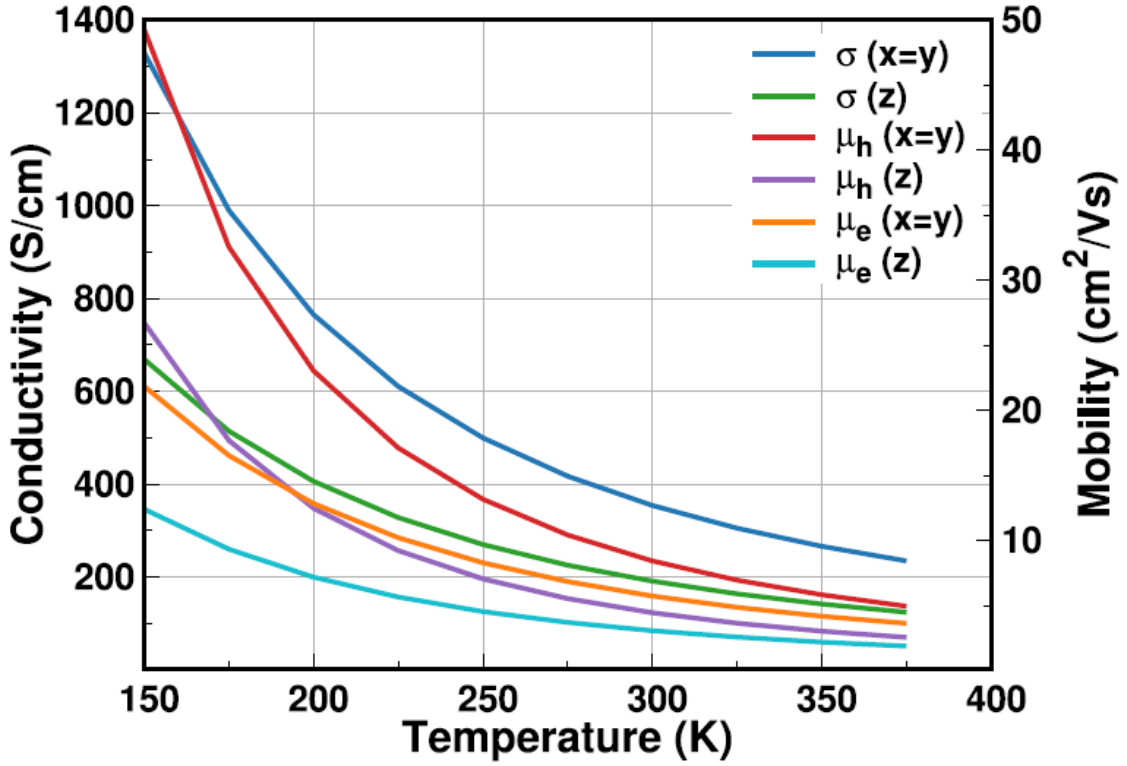
PIN Junction – Electrostatics

- **Design rules:** Absorber width of 500 nm + graded junction = balance of optical absorption and rapid carrier extraction



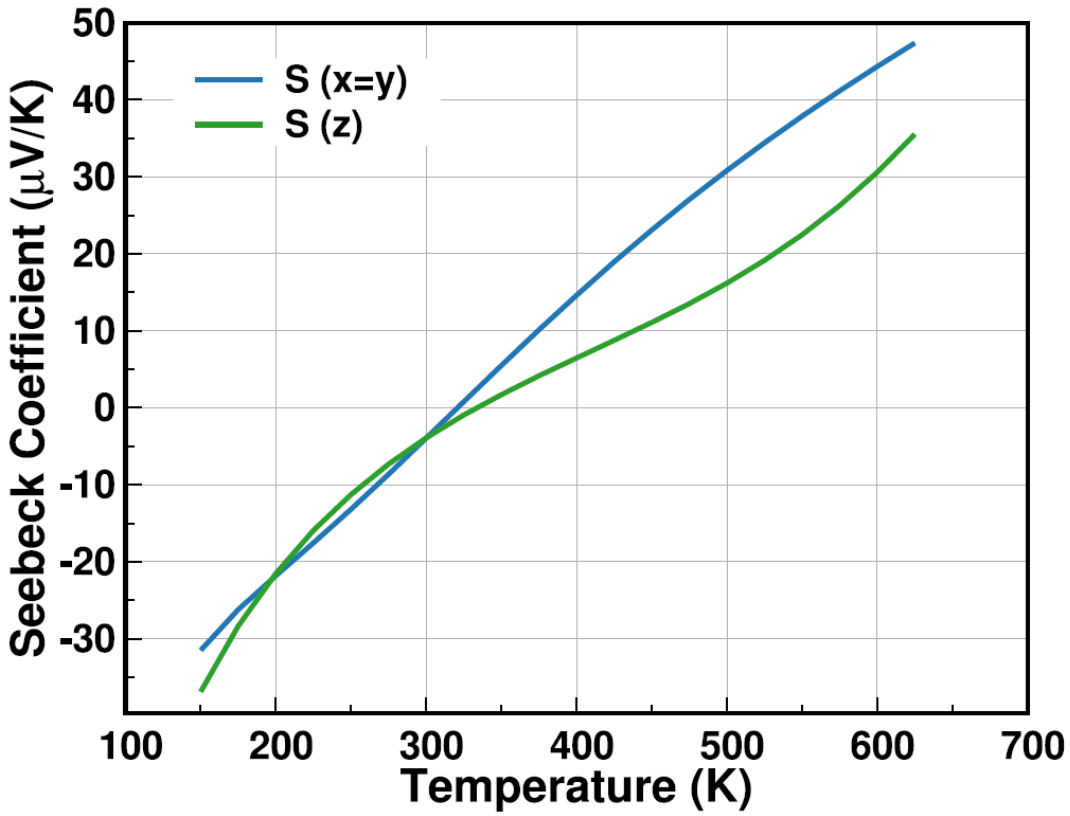
PN Junction Based on Phosphorus Defects - PV

- Impurity band limits mobility (<10 cm^2/Vs at 300 K)
- ✓ Conduction reaches 355 S/cm at 300 K
- ✓ ≈2× higher conductivity in the *xy*-plane than along *z*, ≈50-100x lower than B system
- Impurity band conduction = high doping ⇒ suited for tunnel, PIN and P^+N junction architectures
- × Limited rectifying operation
- **Design rule:** Orient the *z*-axis parallel to the junction for higher conductivity

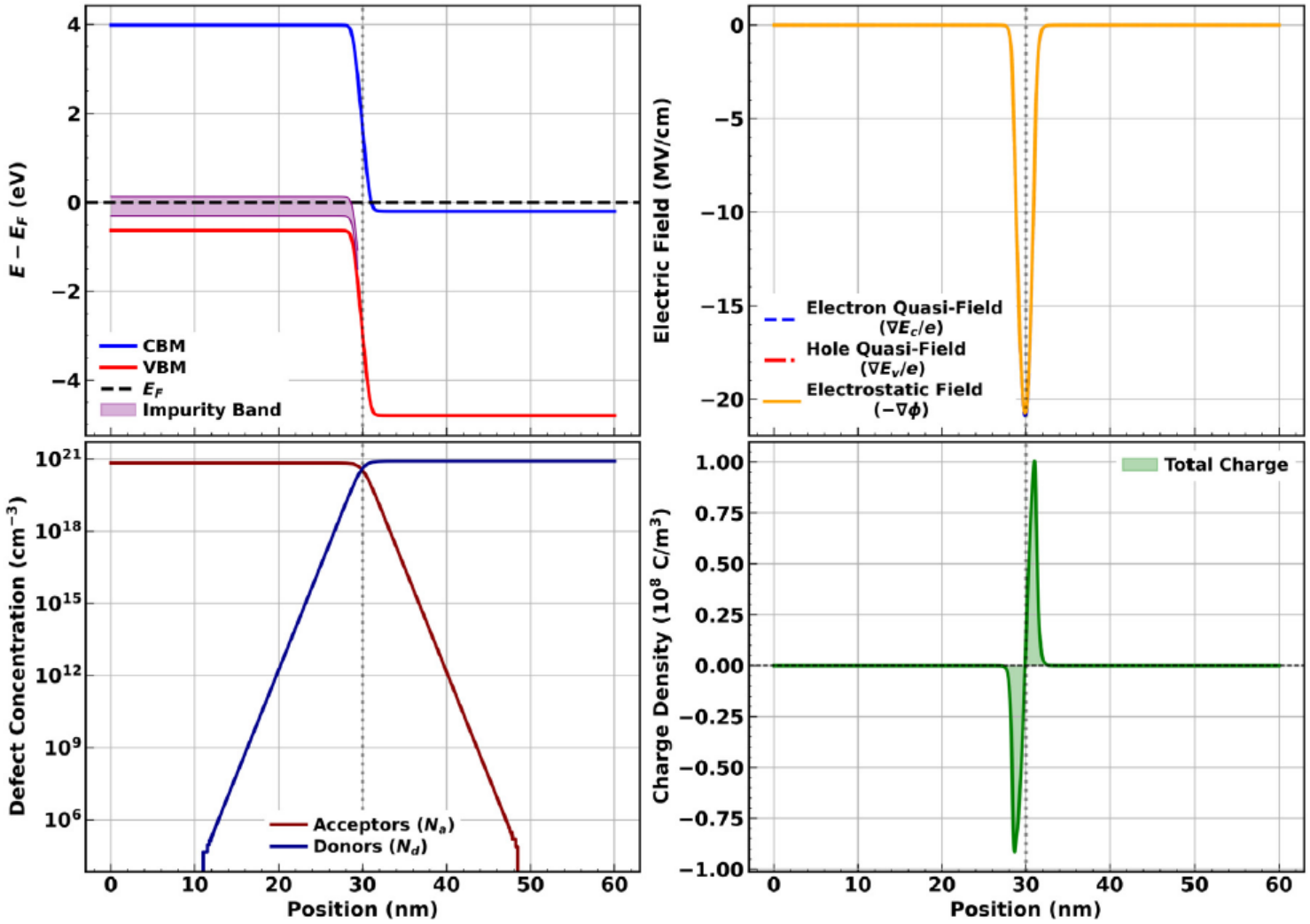


Seebeck Coefficient of PV-doped Diamond

- Seebeck coefficient changes sign with temperature + goniopolar regime near 325 K ($S_{xy} > 0$, $S_z < 0$)
- ✓ Sign change enables thermovoltage compensation (e.g. T_C = 150 K, T_H = 493 K)
- ✓ Potential for thermal stabilisation through the temperature-dependent reversal of the Peltier effect
- ✓ Sign crossover temperature potentially tunable via defect concentration and crystal orientation



PN Device – Electrostatics

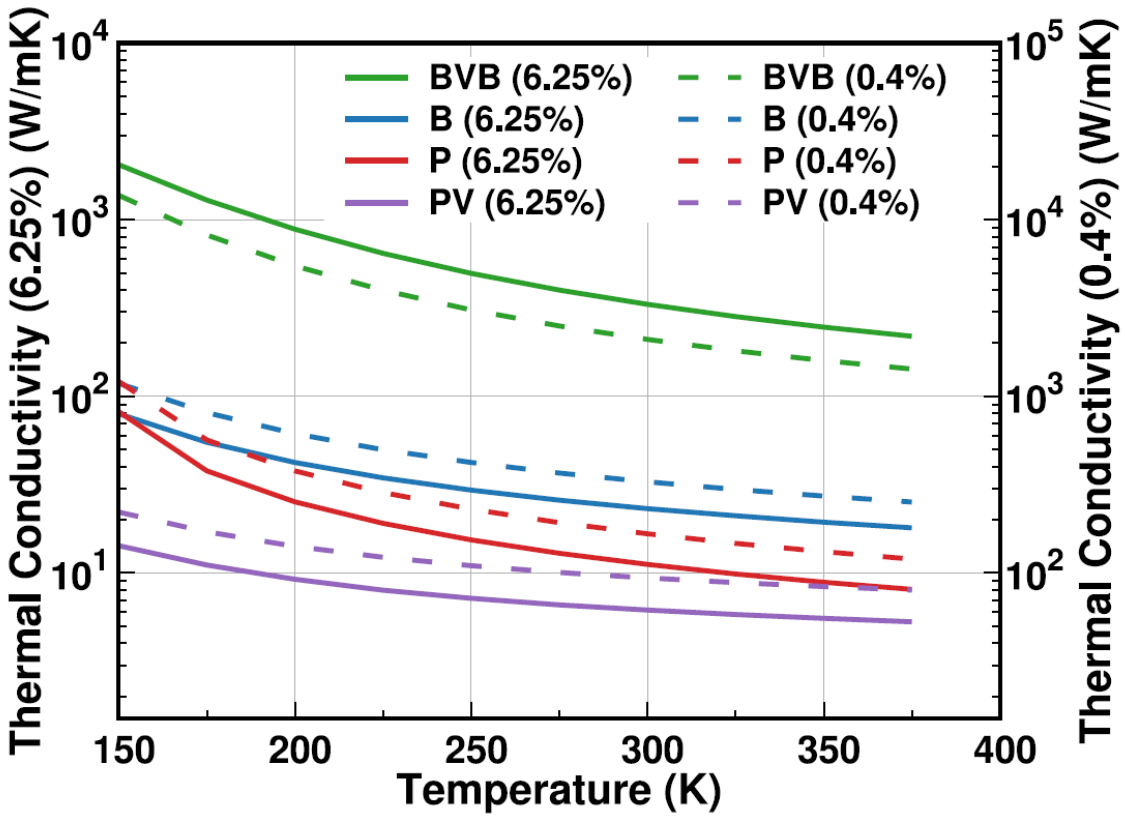


Thermal Conductivity

- High thermal conductivity = heat dissipation under concentrated illumination and high-power operation
- Thermal transport largely isotropic despite defect-induced symmetry breaking

✓ BVB absorber retains >2000 W/mK at 300 K ⇒ the thickest region and primary source of heat generation

- P and N contacts = reduced thermal conductivity ≈328 and ≈166 W/mK
- PV defects = lowest thermal conductivity (≈90 W/mK), still above absorbers such as GaAs and CdTe



Conclusions

- ✓ BVB defect enhances sub-bandgap absorption aligned with the solar spectrum while retaining diamond's exceptional carrier mobility and thermal conductivity
- ✓ PV defect enables p-type behaviour through impurity-band conduction, allowing a PN junction based on a single dopant species
- ✓ Seebeck sign reversal opens pathways for thermoelectric and thermal-management applications
- **Future plan:** Incorporate defect-mediated recombination processes and non-equilibrium carrier dynamics

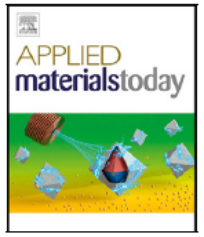
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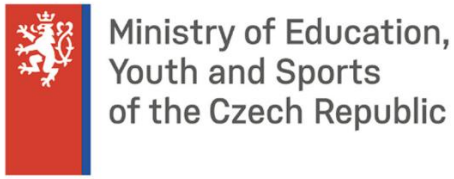


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