

Ex-situ Group V Doping of CdTe using Solution-based Processes

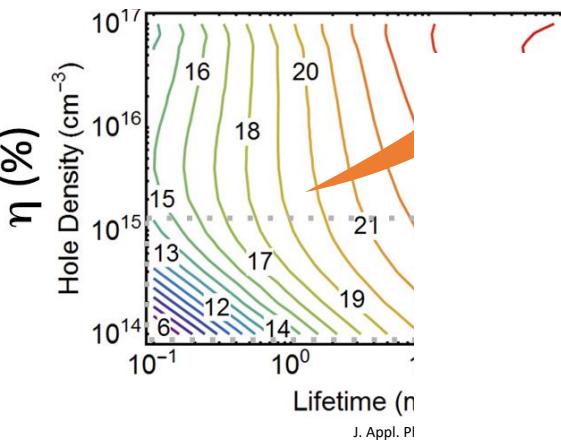
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Group V Doping of CdTe

1 IA 1A	
1 H Hydrogen $1s^1$	2 IIA 2A
3 Li Lithium $[He]2s^1$	4 Be Beryllium $[He]2s^2$
11 Na Sodium $[Ne]3s^1$	12 Mg Magnesium $[Ne]3s^2$
19 K Potassium $[Ar]4s^1$	20 Ca Calcium $[Ar]4s^2$
37 Rb Rubidium $[Kr]5s^1$	38 Sr Strontium $[Kr]5s^2$
55 Cs Cesium $[Xe]6s^1$	56 Ba Barium $[Xe]6s^2$
87 Fr Francium $[Rn]7s^1$	88 Ra Radium $[Rn]7s^2$
89-103 Rf Rutherfordium $[Rn]5f^{14}6d^27s^2$ *	104 Db Dubnium $[Rn]5f^{14}6d^37s^2$ *
	105 Sg Seaborgium $[Rn]5f^{14}6d^47s^2$ *
	106 Bh Bohrium $[Rn]5f^{14}6d^57s^2$ *
	107 Hs Hassium $[Rn]5f^{14}6d^67s^2$ *
	108 Mt Meitnerium $[Rn]5f^{14}6d^77s^2$ *
	109 Ds Darmstadtium $[Rn]5f^{14}6d^87s^2$ *
	110 Rg Roentgenium $[Rn]5f^{14}6d^97s^2$ *
	111 Cn Copernicium $[Rn]5f^{14}6d^{10}7s^2$ *
	112 Uut Ununtrium $[Rn]5f^{14}6d^{10}7s^{2+}$ *
	113 Fl Flerovium $[Rn]5f^{14}6d^{10}7s^{2+}$ *
	114 Uup Ununpentium $[Rn]5f^{14}6d^{10}7s^{2+}p^3$ *
	115 Lv Livermorium $[Rn]5f^{14}6d^{10}7s^{2+}p^4$ *
	116 Uus Ununseptium $[Rn]5f^{14}6d^{10}7s^{2+}p^5$ *
	117 Uuo Ununoctium $[Rn]5f^{14}6d^{10}7s^{2+}p^6$ *



Group V



13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
5 B Boron $[He]2s^22p^1$	6 C Carbon $[He]2s^22p^2$	7 N Nitrogen $[He]2s^22p^3$	8 O Oxygen $[He]2s^22p^4$	9 F Fluorine $[He]2s^22p^5$	10 Ne Neon $[He]2s^22p^6$
13 Al Aluminum $[Ne]3s^23p^1$	14 Si Silicon $[Ne]3s^23p^2$	15 P Phosphorus $[Ne]3s^23p^3$	16 S Sulfur $[Ne]3s^23p^4$	17 Cl Chlorine $[Ne]3s^23p^5$	18 Ar Argon $[Ne]3s^23p^6$
29 Cu Copper $[Ar]3d^{10}4s^1$	30 Zn Zinc $[Ar]3d^{10}4s^2$	31 Ga Gallium $[Ar]3d^{10}4s^24p^1$	32 Ge Germanium $[Ar]3d^{10}4s^24p^2$	33 As Arsenic $[Ar]3d^{10}4s^24p^3$	34 Se Selenium $[Ar]3d^{10}4s^24p^4$
26 Fe Iron $[Ar]3d^64s^2$	27 Co Cobalt $[Ar]3d^74s^2$	28 Ni Nickel $[Ar]3d^84s^2$	29 Ag Silver $[Kr]4d^{10}5s^1$	30 Cd Cadmium $[Kr]4d^{10}5s^2$	31 In Indium $[Kr]4d^{10}5s^25p^1$
44 Ru Ruthenium $[Kr]4d^75s^1$	45 Rh Rhodium $[Kr]4d^85s^1$	46 Pd Palladium $[Kr]4d^{10}$	47 Ag Silver $[Kr]4d^{10}5s^1$	48 Cd Cadmium $[Kr]4d^{10}5s^2$	49 In Indium $[Kr]4d^{10}5s^25p^1$
76 Os Osmium $[Xe]4f^{14}5d^66s^2$	77 Ir Iridium $[Xe]4f^{14}5d^76s^2$	78 Pt Platinum $[Xe]4f^{14}5d^96s^1$	79 Au Gold $[Xe]4f^{14}5d^{10}6s^1$	80 Hg Mercury $[Xe]4f^{14}5d^{10}6s^2$	81 Tl Thallium $[Xe]4f^{14}5d^{10}6s^26p^1$
108 Hs Hassium $[Rn]5f^{14}6d^67s^2$ *	109 Mt Meitnerium $[Rn]5f^{14}6d^77s^2$ *	110 Ds Darmstadtium $[Rn]5f^{14}6d^87s^2$ *	111 Rg Roentgenium $[Rn]5f^{14}6d^97s^2$ *	112 Cn Copernicium $[Rn]5f^{14}6d^{10}7s^2$ *	113 Uut Ununtrium $[Rn]5f^{14}6d^{10}7s^{2+}$ *
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Configurations denoted with a * are unknown and the listed values are predicted.

- Group V doping into the Te site to play as the acceptor

Group V Doping Approaches in CdTe In situ vs Ex-situ

Pros:

- Higher dopant concentration $\sim 1 \times 10^{18}$
- Better control of Group V ions distribution

Cons:

- Low activation ratio $\sim 1\%$
- Possible dopant segregation

Pros:

- Higher activation ratio $\sim 5\%$
- Less dopant segregation

Cons:

- Lower dopant concentration $\sim 1 \times 10^{16}$
- Fixed distribution



Exceeding 20% efficiency with in situ group V doping in polycrystalline CdTe solar cells 2019

W. K. Metzger^{①*}, S. Grover², D. Lu², E. Colegrove¹, J. Moseley¹, C. L. Perkins^①, X. Li², R. Mallick², W. Zhang², R. Malik², J. Kephart², C.-S. Jiang¹, D. Kuciauskas^①, D. S. Albin¹, M. M. Al-Jassim¹, G. Xiong² and M. Gloeckler³

2022 ~ 22%



Low-temperature and effective ex situ group V doping for efficient polycrystalline CdSeTe 2021 solar cells 18%

Deng-Bing Li^①, Canglang Yao¹, S. N. Vijayaraghavan^②, Rasha A. Awni^①, Kamala K. Subedi¹, Randy J. Ellingson¹, Lin Li², Yanfa Yan^{①✉} and Feng Yan^{②✉}

2022 ~ 19%



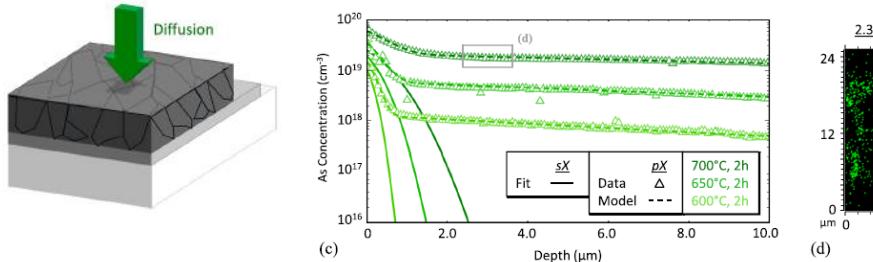
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Ex-situ Doping Approaches and Challenges in Polycrystalline CdTe

• Dry diffusion doping

- Over-pressure of Cd group V covalent compounds.,
 - e.g., Cd_3As_2 , Cd_3P_2



High diffusion temperature (550~700 °C) may not be suitable for the CdTe module manufacturing

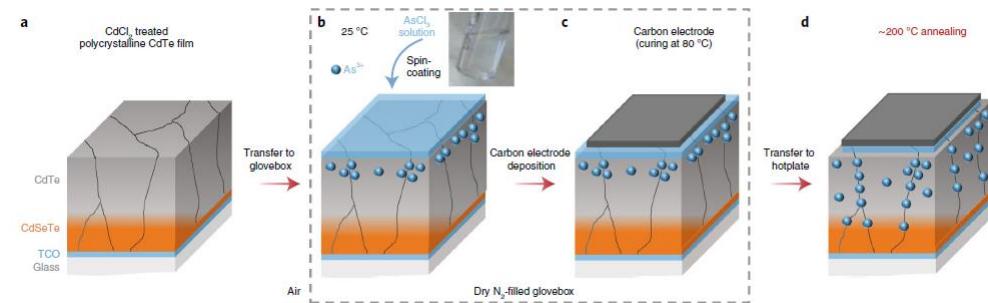
J. Phys. D: Appl. Phys. 51 (2018) 075102

- Group V chalcogenides layer,
 - e.g., Sb_2Te_3 , Bi_2Te_3 as back contact,
Low efficiency without Cu doping

AIP Advances 1, 042152 (2011)
Solar Energy Materials & Solar Cells 121 (2014) 92–98

• Wet diffusion doping

- Group V halides ionic compounds
 - e.g., PCl_3 , AsCl_3 , SbCl_3 ,



Nature Energy, 6, 715–722 (2021)

Low diffusion temperature,
but compounds sensitivity to ambient moisture and
toxicity.

*Need air stable and less-toxicity ex-situ low
temperature diffusion process*

Challenges to Conduct the ex-situ Group V Doping in CdTe

- Understanding ex-situ Diffusion Doping mechanism
- Higher diffusion barrier of Group V in the CdTe Grain Interiors(GIs)/Grain Boundaries (GBs)
- Complicated surface chemistry of the diffusion doped CdTe surface
- Suitable back contact for the diffusion doped CdTe.
- Alternative group V dopants for ex-situ diffusion
- Desired activation process for the ex-situ diffusion doped CdTe
- Others, e.g., impurities (unintentional dopants)

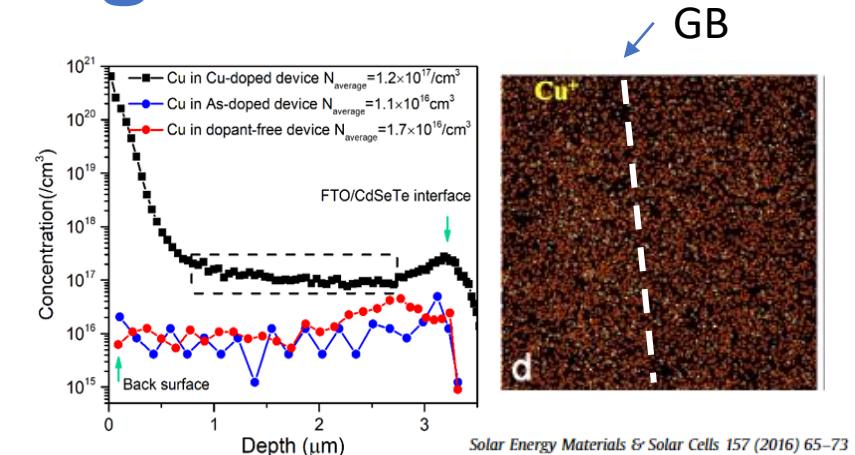
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Solution-processed Doping in CdTe

- Cu doping using the solution means

- CuCl CdCl₂ treated CdTe
- CuCl₂ → *P-type doping at Cd vacancies*
 - Surface reaction: Cu^{+/2+} + Te = Cu₂Te
- CuSCN Defect chemistry: V_{Cd}⁻ + Cu⁺ = Cu_{Cd}⁺ → hole
- CuNO₃ • Cu ions faster diffusion in CdTe
- others • Cu uniform distribution in the GBs/GIs
- Cu activation ratio ~ <1%



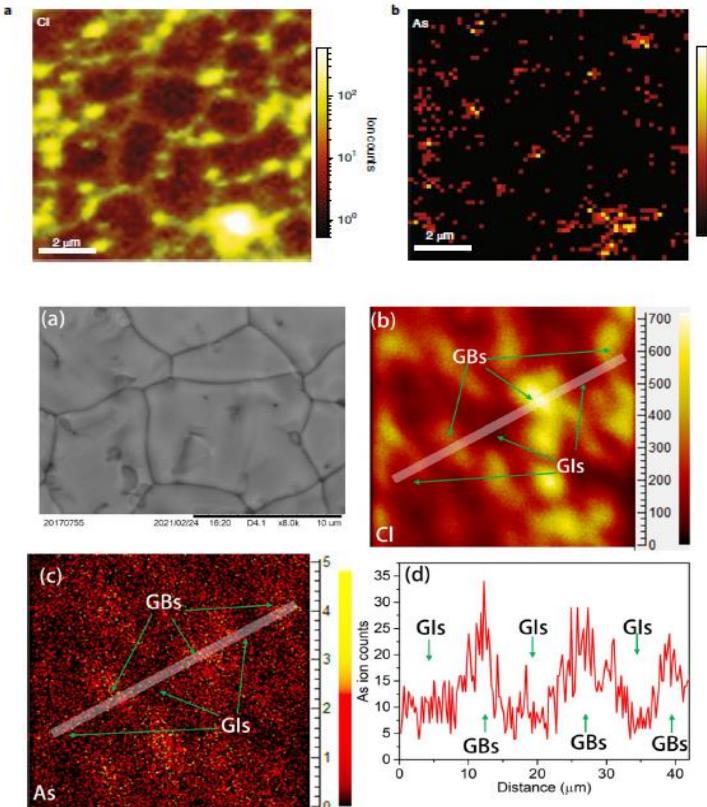
Solar Energy Materials & Solar Cells 157 (2016) 65–73

- Group V solutions doping in CdTe

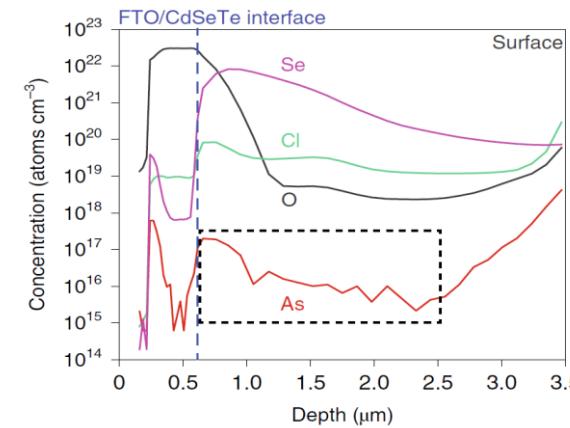
- Group V halides in solutions
 - PCl₃, AsCl₃, SbCl₃, BiCl₃, etc
 - Diffusion barrier: Cations < anions
 - Cations diffusion barrier similar with Cu

Dopants	defect states	Diffusion constant, D ₀ , cm ² s ⁻¹	Diffusion activation energy, E _D , eV
intrinsic	V _{Cd} ²⁻		1.08 (cal)
	Cd ⁰		0.35
	Cd _i ⁺		0.39
Cu	total	7.73×10 ⁻⁷ (exp)	0.33 (exp)
	total	7.4×10 ⁻⁶ (bulk, exp), 2.3 (GB, exp)	0.84 (bulk, exp), 1.1 (GB, exp)
	Cu _{Cd} ⁻		1.23 (cal) 0.72 (cal)
P	total	4.86 ×10 ⁻³ (bulk), 6.61×10 ² (GB)	2.10 (bulk, exp), 1.97 (GB, exp)
	P _i ³⁺		0.43 (Te rich, cal)
	P _i ³⁻		1.08 (Cd rich, cal)
As	total	9.4×10 ⁻² (bulk), 1.05×10 ⁵ (GB)	2.18 (bulk, exp), 2.34 (GB, exp)
	As _i ³⁺		0.49 eV (Te rich, cal)
	As _i ³⁻		0.84 eV (Cd rich, cal)
Sb	total	1.15×10 ¹ (bulk), 4.39×10 ¹ (GB)	2.52 (bulk, exp), 1.71 (GB, exp)
	Sb _{Cd} ⁺		0.55 eV (cal)
	Sb _i ³⁺		1.03 (cal)
	Sb _i ³⁺		0.20 (Te rich, cal)
	Sb _i ³⁻		0.61 (Cd rich, cal)
Bi	total	10 ⁻¹⁰	0.3-0.4 (exp)

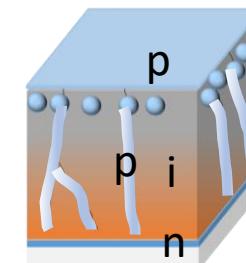
How do the Solution-based Group V halides Diffuse into the Polycrystalline CdTe?



1. Initially, diffuse along the grain boundaries and segregate in GBs
2. Then, diffuse from GIs to GBs.
3. However, the diffusion from the GBs to the GIs is limited, which is different to the Cu diffusion.
4. More characterization needed.



A potential *new p-i-n structure device structure* using the ex-situ group V doping: **GB is p-doped, while GI is intrinsic**



Challenges to Conduct the ex-situ Group V Doping in CdTe

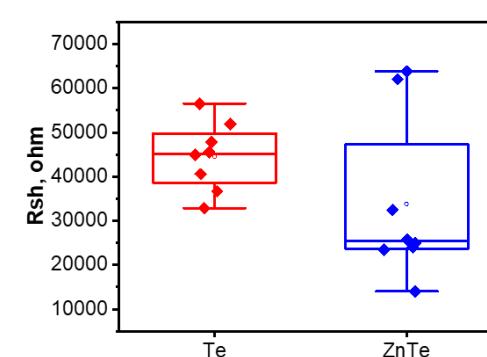
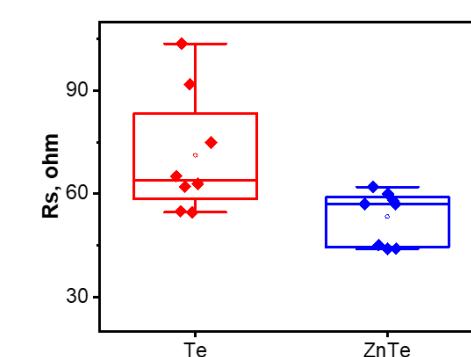
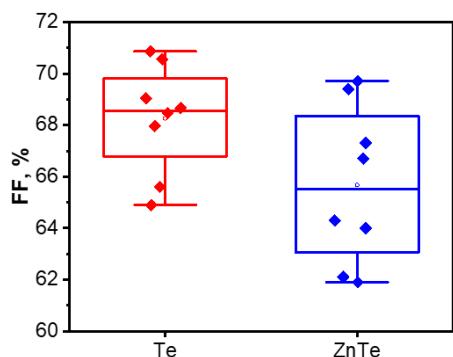
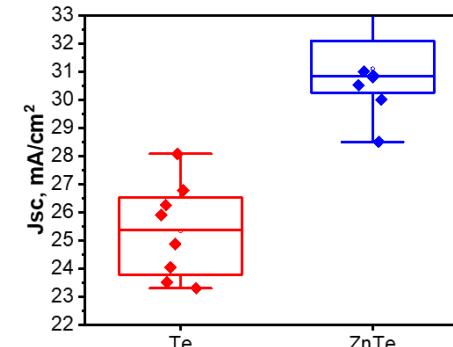
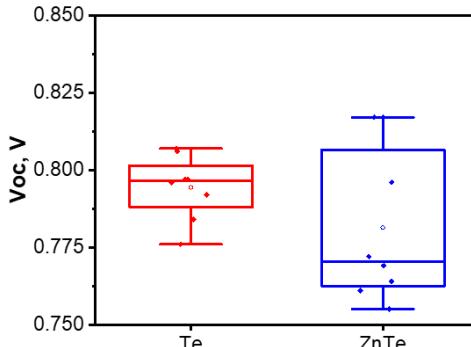
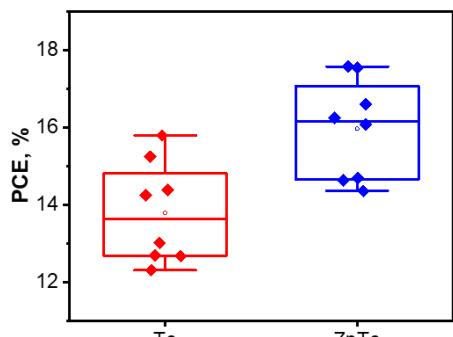
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- Others, e.g., impurities (unintentional dopants)

Alternative Back Contact for the Solution processed Group V Diffusion doped CdTe

- Carbon back contact
 - 18% efficiency
 - Suitable work function
 - Easy to operate in the glovebox
 - Concern:
 - High resistivity
 - Porous interface with CdTe
 - Unintentional impurities
 - Au back contact
 - Thermal evaporated Au electrode
- (a) SEM image showing a porous surface layer, scale bar 1 μm. (b) SEM image showing a smoother surface layer, scale bar 15 μm.
-
- The diagram illustrates the CdTe solar cell structure and the Group V diffusion process. Part (a) shows a cross-section of the cell with layers: CdCl₂ treated polycrystalline CdTe film, CdTe, CdSeTe, TCO, and Glass. Part (b) shows the CdTe film being treated with 25 °C AsCl₃ in air. Part (c) shows the Group V diffusion process in a dry N₂ filled glovebox. Part (d) shows the final structure with a Carbon alternative back contact (e.g. Au).
-
- A graph showing the Current density (mA/cm²) versus Voltage (V) for the Au back contact. The curve starts at approximately 28 mA/cm² at 0.0 V, remains relatively flat until about 0.4 V, then decreases sharply to 0 mA/cm² at approximately 0.8 V. The text "PCE ~18.5%" is indicated on the graph.
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Alternative Back Contact for the Solution processed Group V Diffusion doped CdTe

- ZnTe and Te back contact deposited using sputtering



Other back contact for the heavily doped back surface needed.

Opportunities to Conduct the ex-situ Group V Doping in CdTe via solution process

- Ex-situ Diffusion Doping mechanism
- Higher diffusion barrier of Group V in the CdTe Grain Interiors(GIs)/Grain Boundaries (GBs)
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- Suitable back contact for the diffusion doped CdTe.
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- Others, e.g., impurities (unintentional dopants)

Hope to get a higher device performance after addressing the above challenges >22%

Acknowledgements

Collaborators:

UT: Dengbing Li, Yanfa Yan, Michael Heben, Randy Ellingson

CSU: Tushar Shimpi, Jim Site, W. S. Sampath,

First Solar: Dingyuan Lu, Xiaoping Liu, Gang Xiong

NREL: Matt Reese

Graduate students: UA: Xiaomeng Duan, Harigovind Gokul

Menon, UT: Sabin Neupane,

6th Annual CdTe PV Workshop
October 20-21, 2022
University of Toledo



CMMI-2019473



DE-EE0009368