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

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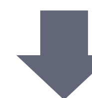
Group V Doping of CdTe

Group V



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

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

Pros:
- Higher dopant concentration ~1x10^{18}
- Better control of Group V ions distribution

Cons:
- Low activation ratio ~1%
- Possible dopant segregation

Pros:
- Higher activation ratio ~5%
- Less dopant segregation

Cons:
- Lower dopant concentration ~ 1x10^{16}
- Fixed distribution

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

W. K. Metzger[1*], S. Grover[2], D. Lu[2], E. Colegrove[1], J. Moseley[1], C. L. Perkins[1], X. Li[2], R. Mallick[2], W. Zhang[2], R. Malik[2], J. Kephart[2], C.-S. Jiang[1], D. Kuciauskas[1], D. S. Albin[1], M. M. Al-Jassim[1], G. Xiong[2] and M. Gloeckler[3]

2022 ~ 22%

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

18%

Deng-Bing Li[1], Canglang Yao[1], S. N. Vijayaraghavan[2], Rasha A. Awni[1], Kamala K. Subedi[1], Randy J. Ellingson[1], Lin Li[2], Yanfa Yan[1] and Feng Yan[2]

2022 ~ 19%

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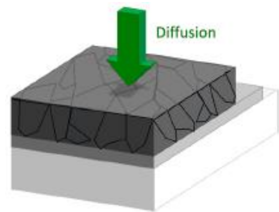
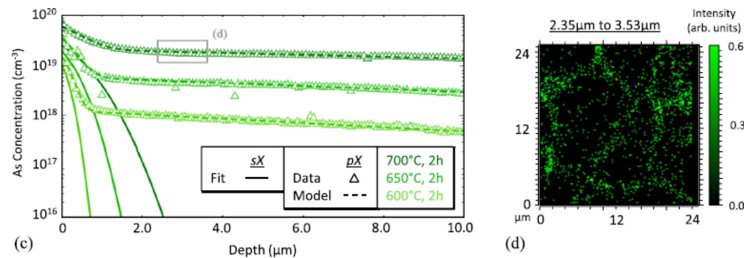
Ex-situ Doping Approaches and Challenges in Polycrystalline CdTe

- **Dry diffusion doping**
  - Over-pressure of Cd group V covalent compounds.,
    - e.g., Cd_3As_2, Cd_3P_2

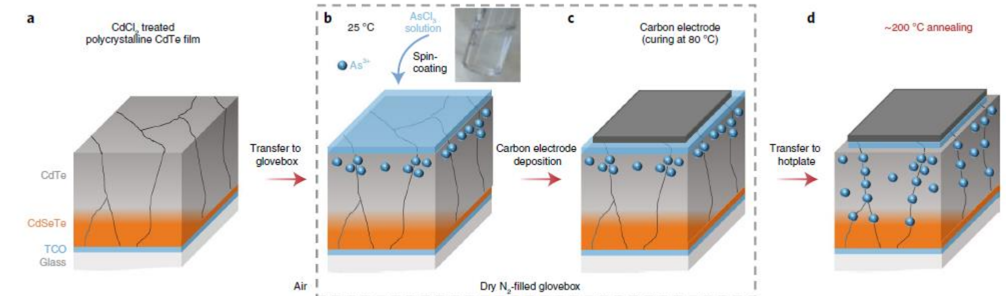




High diffusion temperature (550~700 ^oC) may not be suitable for the CdTe module manufacturing

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

- **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.

- 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

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

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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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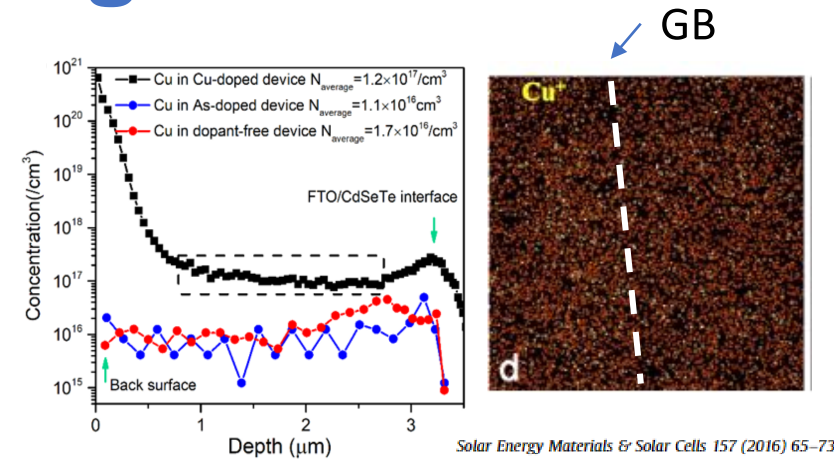
Solution-processed Doping in CdTe

- Cu doping using the solution means
  - CuCl
  - $CuCl_2$
  - CuSCN
  - $CuNO_3$
  - others

$CdCl_2$ treated CdTe

P-type doping at Cd vacancies

- Surface reaction: $Cu^{+/2+}$ + Te = Cu_2Te
- Defect chemistry: V_{Cd}'' + Cu^{+} = Cu_{Cd}' → hole
- Cu ions faster diffusion in CdTe
- Cu uniform distribution in the GBs/GIs
- Cu activation ratio ~ <1%



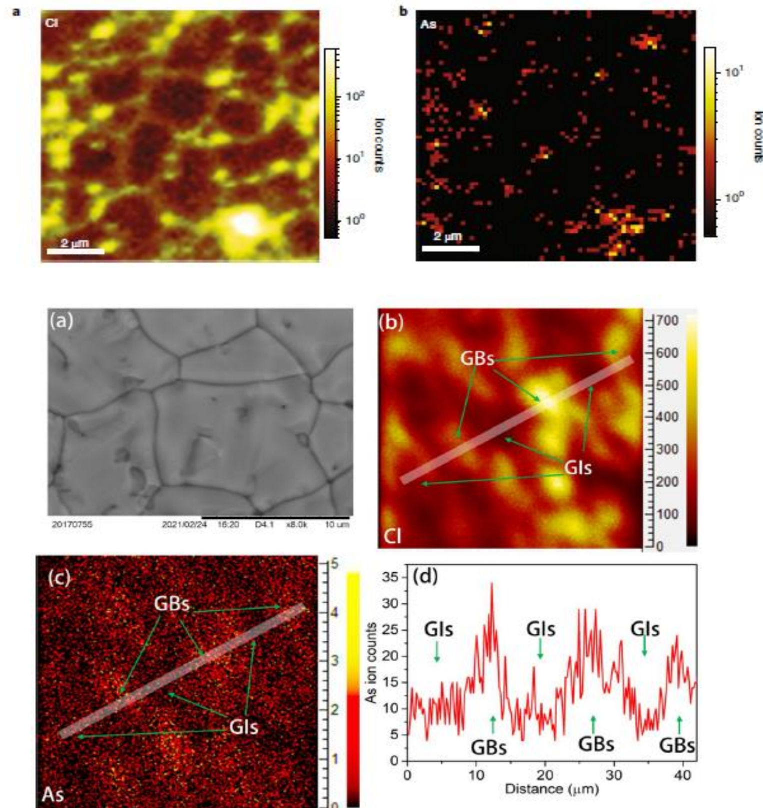
Solar Energy Materials & Solar Cells 157 (2016) 65–73

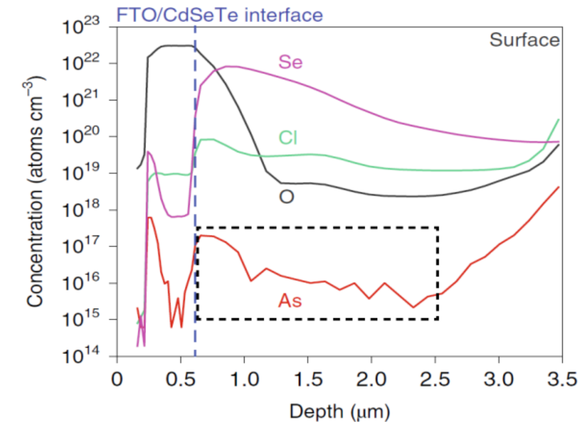
- Group V solutions doping in CdTe
  - Group V halides in solutions
    - PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$, etc
    - Diffusion barrier: Cations < anions
    - Cations diffusion barrier similar with Cu

Diffusion constant and activation energy of intrinsic and extrinsic defects in CdTe

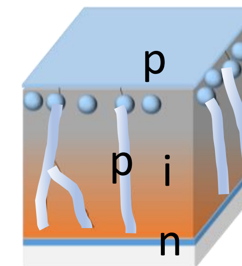
Dopants	defect states	Diffusion constant, D_0, cm^2s^{-1}	Diffusion activation energy, E_D, eV
intrinsic	V_{Cd}^{2-}		1.08 (cal)
	Cd_i^0		0.35
	Cd_i^+		0.39
Cu	total	7.73×10^{-7} (exp)	0.33 (exp)
Cu	total	7.4×10^{-6} (bulk, exp), 2.3 (GB, exp)	0.84 (bulk, exp), 1.1 (GB, exp)
	Cu_{Cd}^-		1.23 (cal)
			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)

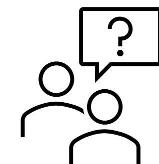
How do the Solution-based Group V halides Diffuse into the Polycrystalline CdTe?





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





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.

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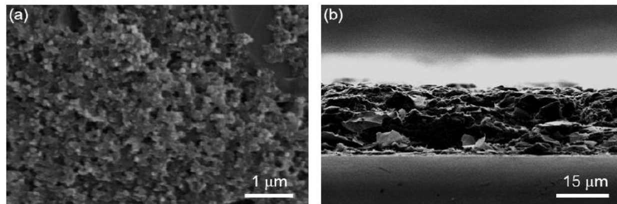
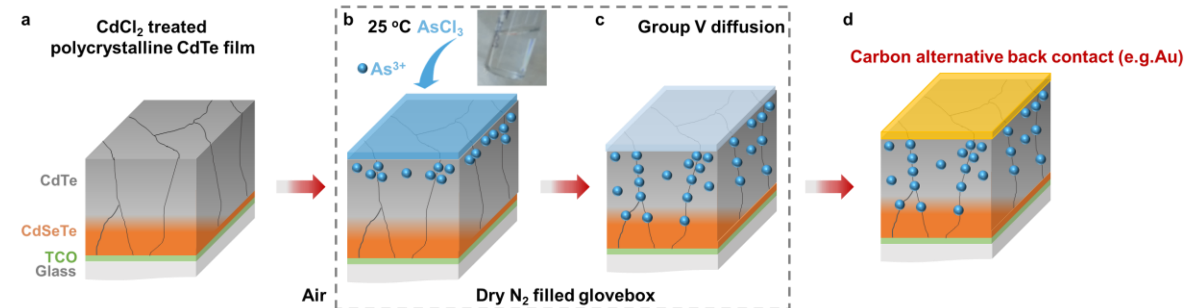
Alternative Back Contact for the Solution processed Group V Diffusion doped CdTe

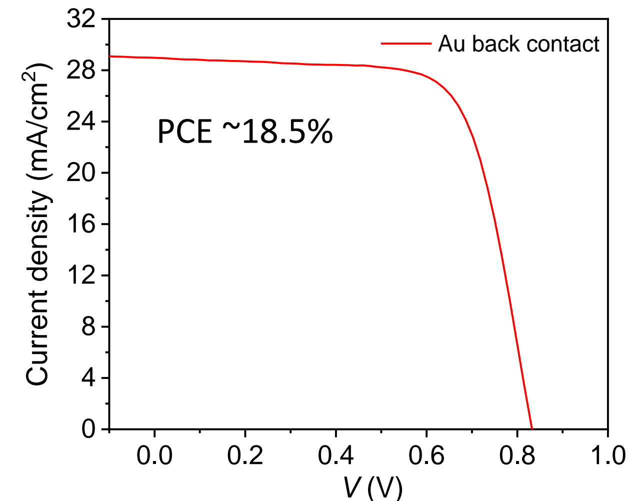
- Carbon back contact
  - 18% efficiency
  - Suitable work function
  - Easy to operate in the glovebox



  - Concern:
    - High resistivity
    - Porous interface with CdTe
    - Unintentional impurities

- Au back contact
  - Thermal evaporated Au electrode





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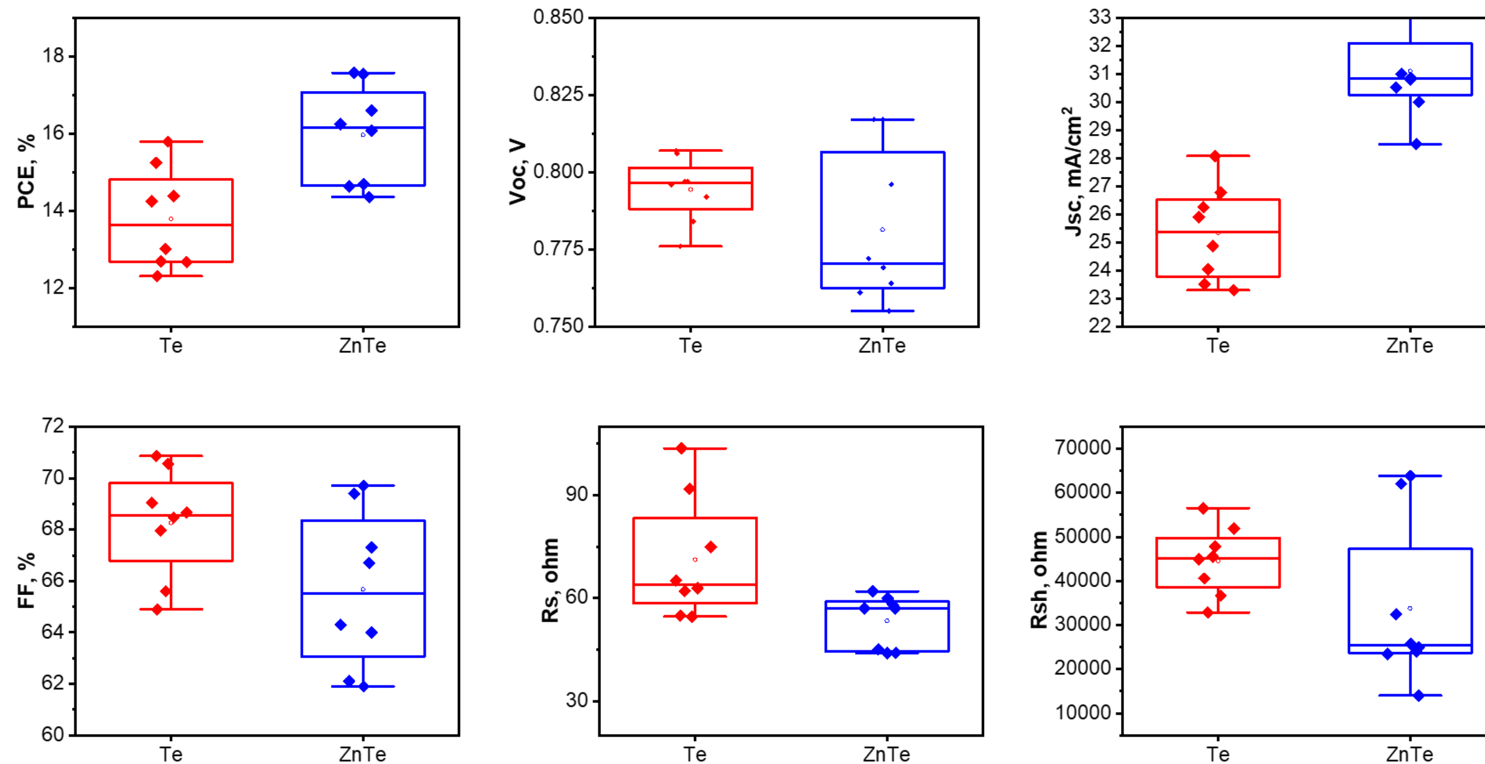
Alternative Back Contact for the Solution processed Group V Diffusion doped CdTe

- ZnTe and Te back contact deposited using sputtering



Other back contact for the heavily doped back surface needed.

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

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

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

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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,

CMMI-2019473

DE-EE0009368