Joint EPS-SIF International School on Energy

Energy Innovation and Integration for a Clean Environment

Sb_2Se_3

the future of thin-film photovoltaics ?

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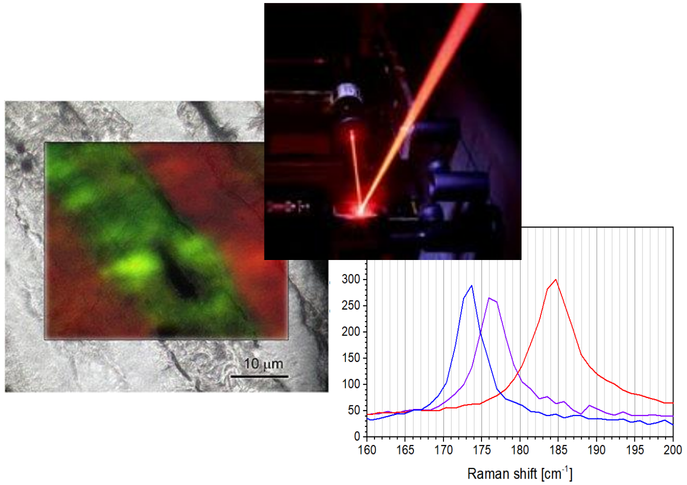
Introduction

Prof. Danilo Bersani

- Optical characterization of materials
- Raman and micro-Raman spectroscopy



PHD IN PHYSICS UNIPR

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INSTITUTE OF MATERIALS FOR ELECTRONICS AND MAGNETISM

Dott. Stefano Rampino

- Materials for photovoltaics
  - Thin-films depositions
  - Innovative applications for solar cells

Why Sb_2Se_3? The need for alternative materials

THIN-FILM SOLAR CELLS

PROs:

- Low cost materials and processes
- Low toxicity

amorphous silicon (a-Si)
PCE cell: 14% | PCE module: 9.2%

- High efficiency
- Reliable and well assessed production process

cadmium Telluride (CdTe)
PCE cell: 22.1% | PCE module: 19.0%

- High efficiency
- Low Toxicity

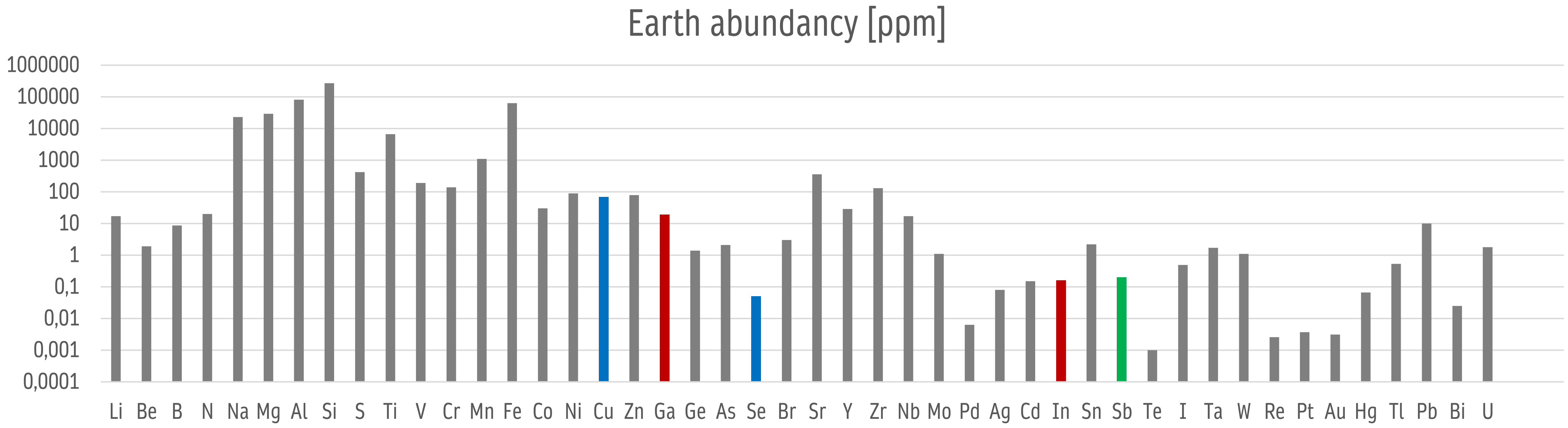
copper indium gallium selenide (CIGS)
PCE cell: 23.4% | PCE module: 19.2%

CONs:

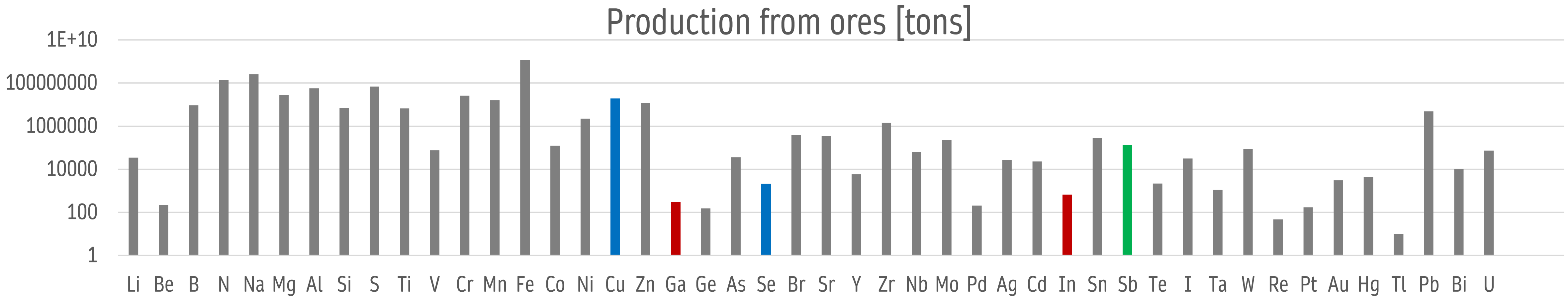
- Low efficiency (no big improvement since 2015)
- **Cadmium** toxicity/carcinogenicity (high recovery cost)
- **In** and **Ga** are expensive (not competitive with same efficiency crystalline Si)

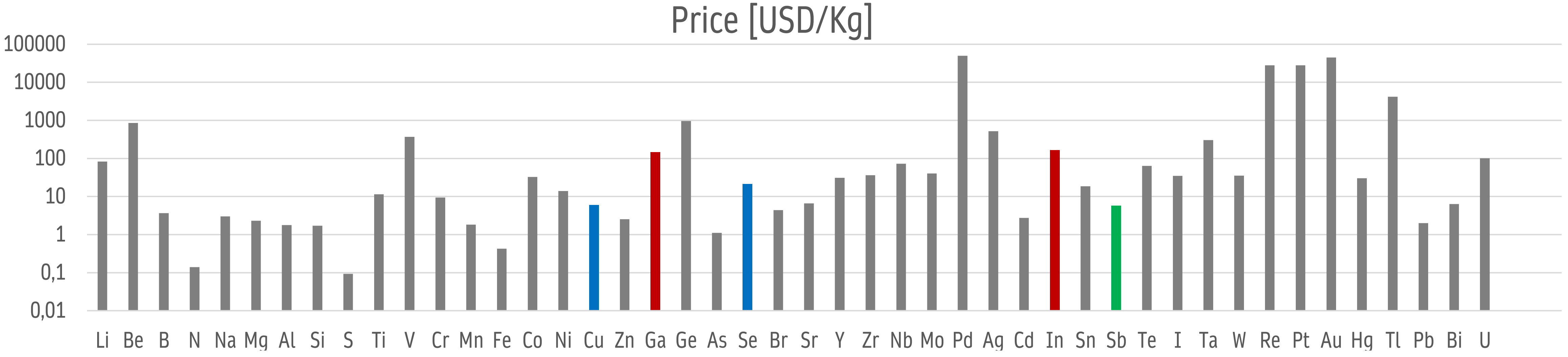
Need for a **low-toxicity, abundant,** and **cheap** alternative!

Why Sb_2Se_3? The need for alternative materials



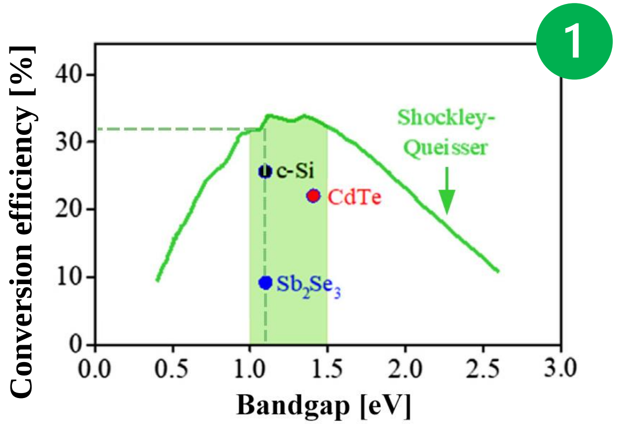
Why Sb_2Se_3? The need for alternative materials

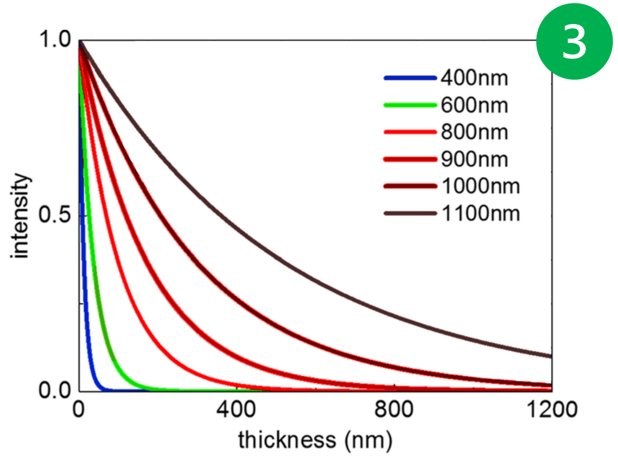


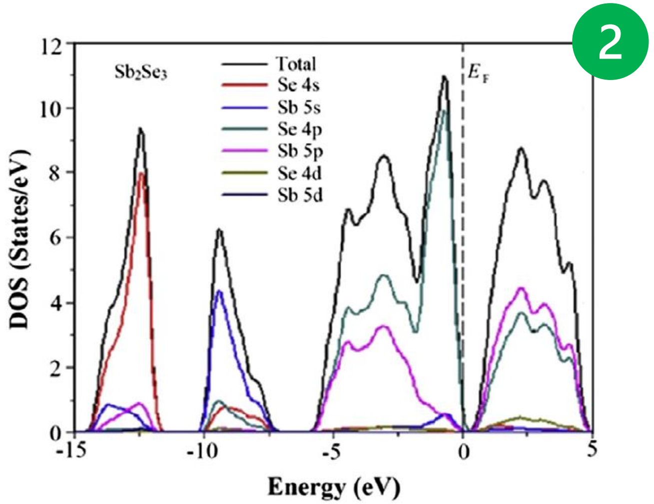


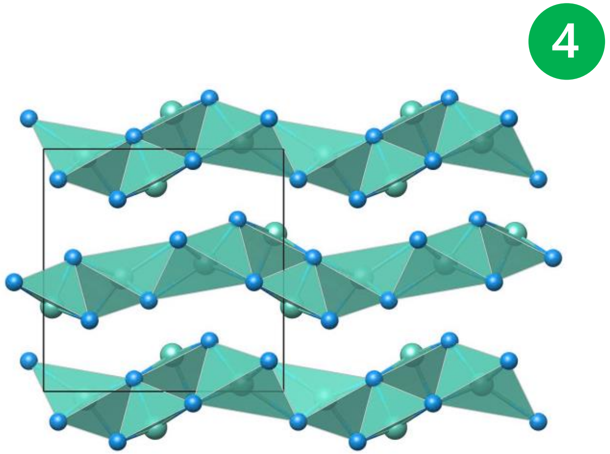
Sb_2Se_3 (ASe) is a very promising material…

1. Optimal bandgap
2. High density of states near the band-gap
3. High absorption coefficient and sufficiently good charge transport properties (photon penetration depth < charge diffusion length 1.7 μm)
4. The columnar crystal structure has almost “dangling-bonds”-free grain boundaries







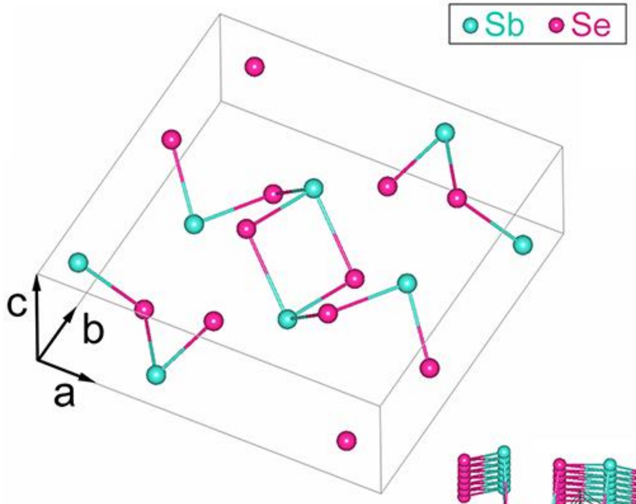


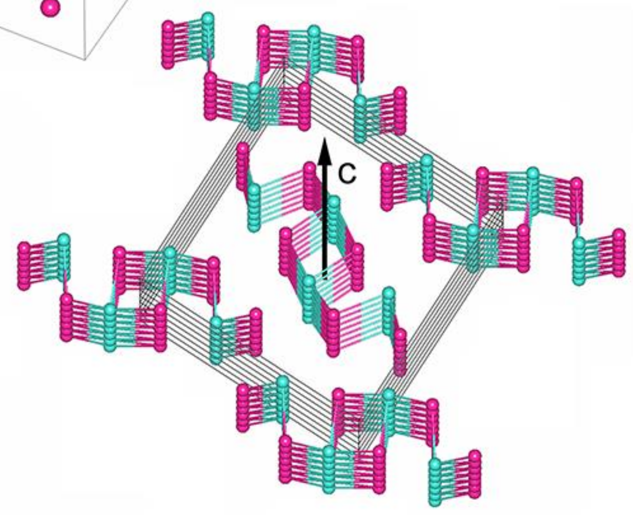
...with some challenges

1. Columnar crystal structure
   ➡ highly anisotropic properties

2. Typical free charge-carrier density is low: $\sim 10^{13}$ cm^{-3} (10^{16} cm^{-3} is generally required for solar cells)

3. High activation energies (from 0.2 to 1.0 eV) have been often measured
   ➡ deep trap levels in the band-gap (negatively affecting V_{OC})





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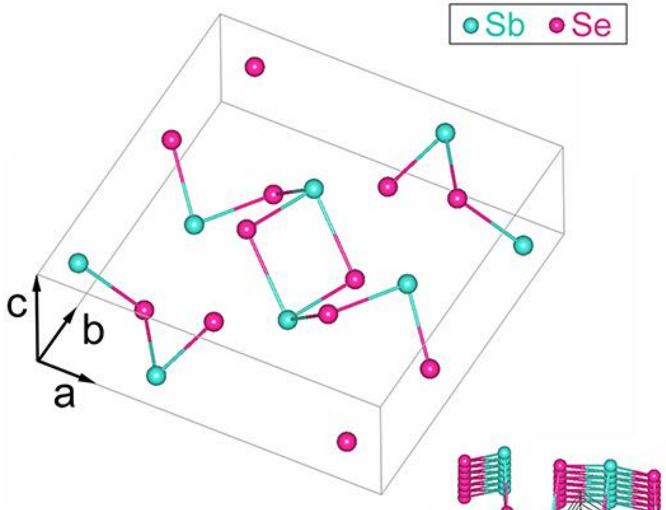
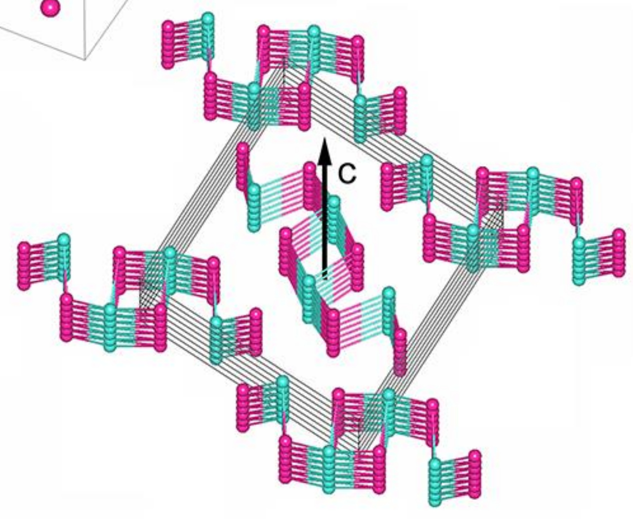


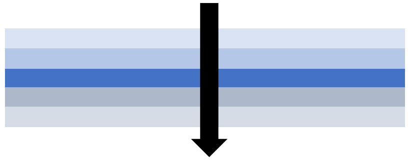


1 + 2

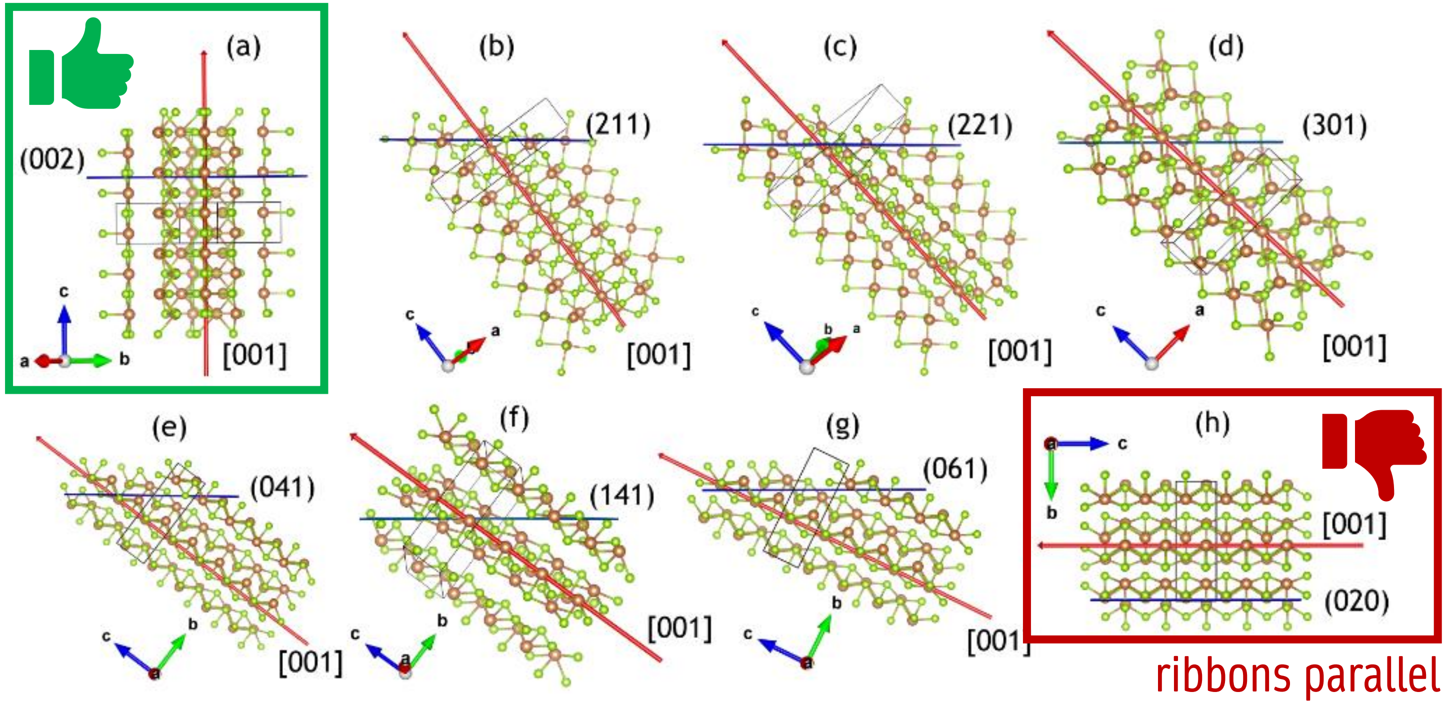
means that transport properties are
very bad in any direction
across the column-like structures (“ribbons”)

...with some challenges

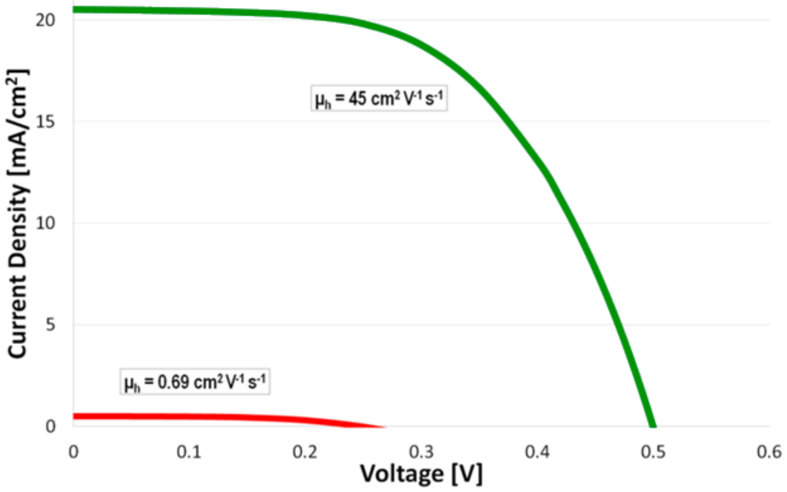
In a thin-film solar cell layered structure:



ribbons perpendicular to the substrate



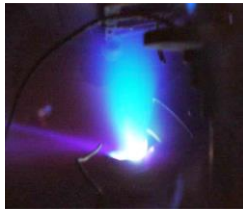
ribbons parallel to the substrate



Simulated J-V curve of ASe/Mo solar cells, assuming a hole mobility of 45 $cm^2\ V^{-1}\ s^{-1}$ (perpendicular orientation - green line) and of 0.69 $cm^2\ V^{-1}\ s^{-1}$ (parallel orientation - red line)

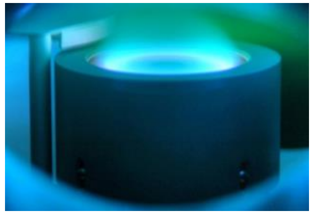
Deposition techniques used for ASe thin-films

LT-PED
Low Temperature Pulsed Electron Deposition



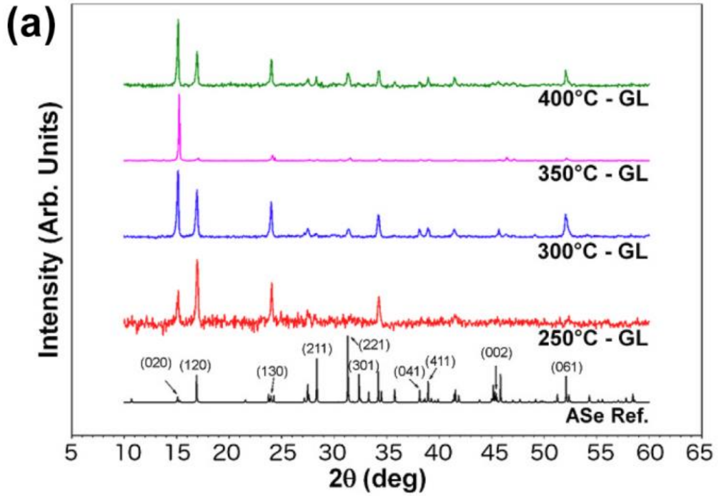
- high energy ($E_{partic.} \approx$ 1-10 keV)
  (film crystallization is favored also when low substrate temperature is used)
- low cost
- **very good deposition rate** (7.5Å/s)
- **target is "ablated"**
  (stoichiometric transport of elements from target to substrate, even for compounds with complex stoichimetry and/or not-congruent melting point, also for long deposition time)

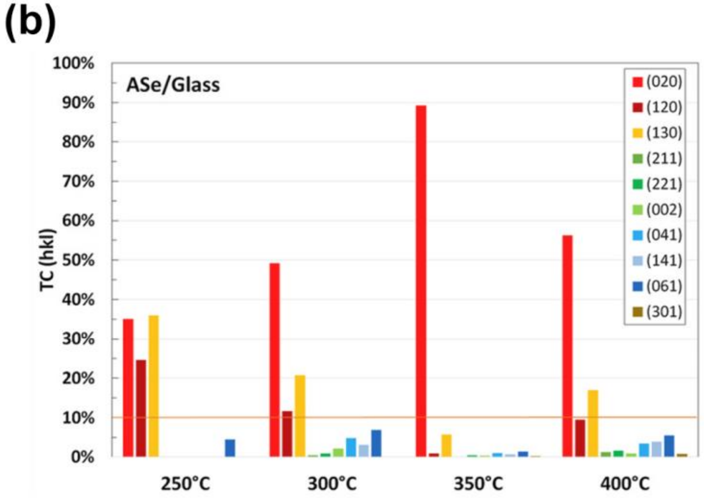
MS
Magnetron Sputtering



- high energy ($E_{partic.} \approx$ 10-100 eV)
  (film crystallization is favored also when low substrate temperature is used)
- low cost
- good deposition rate (2Å/s)
- target is "eroded" almost stoichiometrically
  (less problems when binary compounds with congruent melting point, like Sb_2Se_3, are used)
- **easy extension to large areas and industrial production**

ASe thin-films by PED



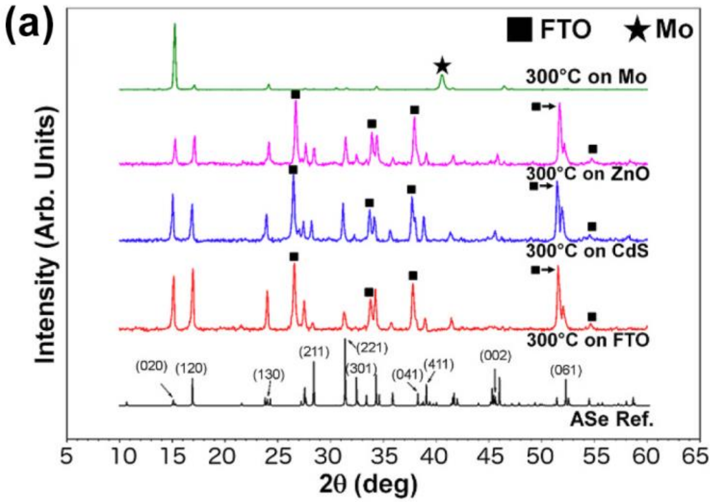


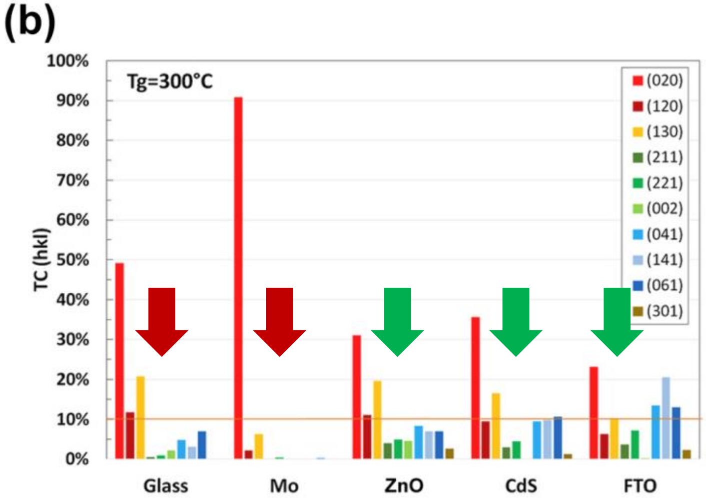
CRYSTALLIZATION:

- Optimal substrate temperature: >300°C

GRAIN TEXTURE ALIGNEMENT:

- On glass and Mo substrates ribbons lying parallel to the substrate are dominant
- On ZnO, CdS and FTO ribbons orientations have a higher vertical component





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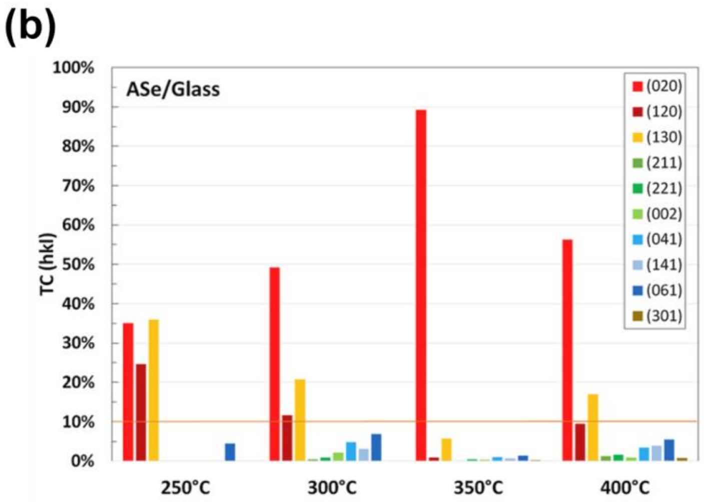
ASe thin-films by PED

$$\mathrm{TC}(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\sum_n \frac{I(h'k'l')}{I_0(h'k'l')}} \times 100\%$$

A Texture Coefficient TC(hkl)>10% means preferential orientation along (hkl)

BAD ORIENTATIONS

GOOD ORIENTATIONS



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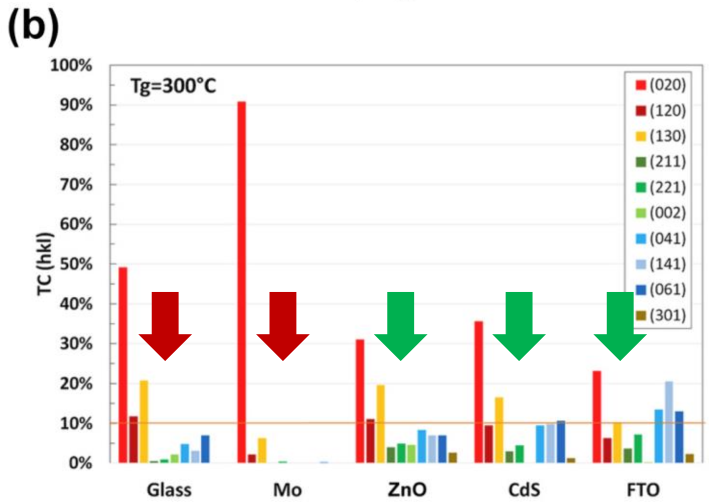
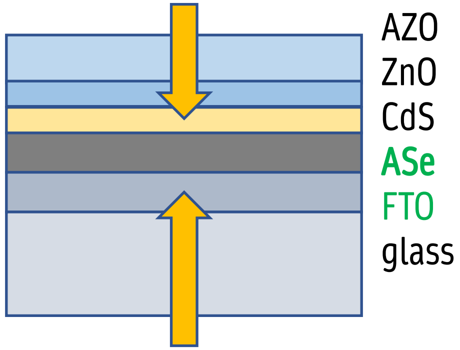
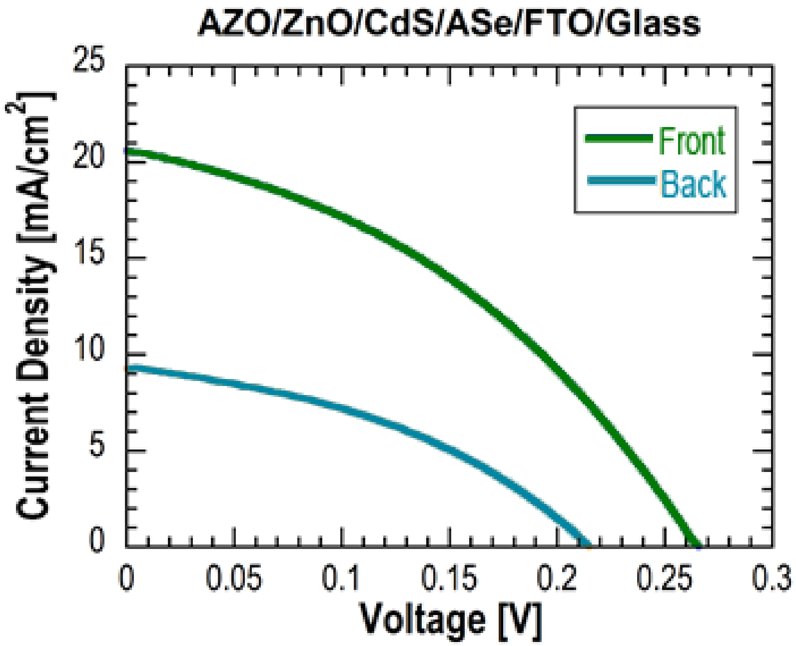


Test of solar cells based on ASe films by PED

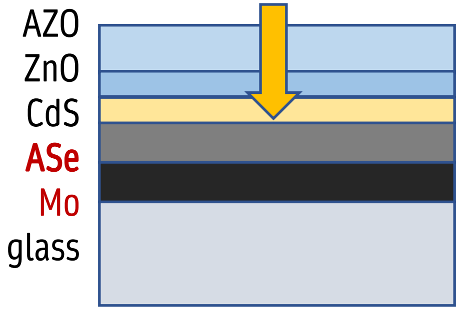
ASe deposited on FTO (bifacial cell on transparent FTO back contact)



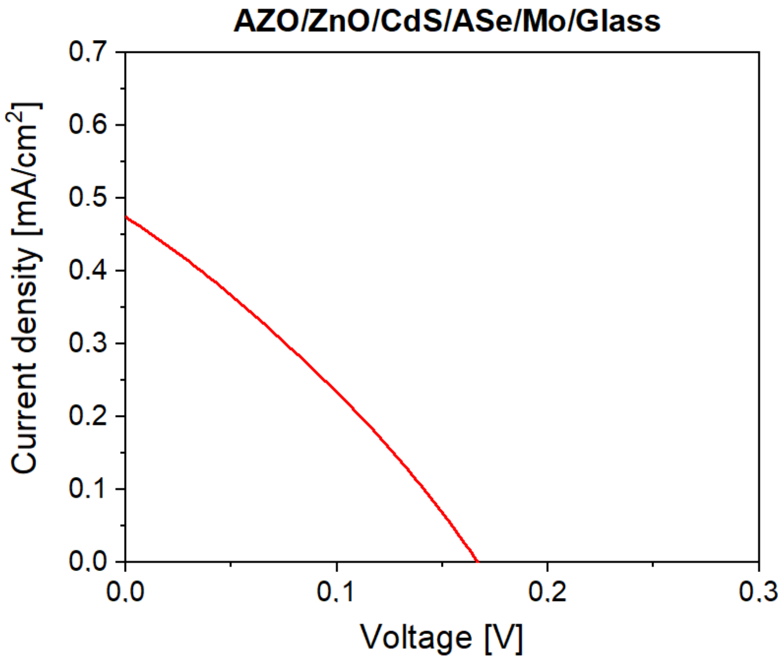


Jsc	20.28 mA cm^{-2}
Voc	256 mV
FF	39.2%
PCE	2.1%
Rs	2.2 Ω cm^{-2}
Rsh	94 Ω cm^{-2}

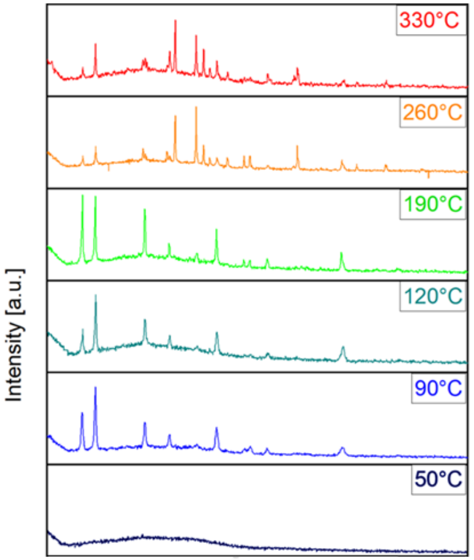
ASe deposited on Mo (standard cell on Mo back contact)

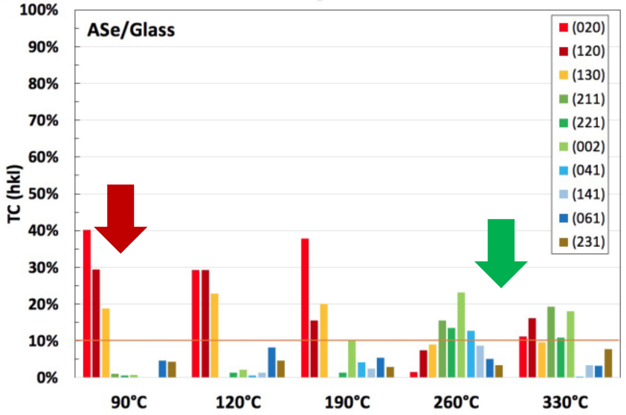


Jsc is almost 50 times lower



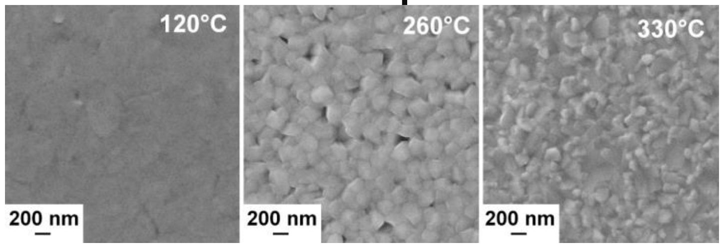
ASe thin-films by MS





CRYSTALLIZATION:

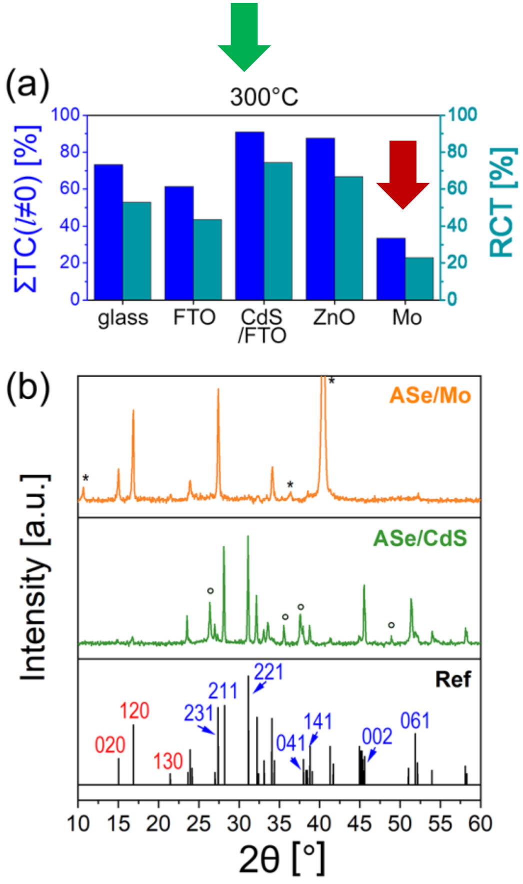
- Crystallization occurs for T>90°C
- Optimal substrate temperature for T>260°C



GRAIN TEXTURE ALIGNEMENT:

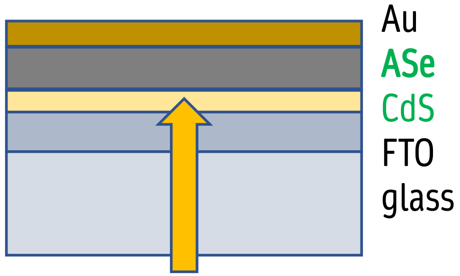
ΣTC(l≠0) is the summation of TC values for orientations not lying parallel to the substrate

- At 300°C "good" preferential orientations of ribbons are higher than in films by PED
- CdS induces the best orientation
- Mo induces the worst orientation

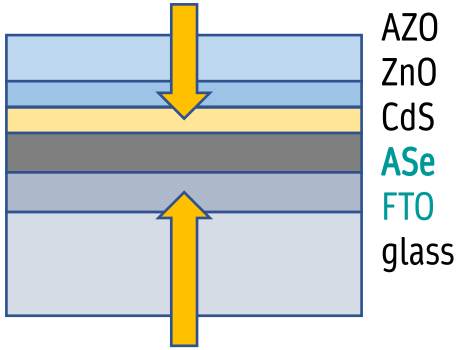


Test of solar cells based on ASe films by MS

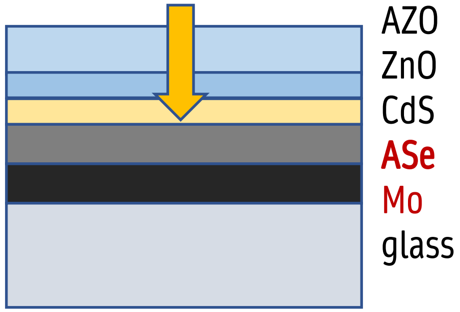
ASe deposited on CdS (superstrate cell on transparent CdS/FTO)



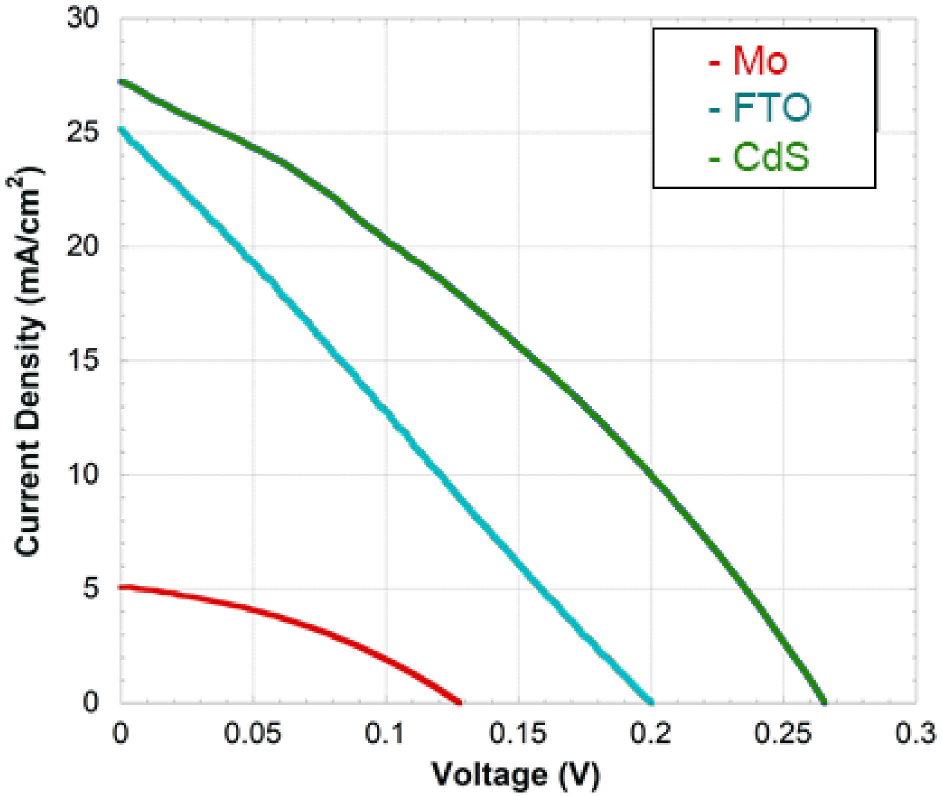
ASe deposited on FTO (bifacial cell on transparent FTO back contact)



ASe deposited on Mo (standard cell on Mo back contact)

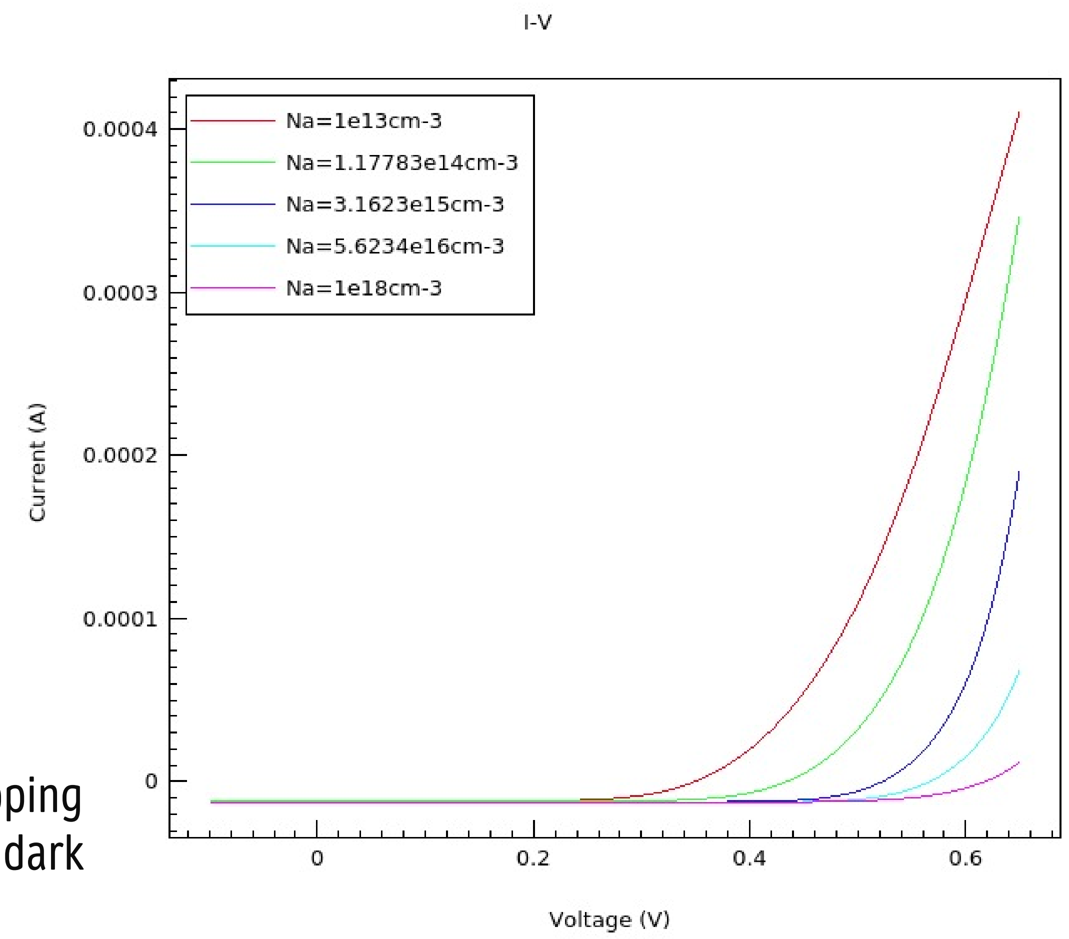


Jsc	27.06 mA cm^{-2}
Voc	266 mV
FF	32.7%
PCE	2.36%
Rs	1 Ω cm^{-2}
Rsh	70 Ω cm^{-2}



Doping of ASe films

- PCE is still low also because of ASe low free charge-carrier density
- The right doping may improve material conductivity
- Effective doping is expected to increase V_{OC} in solar cells

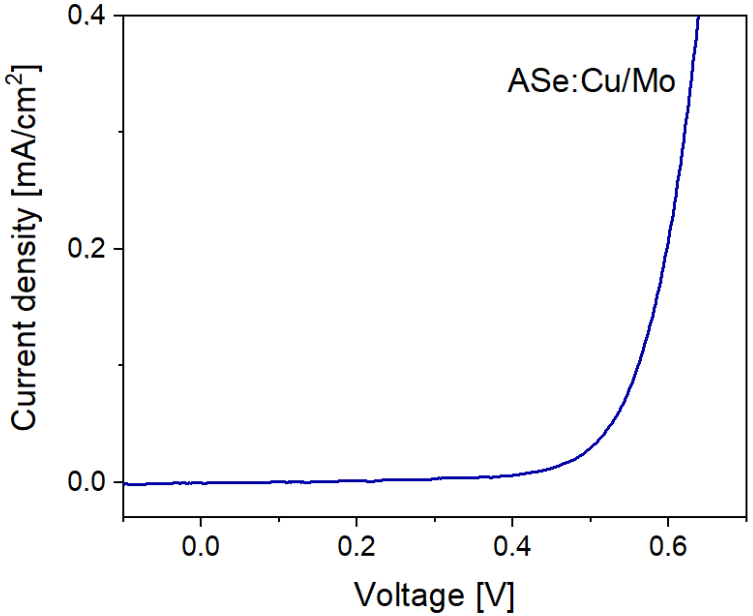


simulation of the possible effect of doping on ASe I-V characteristics in dark

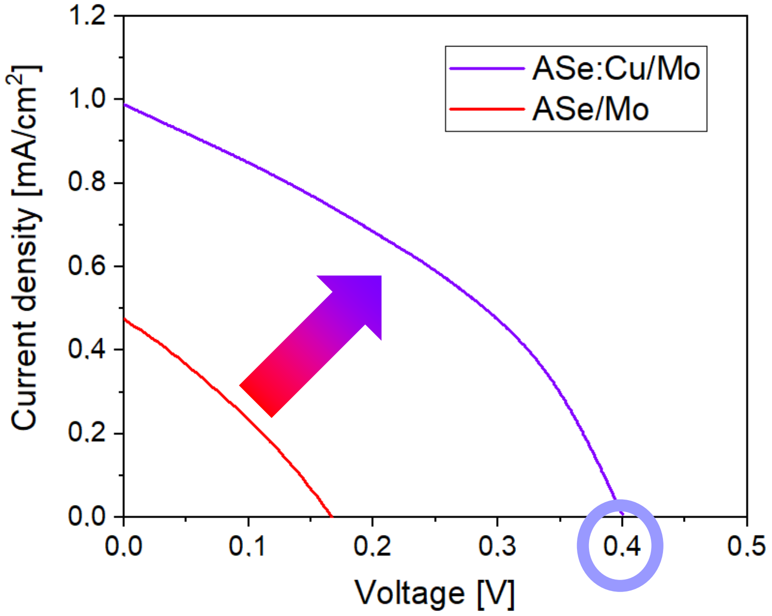
Preliminary results on Cu doping

- Preliminary test have been made with Cu doping
- A doped Cu target has been employed for the deposition of ASe:Cu thin-films by PED
- Effective doping is clearly visible

in dark



under illumination



Conclusions

ACHIEVED GOALS:

- The best growth conditions have been found for both techniques (PED and MS) in order to improve efficient ribbons orientation
- Preliminary experiments have been performed to improve the charge carriers' density by doping (Cu) with promising results
- The effect of both improvements has been successfully verified by testing the cells performance

NEXT STEPS:

- Trying different dopants (and test their effect on deep-levels defects)
- Optimization of the other layers in the cell (buffer layer, back contact with HTL, etc.)

Thank you!

For further questions/details contact me: giulia.spaggiari1@unipr.it / giulia.spaggiari@imem.cnr.it