Thermoelectric performance of Ag_2Se films grown by Pulsed Hybrid Reactive Magnetron Sputtering (PHRMS) on glass and flexible substrates

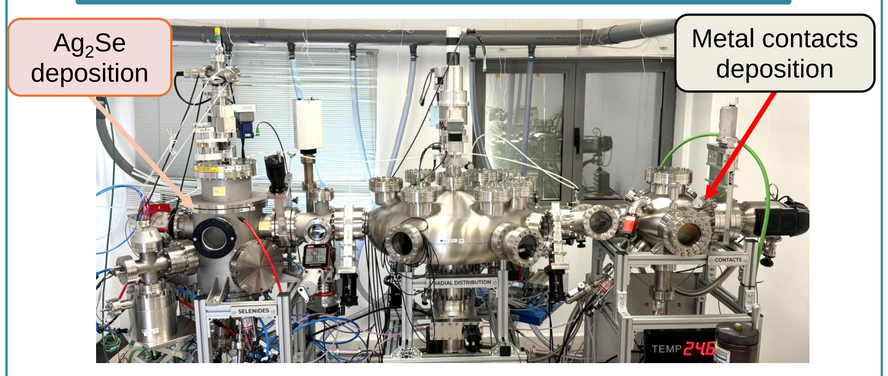
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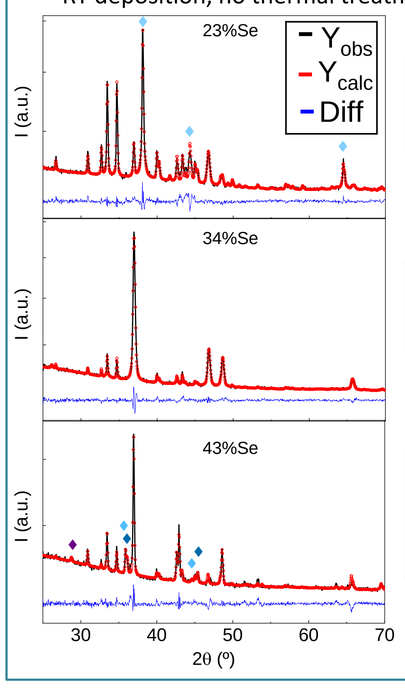
1. Introduction

- Orthorhombic β-Ag_2Se (naumannite) is an n-type semiconductor with maximum reported zT of 1.57 for bulk form at 398 K [1] and 1.33 [2] for thin films.
- Many fabrication approaches require time-consuming sintering processes at elevated pressure and temperature which can lead to inhomogeneity, as over 135°C Ag_2Se experiments a phase transition and acts as a superionic conductor.
- Studying low T synthesis techniques [3-5] is of great interest also for the fabrication of TEG devices in flexible materials based on polymers for powering wearables.
- A slight Se excess from the stoichiometric ratio is beneficial for thermoelectric performance, reducing the carrier concentration to an optimal point [6-7] and eliminating Ag leftovers.

2. Film growth by PHRMS



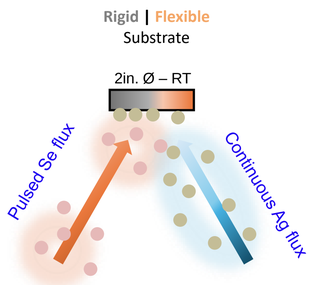
- Semi-industrial multichamber deposition system
- Pulsed Hybrid Reactive Magnetron Sputtering (**PHRMS**): Dual source for Ag_2Se, pulsed thermal evaporation for Se, sputtering for Ag
- RT deposition, no thermal treatment



<33% Se
β-Ag_2Se
Ag cubic

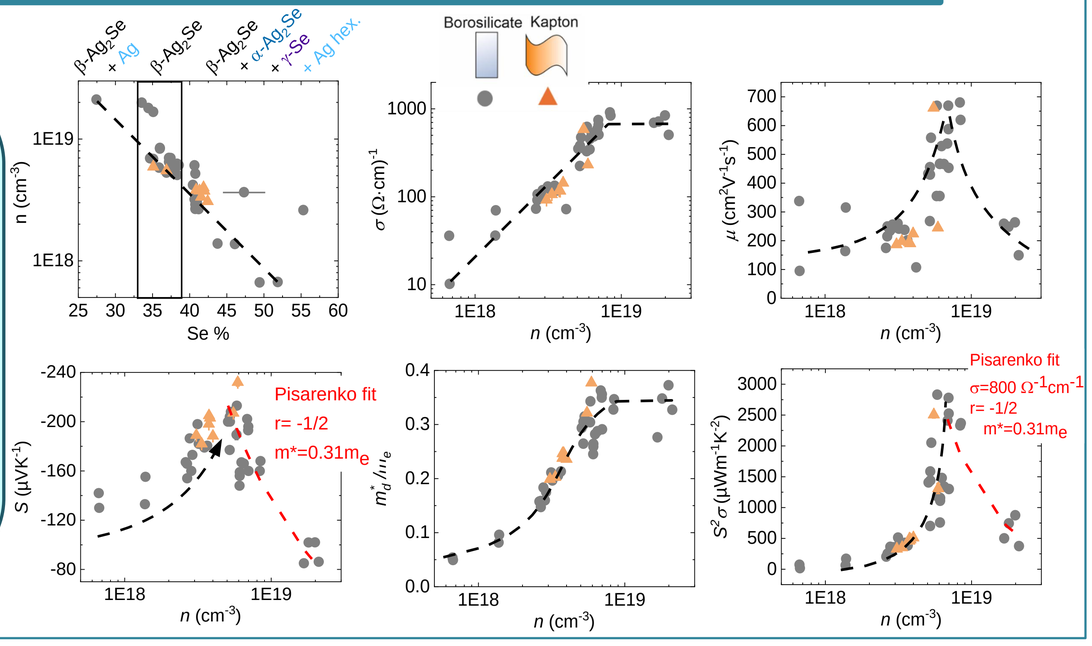
33-38%Se
β-Ag_2Se

>38% Se
β-Ag_2Se
Se cubic
α-Ag_2Se
Ag hex.

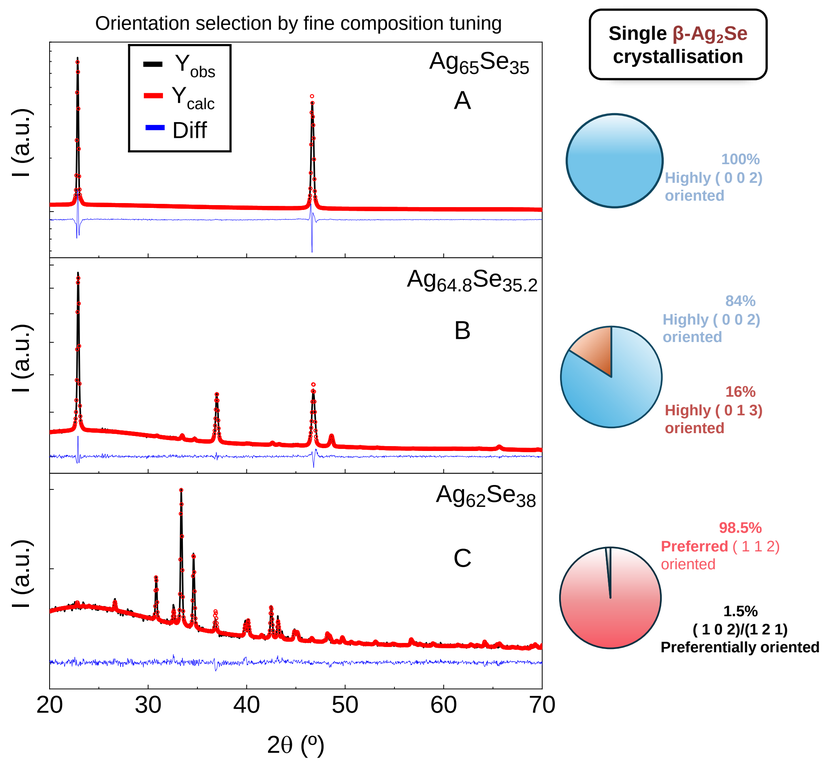


3. Thermoelectric and electrical transport properties

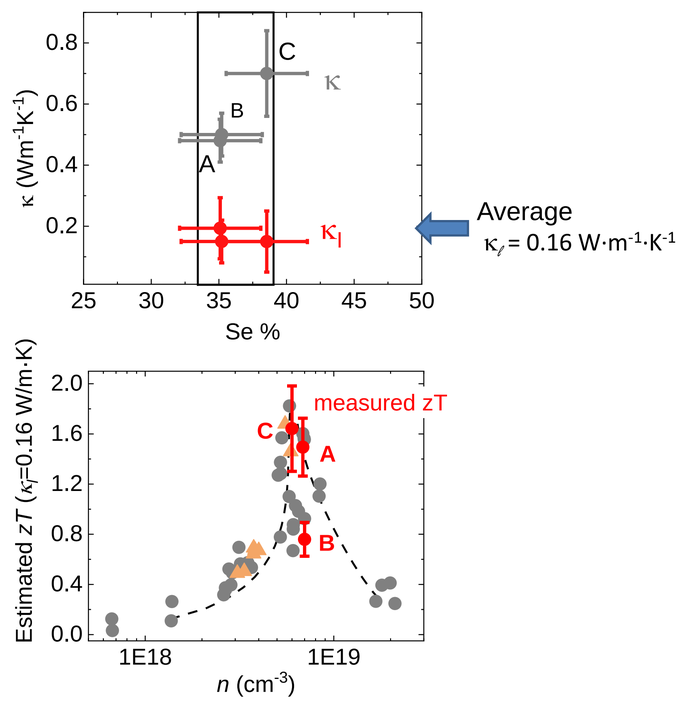
- **Maximum S = -220 ± 20 µV/K** for $Ag_{65}Se_{35}$ (single β-Ag_2Se phase)
- **PF** of **2500** and **2800 µW·m^{-1}·K^{-1} at RT on flexible and solid films** are achieved.
- Optimization of *n* and phase crystallization.
- For single single β-Ag_2Se phase and *n* = 7·10^{18} cm^{-3} mobility and S reaches maximum.



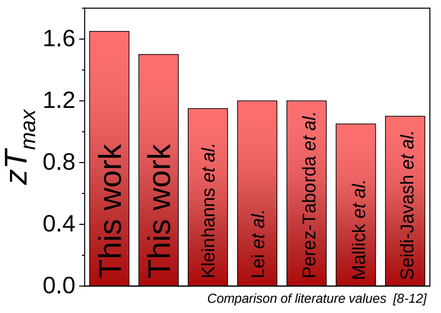
4. Thermal transport



Single β-Ag_2Se crystallisation

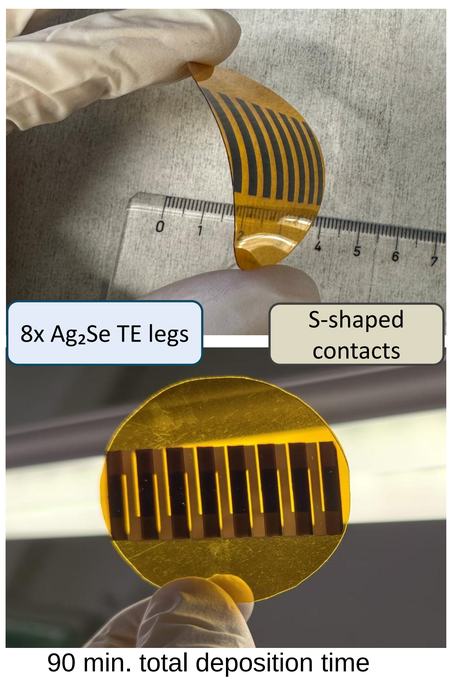


- Time-domain thermo-reflectance (TDTR) used of thermal conductivity
- Same value of κ_l independently of growth orientation → **isotropic lattice thermal transport**
- Maximum **zT values of 1.5 and 1.65 at RT on glass and estimated 1.7 on flexible substrate** are obtained

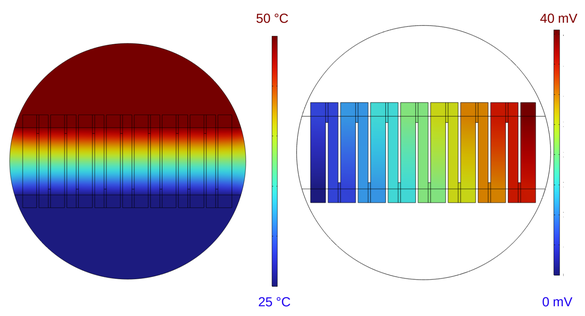


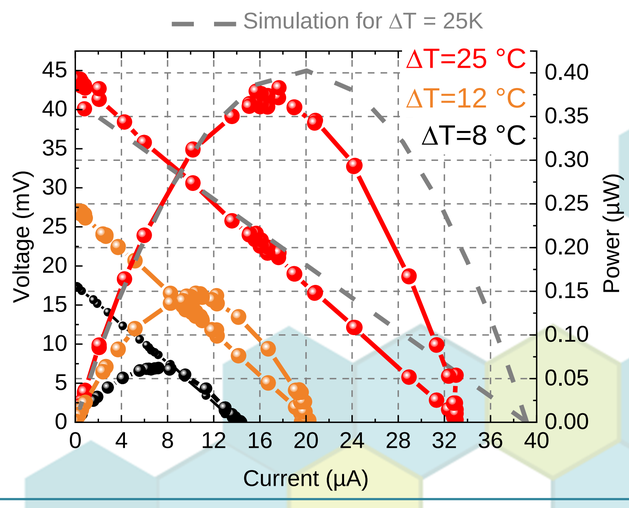
Comparison of literature values [8-12]

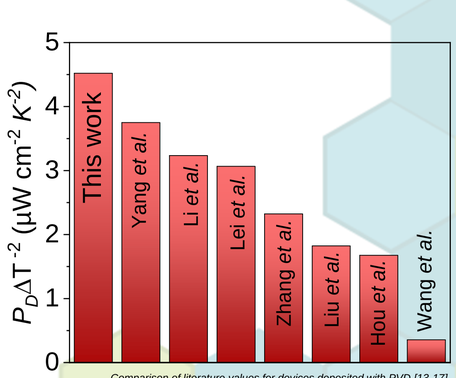
5. Flexible device 2"Ø



90 min. total deposition time







Comparison of literature values for devices deposited with PVD [13-17]

- V_{OC} = 45 mV for ΔT=25K
- P_D = 2.8 mW·cm^{-2}
- S = -225 µV/K
- COMSOL simulation with measured material parameter describes the measured device behavior.

Conclusions

- **High-quality crystalline Ag_2Se thin films were successfully synthesized at RT via PHRM**, demonstrating a fine tuning of composition and carrier concentration n.
- Maximum performance at the range of 5-7·10^{18} cm^{-3}, with **maximum PF values of 2800 µW·m^{-1}·K^{-1} and 2500 µW·m^{-1}·K^{-1} on rigid and flexible films**, respectively.
- The intrinsic nanometric size of the crystallites reduces drastically the lattice thermal conductivity of **Ag_2Se to 0.16 W·m^{-1}·K^{-1} irrespectively from growth orientation**, therefore allowing an isotropic thermal transport approximation in polycrystalline films.
- Assuming isotropic thermal transport, **zT values of 1.65 and 1.5 are measured**, both surpassing highest reported zT values for Ag_2Se.
- The **room temperature-compatible technique** employed in this work allows for **fast flexible device fabrication** avoiding posterior sintering processes at elevated temperature or pressure.
- A **flexible device** was fabricated with state-of-the-art **normalized power density of 4.5 µW·cm^{-2}K^{-2}** assessing the reproducibility, homogeneity and quality of the synthesis process.

References

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