New amorphous materials with applications in optics, optoelectronics, chemistry, medicine and biology prepared by pulsed laser deposition

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Introduction

Chalcogenide glasses and films in focus of many labs:-many **present and potential applications, e.g.:**

- **optical IR elements and memories,** filters, holography
- fibers, photoresists, lasers, gratings, waveguides, amplifiers, …
- planar devices, optical circuits, optical signal processing,
- ionic and optical sensors, microbateries,
- X-ray sensors, analysers, etc.

Many systems studied, mostly sulfides, selenides, recently also tellurides, e. g. GeTe, Ge-Sb-Te, …. and others:

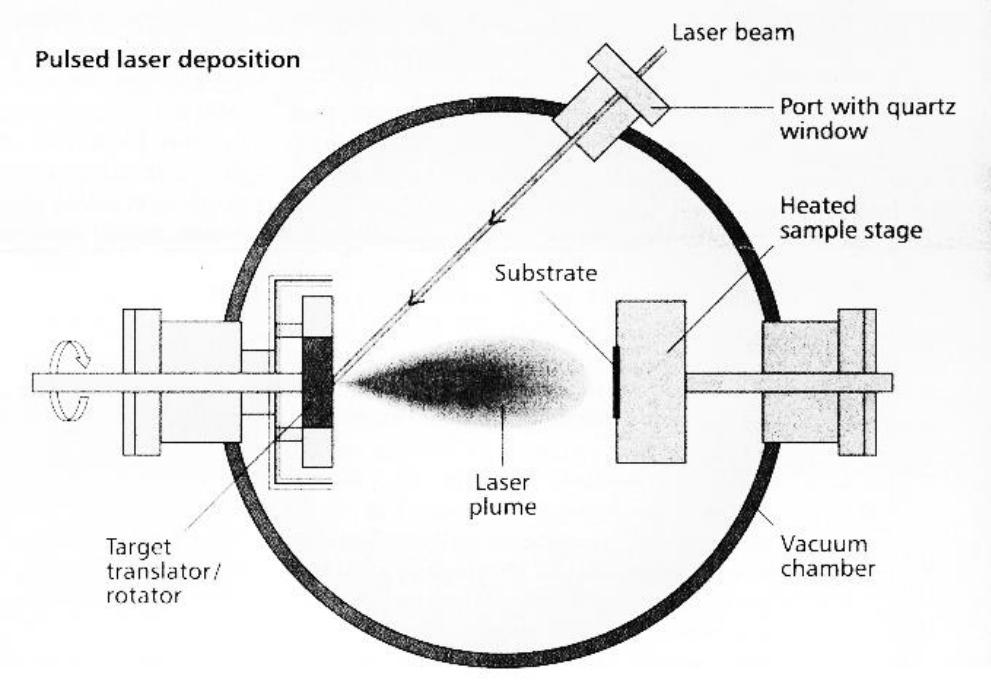
search for new materials, new properties and new effects

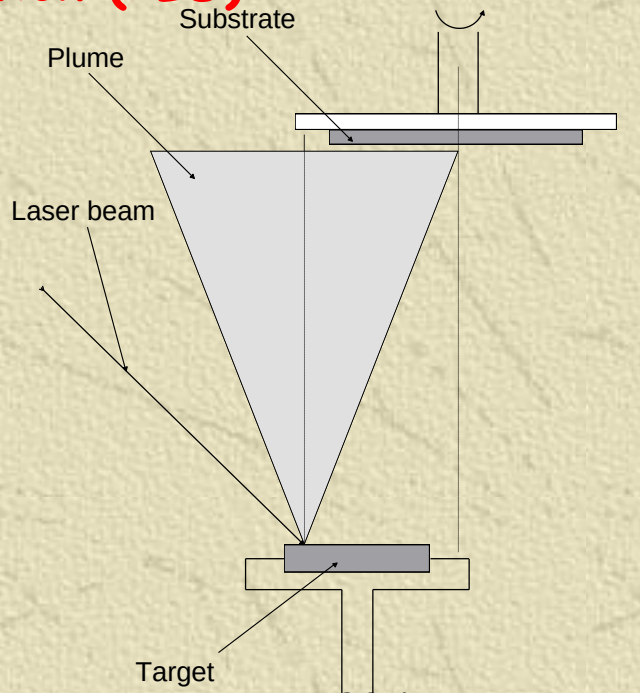
(e.g. for optical storage, optical signal processing, multilevel optical and electrical storage, biology, medicine, ...)

thin films, binary, ternary or multinary systems, no optimal:

- preparation, properties, applications, performance
- **often - difficulties in preparation of thin films, especially binary, ternary, multinary,** with different volatility ⇒

A possible solution: pulsed laser deposition (PLD)





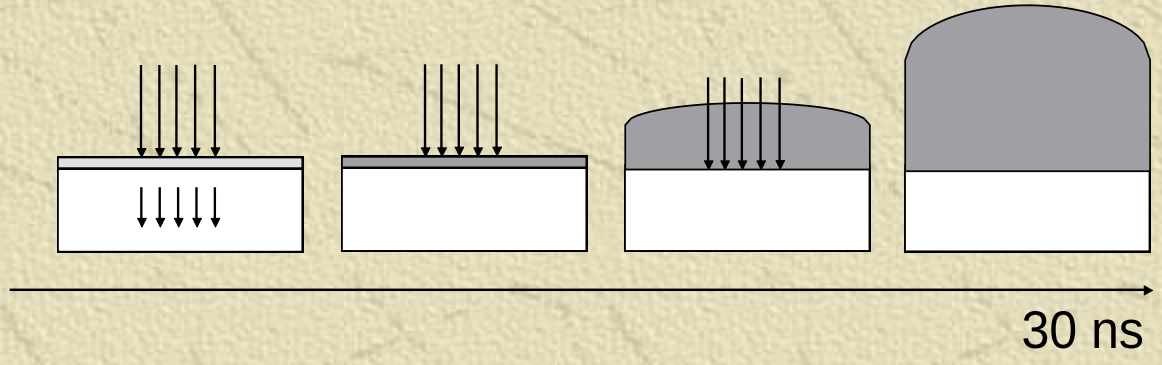
– target off line

Absorption
Thermal conduction

Surface melting

Vaporization
Plasma formation

Plasma emission



short pulses (ns or fs) of high intensity and energy ~ **10^8 - 10^9 W/cm^2 (for ns, for fs much higher, up to 10^{16} W/cm^2)** in UV, VIS or IR region,

our: 248nm, hν = **5 eV, 480 kJ/mol > chemical bonds energies: evaporation, atomization, formation of ionized plume**

- **vapors in plume are very hot (~X.10^3K, dissociation?, new compounds are formed in hot plasma,**
- **quenched quickly by condensation,**
- **the obtained films far from equilibrium**
- **many materials, e.g. multinary compounds with different volatility components. Every pulse evaporates all components, independently on their vapor pressure.**
- **films of unusual composition, e.g. Ga-La-S, PbS-AgI-As-S, Tl-Ag-As-I-S, can be prepared (mostly amorphous).**

- the parameters of pulses (e.g. energy, frequency and number) can be controlled; **the properties of films and their stoichiometry can be controlled as well.**

The mechanism of evaporation and film formation is complex :

- **exfoliation**
- **fragmentation (the energy of fragmentation: much lower than E of evaporation**
- **surface or subsurface evaporation**
- **surface melting**
- **bubles formation**
- **phase explosion** (from superheated liquids) .
- **particulates formation,**
- **plume formation**

- **dissociation, atomization, plasma formation and ionization**

(e.g. **e-**, ions, unusual states, e. g. Cu^{5+}, Cu^{4+}, Cu^{3+} were found)

- **vapors condensation, their interaction, film formation and relaxation, self-annealing**

The **kinetic energy** (temperature) of the **particles in the plume is high (up to keV)** $\Rightarrow$

chemical reactions among particles (fragments) during or after condensation **are quicker** (easier, self-annealing) $\Rightarrow$ the structure of some ablated films can be closer to the structure of target glass – contrary to films prepared by thermal evaporation (TE).

Sometimes **higly oversaturated films with unusual composition and properties are obtained**, e.g. As-rich As-Se system

In some cases, e.g. in As-S system:

a) the fragments in the plume have different rates of condensation- new compounds are formed in the hot plasma → composition change

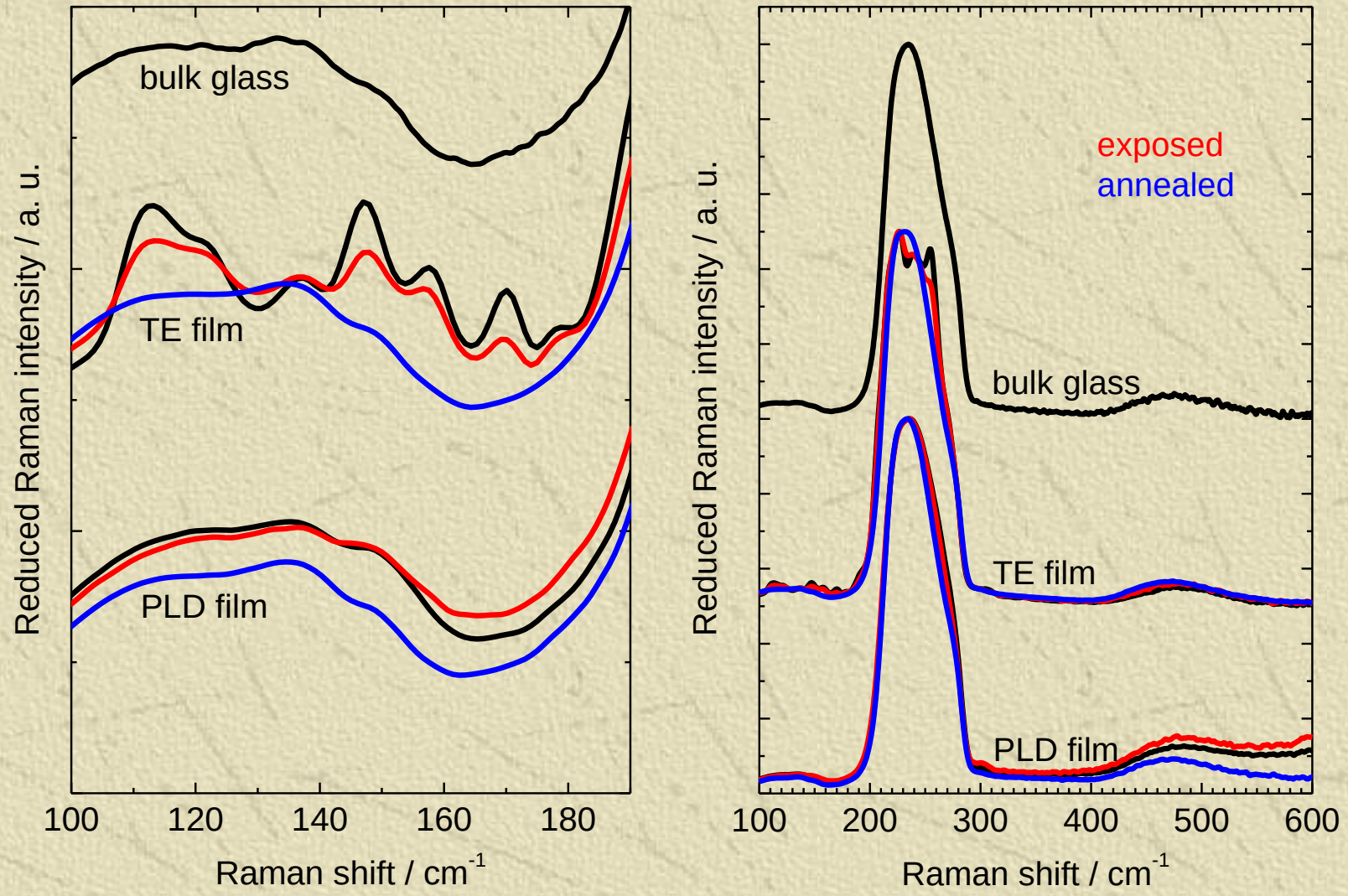
b) **the structure is different from thermally evap. films (TE)**

In this paper: ablated films

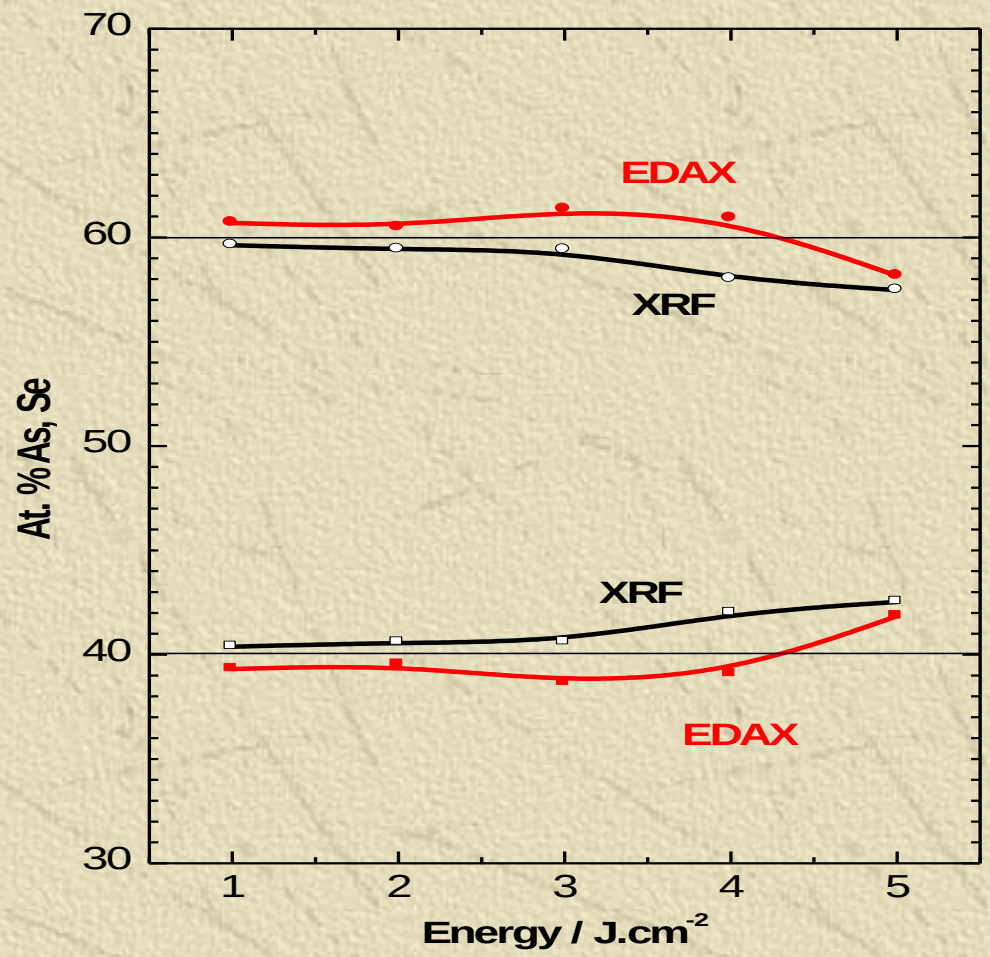
- *As-S, As-Se, Ge-Se, Ge-Ga-Se and RE doped systems*

- *tellurides of eutectic compositions*
(Sn-Te, In-Te, Sb-Te)

- other systems, *e.g. Ag-As-S, Ag-Sb-S and As-In-S:Sm*



Raman spectra of bulk As_2Se_3 glass and As-Se thin films



Composition of As-Se thin films prepared by PLD on energy density of the laser beam:
full squares – As content from EDAX, open squares – As content from XRF, full circles – Se content from EDAX , open circles – Se content from XRF;

The PLD As_2Se_3 films contain (in comparison with TE films) less 'wrong' As-As and Se-Se bonds and less As_4Se_4, As_4Se_3, Se_8 or Se_n particles.

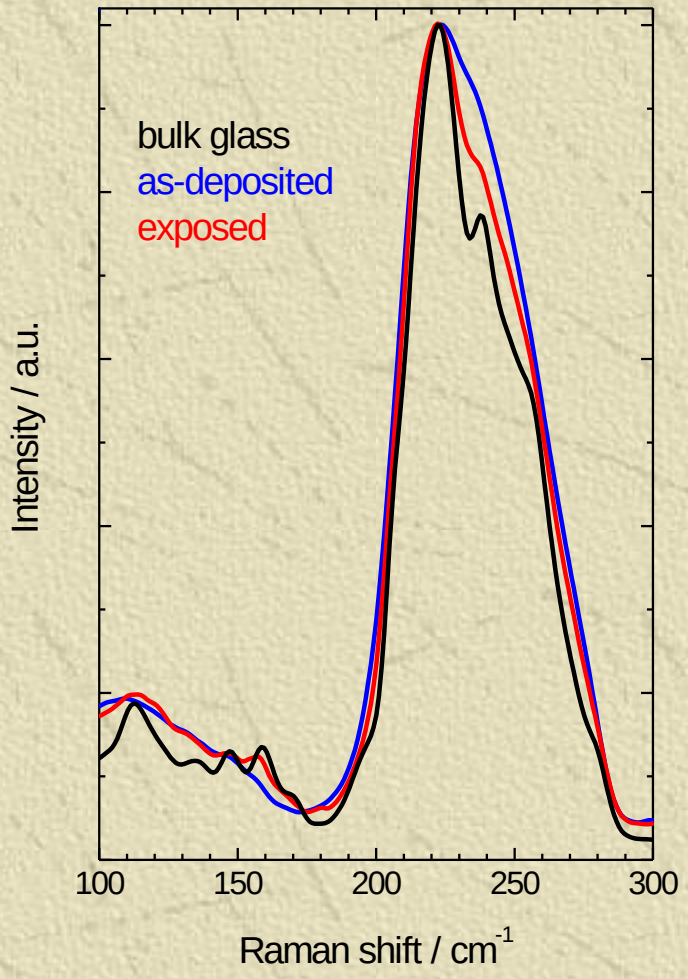
- High kinetic energy of plasma-plume particles enables their interaction ⇒ (Eqs. 1-3), densities of As_4Se_4, As_4Se_3, Se_n are lowered, e.g.

$$As_4Se_4 + (2/n)\ Se_n = 2\ As_2Se_3 \qquad (1)$$

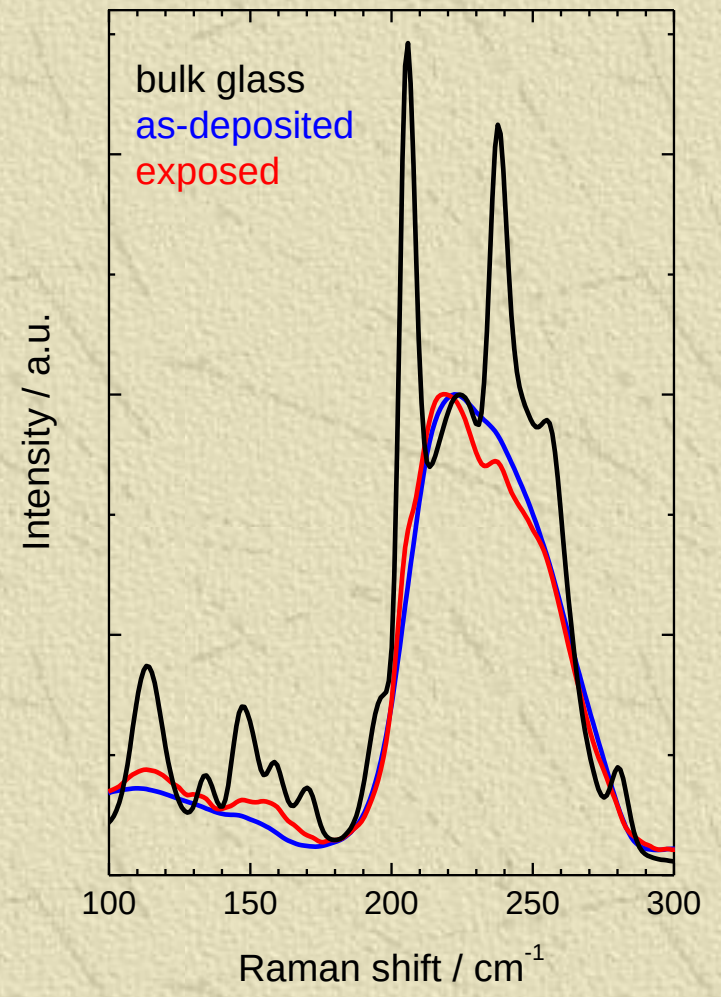
$$As_4Se_3 + (3/n)\ Se_n = 2\ As_2Se_3, \qquad (2)$$

or just

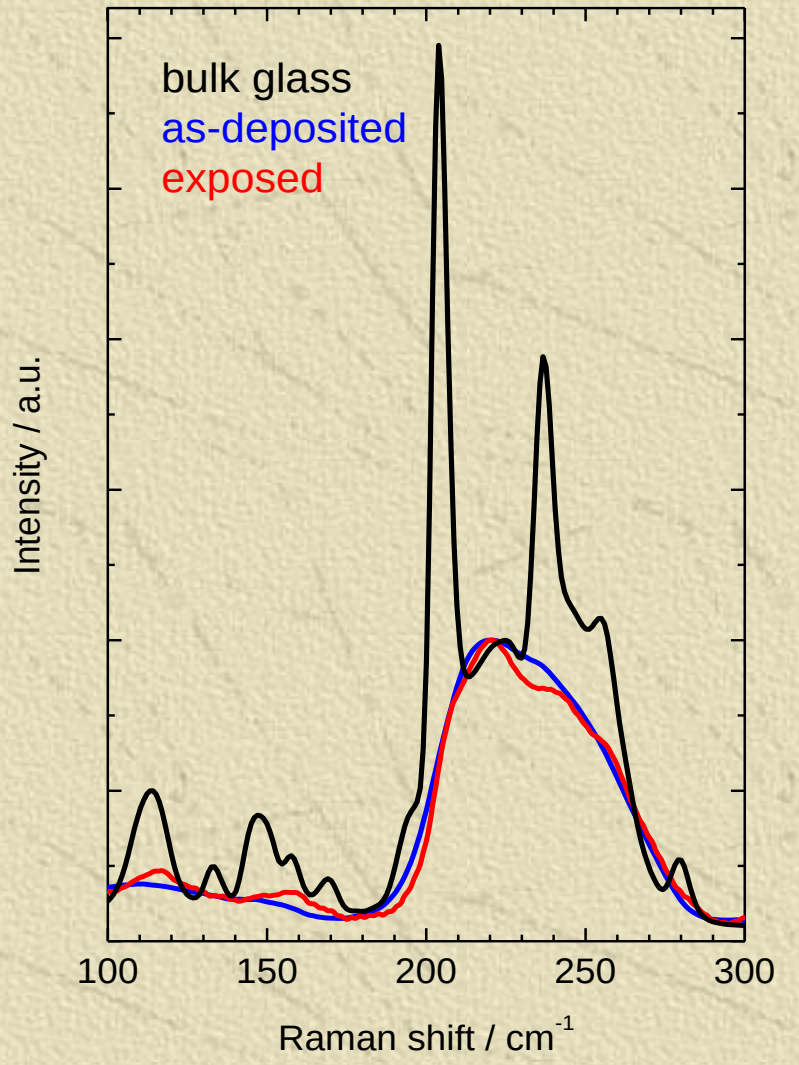
$$|As\text{-}As| + |Se\text{-}Se| = 2|As\text{-}Se| \qquad (3)$$



Raman spectra of bulk **$As_{50}Se_{50}$** glass (full line), as-deposited (dashed line), and exposed (dotted line) PLD $As_{50}Se_{50}$ thin films



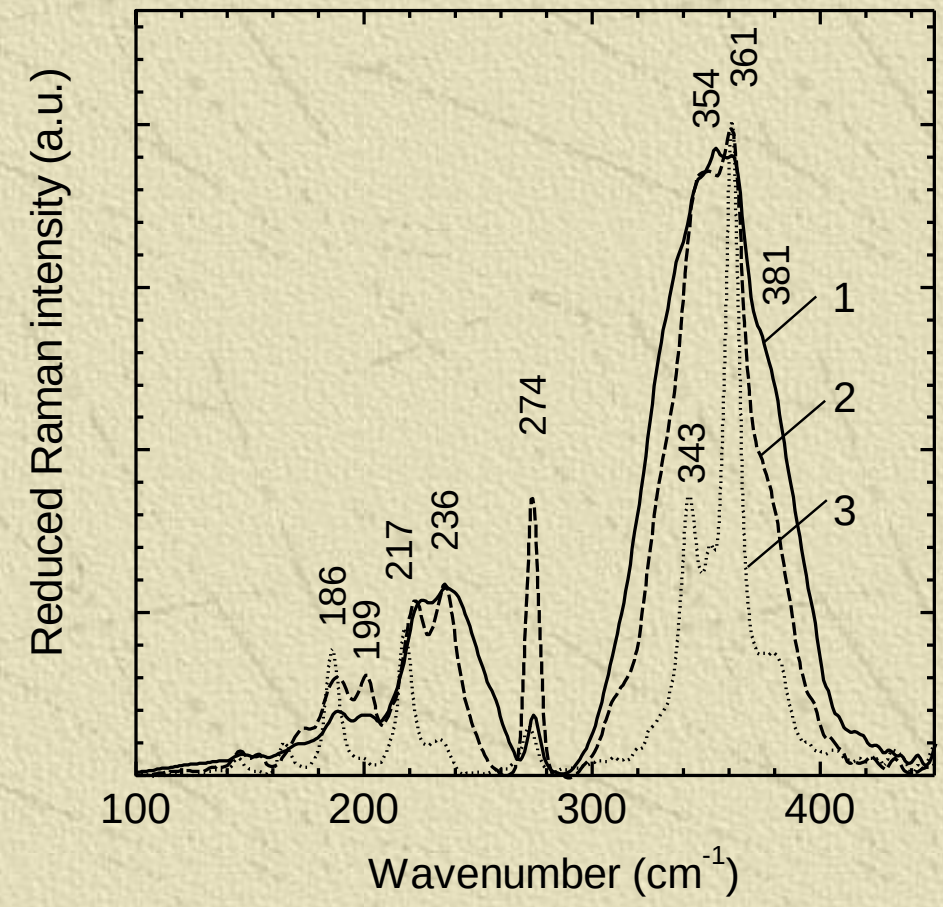
Raman spectra of bulk **$As_{57.14}Se_{42.86}$ (As_4Se_3)** glass (full line), as-deposited (dashed line), and exposed (dotted line) PLD As_4Se_3 thin films



Raman spectra of bulk **$As_{60}Se_{40}$** glass (full line), as-deposited (dashed line), and exposed (dotted line) PLD $As_{60}Se_{40}$ thin films

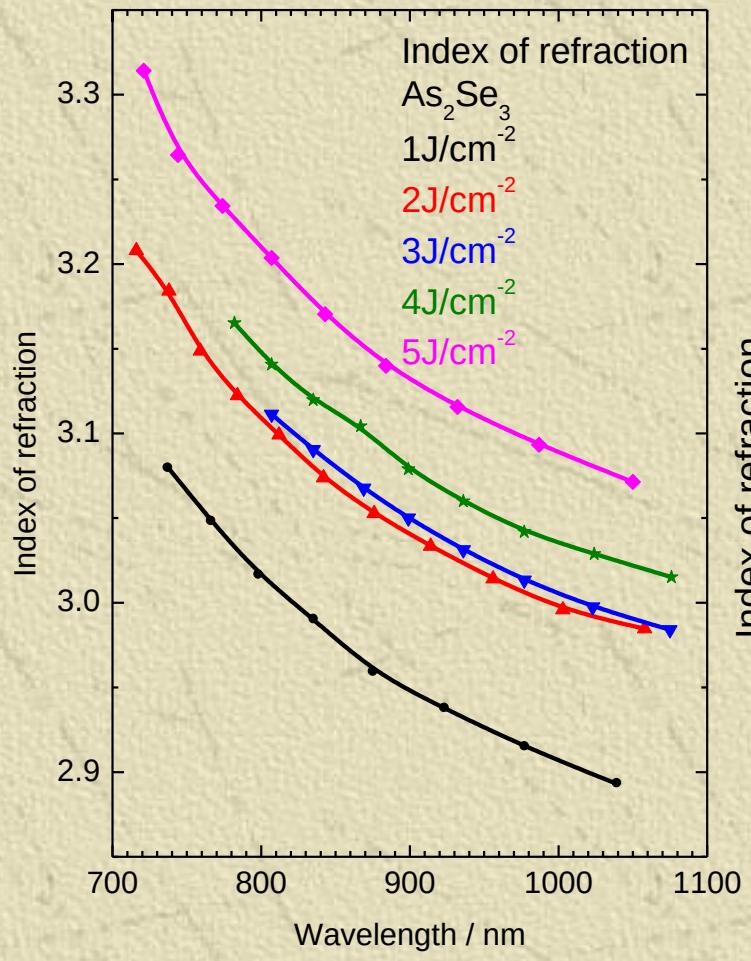
In **As-S system**: thermal dissociation
$2As_2S_3 = As_4S_4 + S_2 \Rightarrow$ change of composition

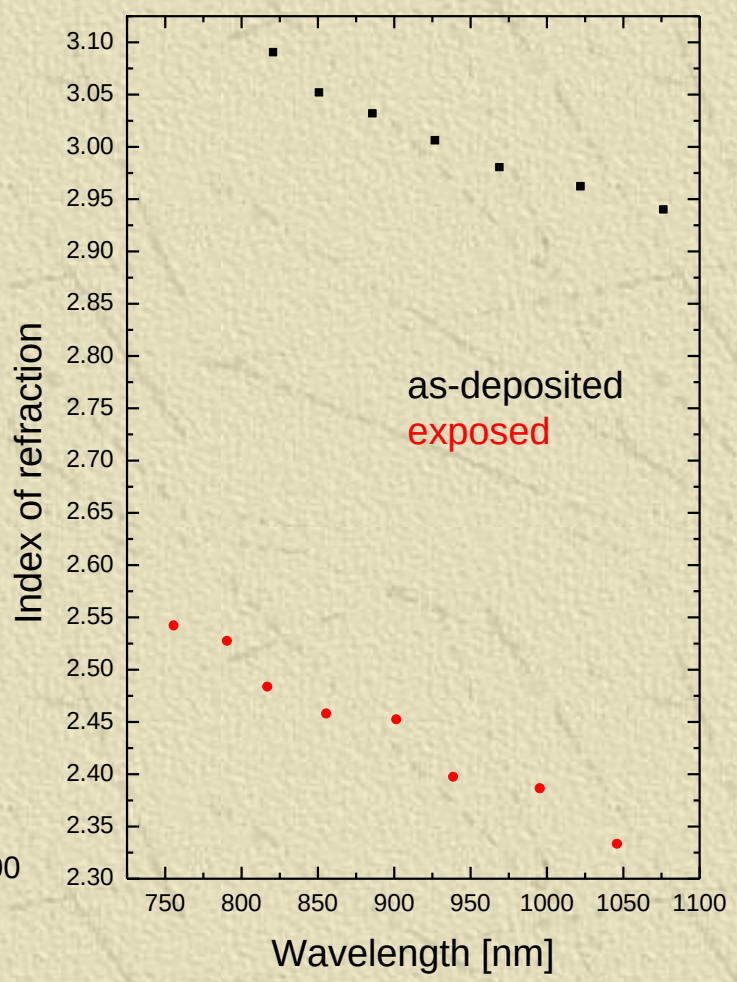
para-realgar, **As_4S_4**, is formed only at high temperatures



$As_{50}S_{50}$ from As_2S_3

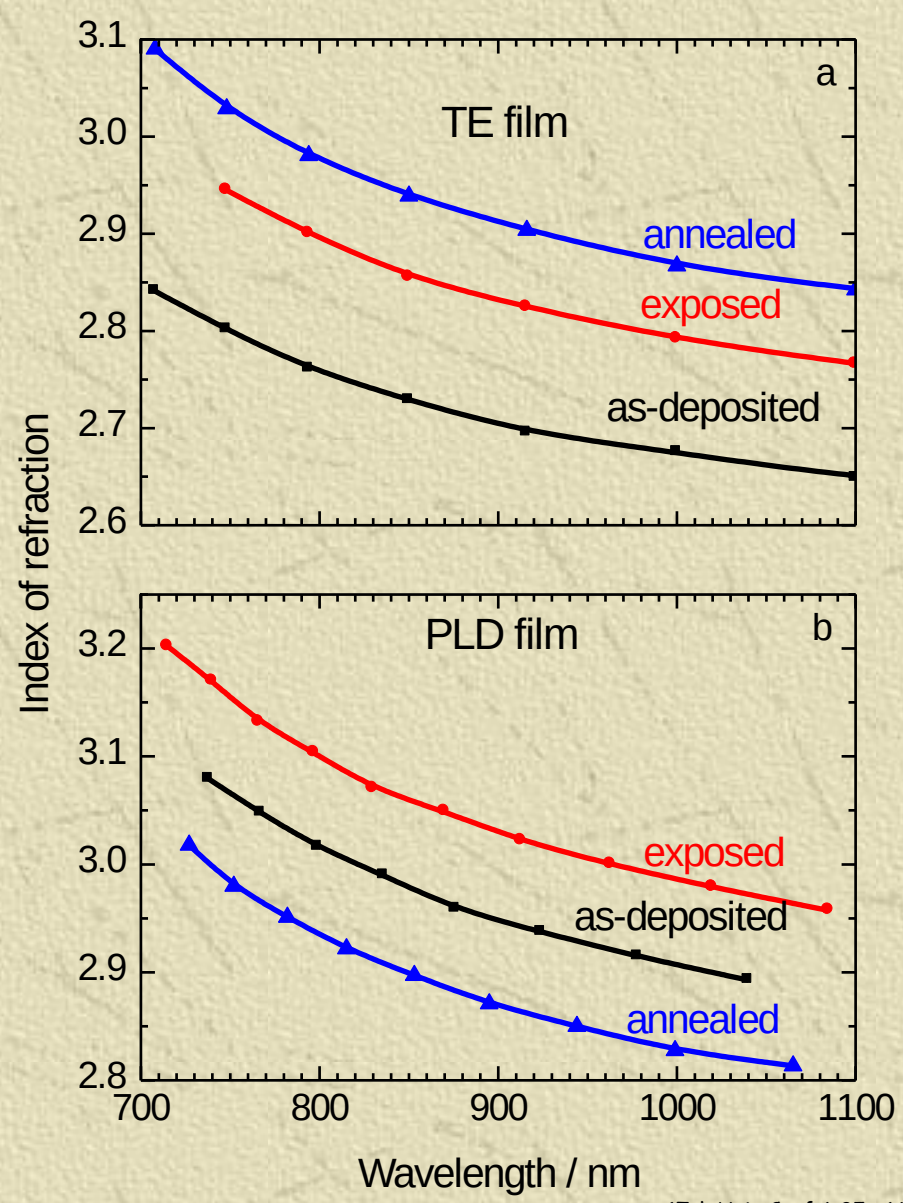
1 as-evaporated
2 exposed
3 annealled





Spectral dependence of index of refraction values for As_4Se_3 PLD thin films

Index of refraction, n, of As_2Se_3 is different from bulk glasses PLD and TE films, Δn can be much larger



In **PLD films**:

index of refraction: the exposure increases, - following **annealing - decreases**

probably by **densification, microliquation, formation of nano-particles?, photolysis, phase separation and thermally-induced expansion** of the amorphous layers.

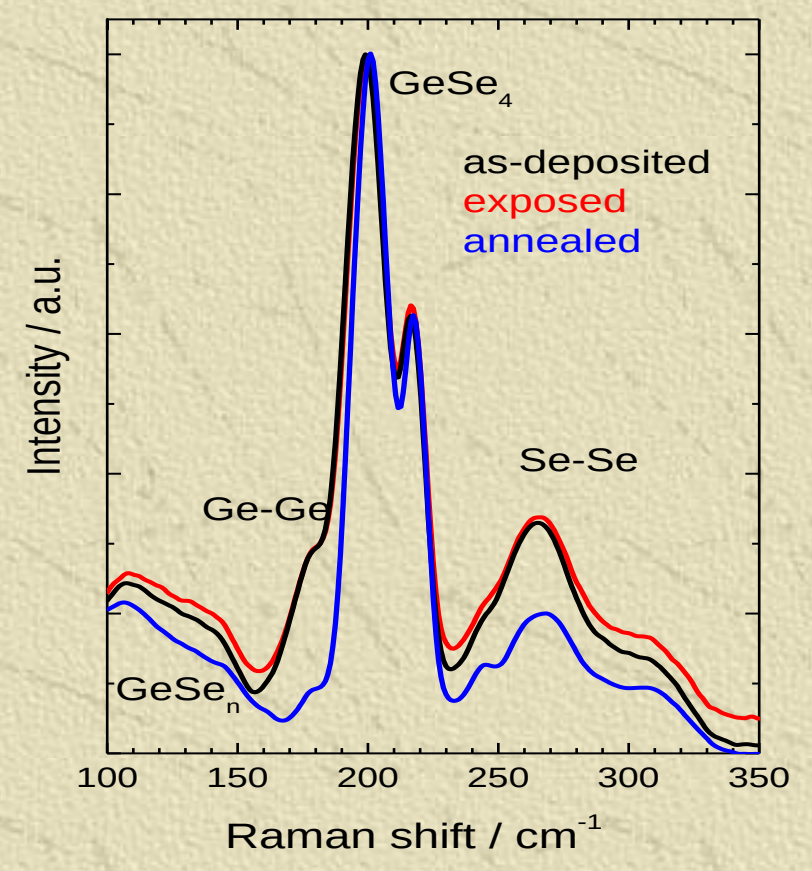
The values of **n are significantly higher in PLD films** in comparison with TE films-

The values of **third-order non-linear susceptibility**, **in PLD films also higher**.

$$\chi^{(3)} = \frac{A}{(4\pi)^4}\left(\frac{E_d}{E_0}\right)^4 = \frac{A}{(4\pi)^4}\left(n_0^2 - 1\right)^4 \qquad (4)$$

In Ge_xSe_{1-x}:
exposure and **annealing** - **decrease** of the density of **Ge-Ge and Se-Se bonds** in $Ge_2(Se_{1/2})_6$ structural units

$$|Ge-Ge| + |Se-Se| \leftrightarrow 2|Ge-Se| \qquad (5)$$



Raman spectra Ge_xSe_{1-x}, $x = 0.24$ *thin films*

A broad Raman band 100-150 cm^{-1} - vibrations of structural units similar to the GeSe formed T > 500°C).

By annealing - decrease of Raman bands of Ge-Ge and Se-Se bonds → more chemically ordered system → higher E_g

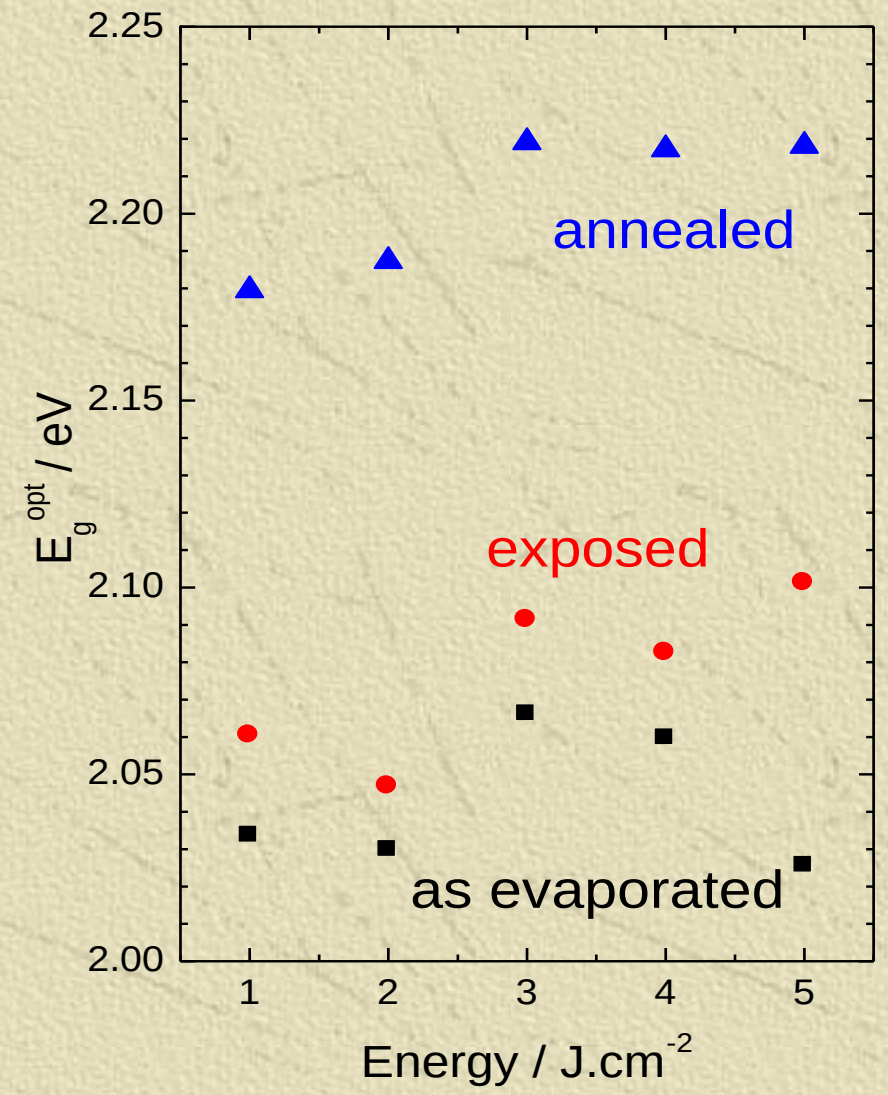
$$x GeSe_{2(s)} \leftrightarrow (x-y)\ GeSe_{2(g)} + y\ GeSe_{(g)} + y/n\ Se_{n(g)}, \quad (6)$$

At T > 500°C, GeSe becoms Se deficient (Chizhikov and Schastlivyi 1964):

$$m GeSe_{(g)} \leftrightarrow m GeSe_{1-p} + (p/n) Se_n \quad (7)$$

Due to high energy of the particles ($GeSe_2$, GeSe, $GeSe_{1-p}$, Se_n, and other fragments of $GeSe_2$) in the plume,

some react together when deposited, (reactions (2) and (3) in the backward direction).



E_g^{opt} , $Ge_{28}Se_{72}$

Slight photobleaching, larger bleaching by annealing

By annealing– decrease of Raman bands of Ge-Ge and Se-Se bonds → more chemically ordered system → higher E_g

Eutectic tellurides – optical and electrical memories
Melting, crystallization, composition is not changed

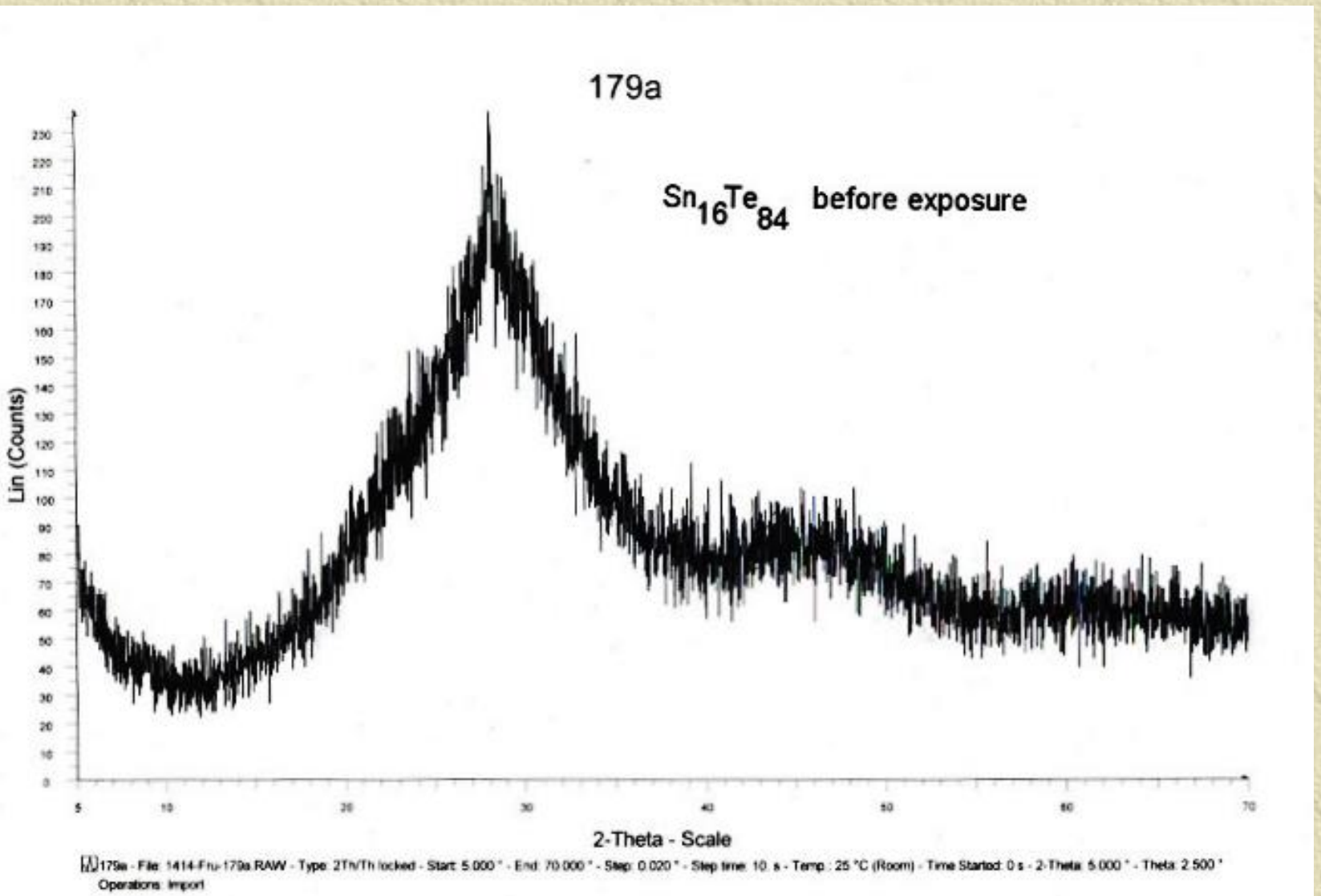
In this paper:
$Sn_{16}Te_{84}$, $In_{13}Te_{87}$, $Sb_{11}Te_{89}$.

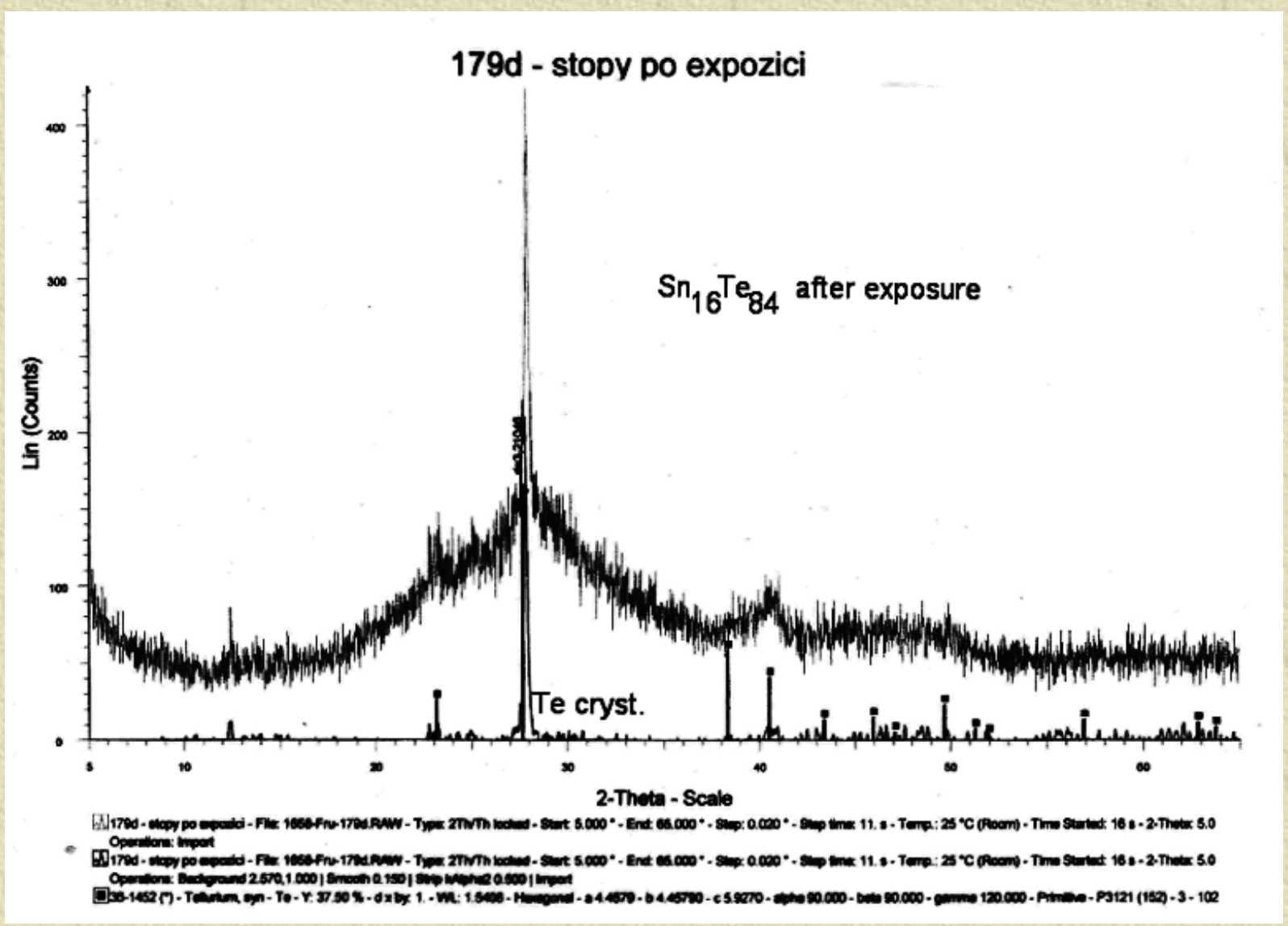
Melting t ≅ 400-420°C

⇔ Bulk samples- **crystalline**
ablated films – **amorphous**, **good optical transmittance up to 18 μm**, untill now- many droplets

Exposure high pressure Hg lamp (~14mW/cm^2) –nearly no changes

Excimer laser pulses – crystallization, prevailing Te crystals the Raman spectra of very low intensity, only small changes


179a
$Sn_{16}Te_{84}$ before exposure
Lin (Counts)
2-Theta - Scale
179a - File: 1414-Fru-179a.RAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 70.000 ° - Step: 0.020 ° - Step time: 10. s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 5.000 ° - Theta: 2.500 °
Operations: Import


179d - stopy po expozici
$Sn_{16}Te_{84}$ after exposure
Te cryst.
Lin (Counts)
2-Theta - Scale
179d - stopy po expozici - File: 1658-Fru-179d.RAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 11. s - Temp.: 25 °C (Room) - Time Started: 16 s - 2-Theta: 5.0
Operations: Import
179d - stopy po expozici - File: 1658-Fru-179d.RAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 11. s - Temp.: 25 °C (Room) - Time Started: 16 s - 2-Theta: 5.0
Operations: Background 2.570,1.000 | Smooth 0.150 | Strip kAlpha2 0.500 | Import
35-1452 (*) - Tellurium, syn - Te - Y: 37.50 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 4.4579 - b 4.45790 - c 5.9270 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P3121 (152) - 3 - 102

$Sn_{16}Te_{84}$

Conclusion

1. **The films** prepared by PLD are often of **different structure** (x TE films) and **different properties**. **Thin films of unusual or complex composition and properties can be prepared**.

2. **The volatile and non-volatile parts** of target material can be deposited at once.

3. **Many materials (e.g. tellurides) can be newly** prepared **as amorphous** due to quenching from high temperatures. **Their physics and chemistry is mostly unknown. Properties are promissing.**

5. The **photoinduced effects are different** – in some cases – higher changes of n, T, R, E_g^{opt}

   Higher changes of n – **higher nonlinearity**

6. Due to **higher index of refraction and larger photoinduced changes** of structure and properties, **the PLD prepared chalcogenide** films
   - materials for **waveguides, optical signal processing, memories,** ….. and for **other applications.**

7. High ionic conductivity, Ag doped
   and other complex systems – ionic sensors, artificial tongue

Acknowledgements

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Thank you for your kind invitation and for your attention