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# XVI, Part 1: Preparation Of Thin Films Of Complex Composition By Pulsed Laser Deposition- A Way for Producing New Amorphous Materials Applicable in Optoelectronics, Chemistry and Biology

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**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.

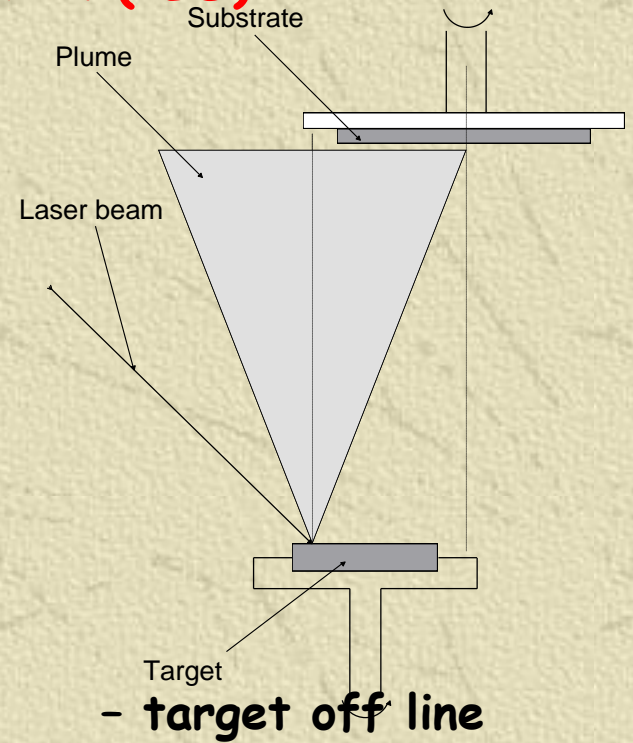
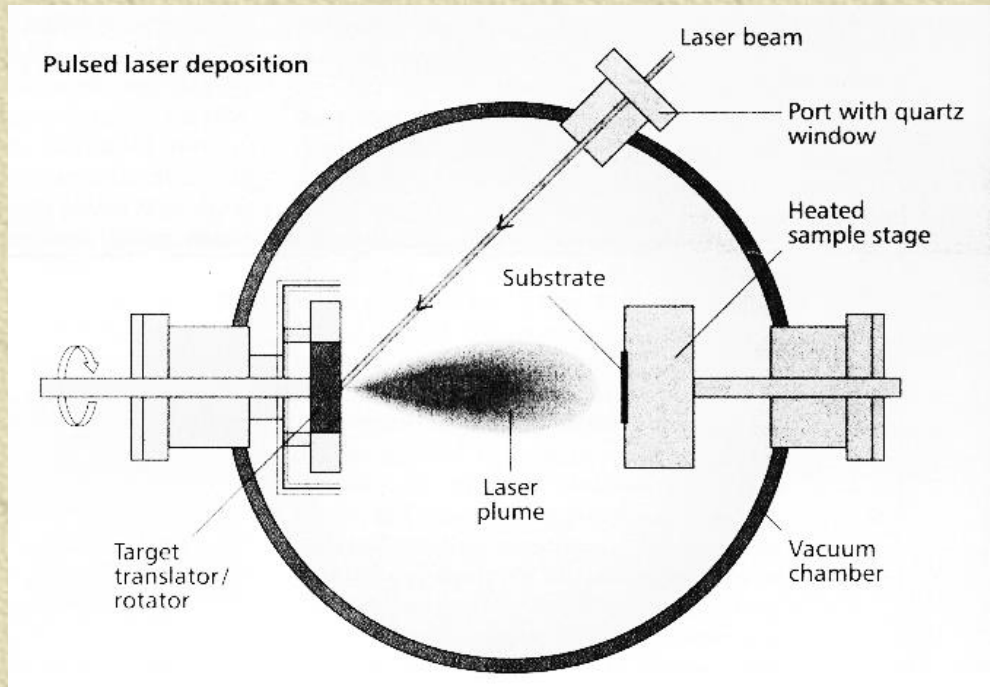
Many systems studied, mostly sulfides, selenides, recently also tellurides, e. g. GeTe, Ge-Sb-Te, .... and others:

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)**

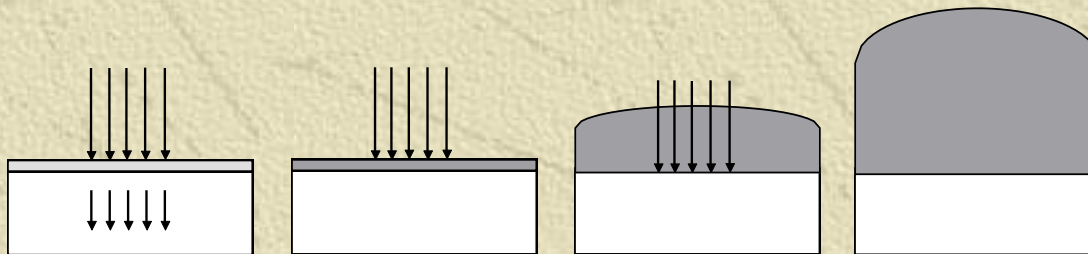


Absorption  
Thermal conduction

Surface melting

Vaporization  
Plasma formation

Plasma emission



30 ns

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

our: 248nm,  $h\nu = 5$  eV, 480 kJ/mol > chemical bonds  
energies: evaporation, atomization, formation of ionized plume

- vapors in plume are very hot ( $\sim X \cdot 10^3$ K, 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
- bubbles 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 highly 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)

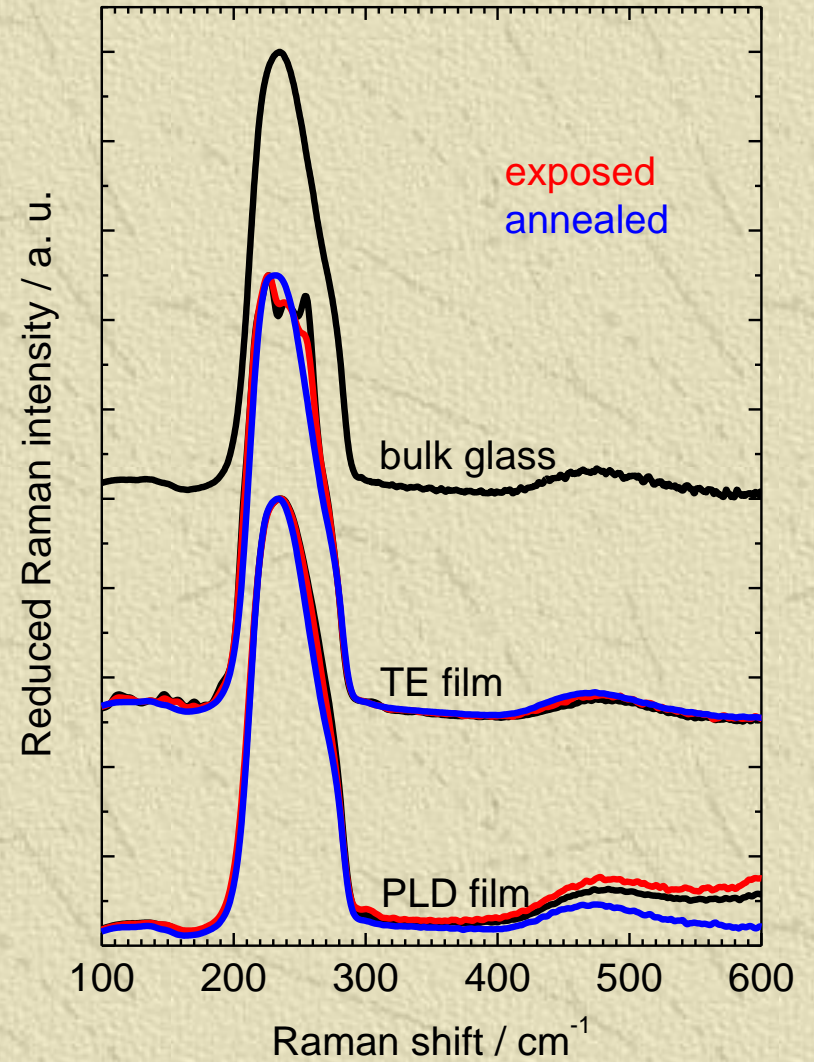
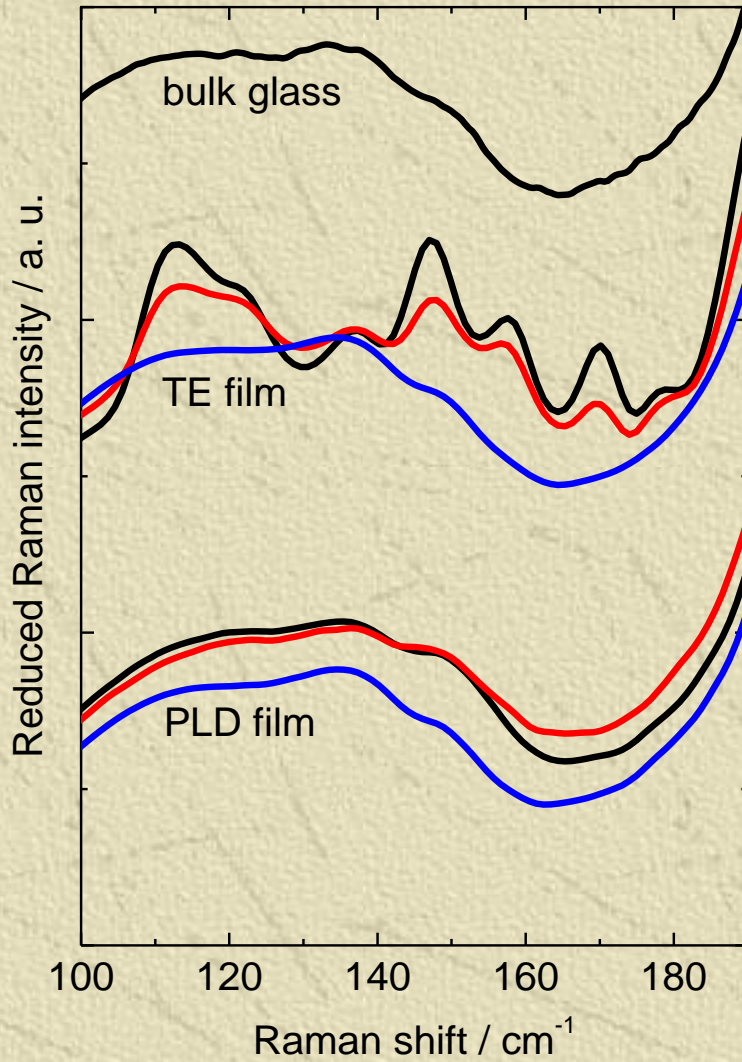
*In this paper: ablated films*

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

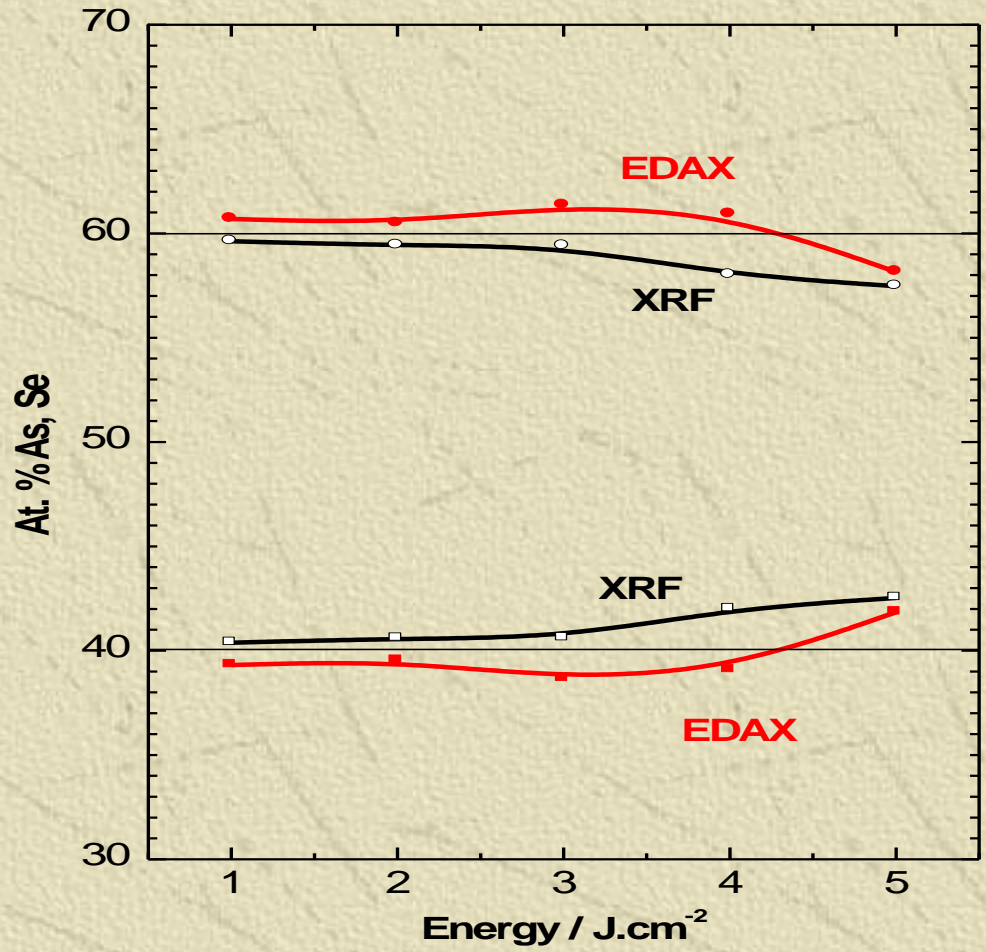
- *tellurides of eutectic compositions*

*(Sn-Te, In-Te, Sb-Te)*

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



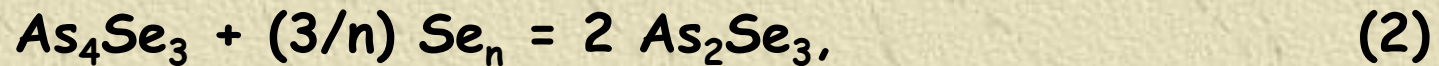
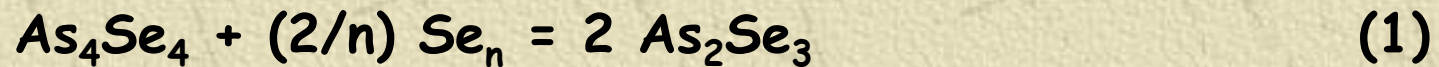
*Raman spectra of bulk  $\text{As}_2\text{Se}_3$  glass and  $\text{As-Se}$  thin films*



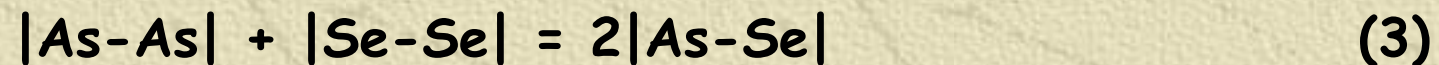
*Composition of As-Se thin films prepared by PLD on energy density of the laser beam:*  
*full squares - As content from EDAX, open squares - As content from XRF,*  
*full circles - Se content from EDAX, open circles - Se content from XRF;*

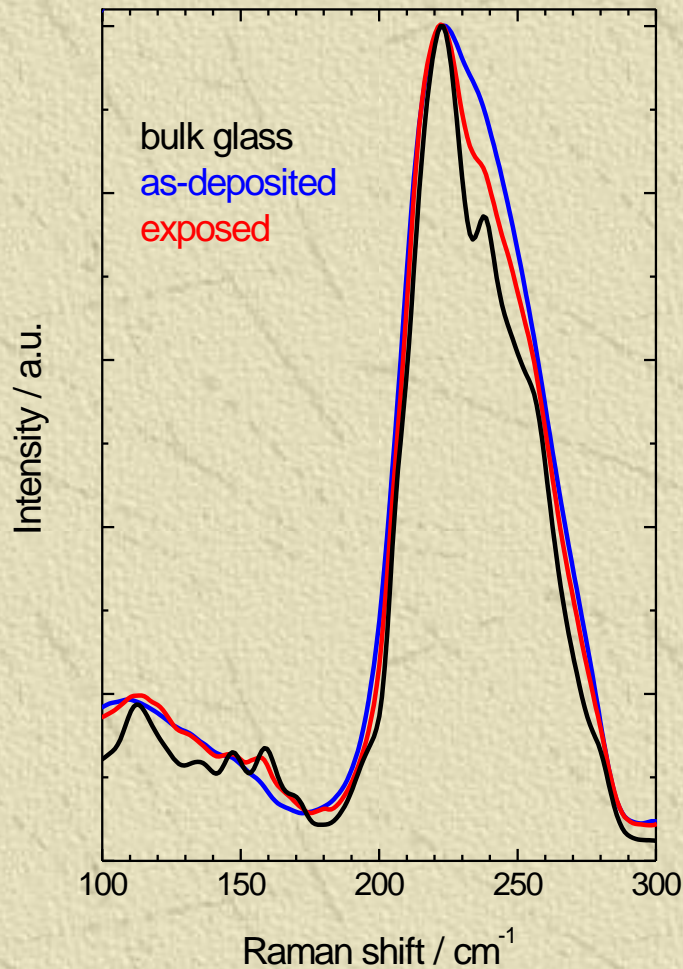
The PLD  $As_2Se_3$  films contain (in comparison with TE films) less 'wrong' As-As and Se-Se bonds and less  $As_4Se_4$ ,  $As_4Se_3$ ,  $Se_8$  or  $Se_n$  particles.

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

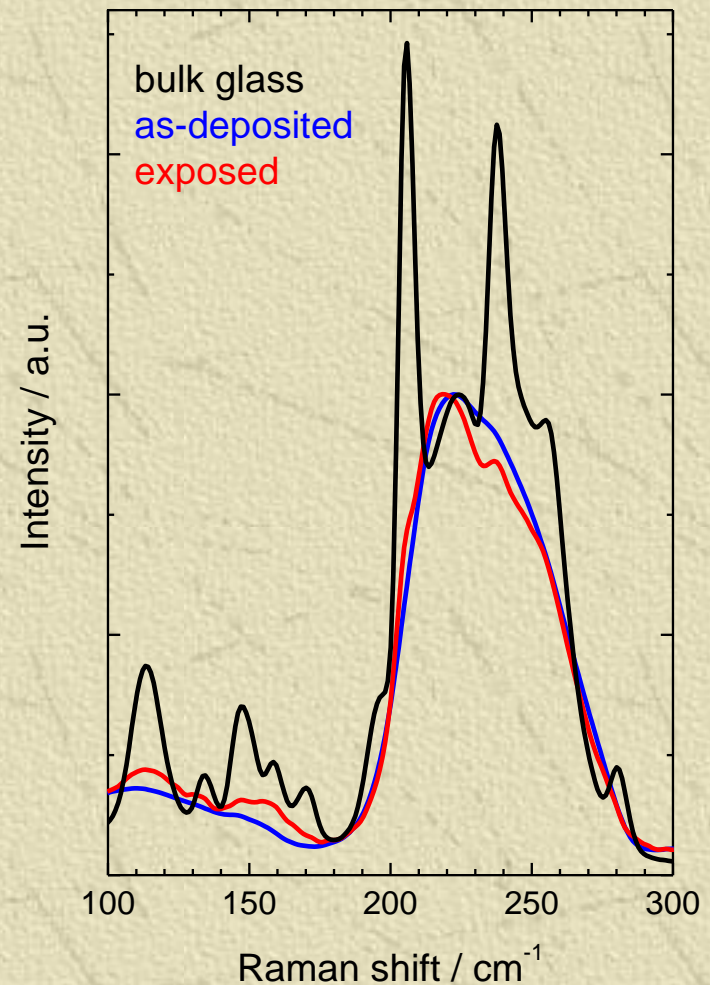


or just

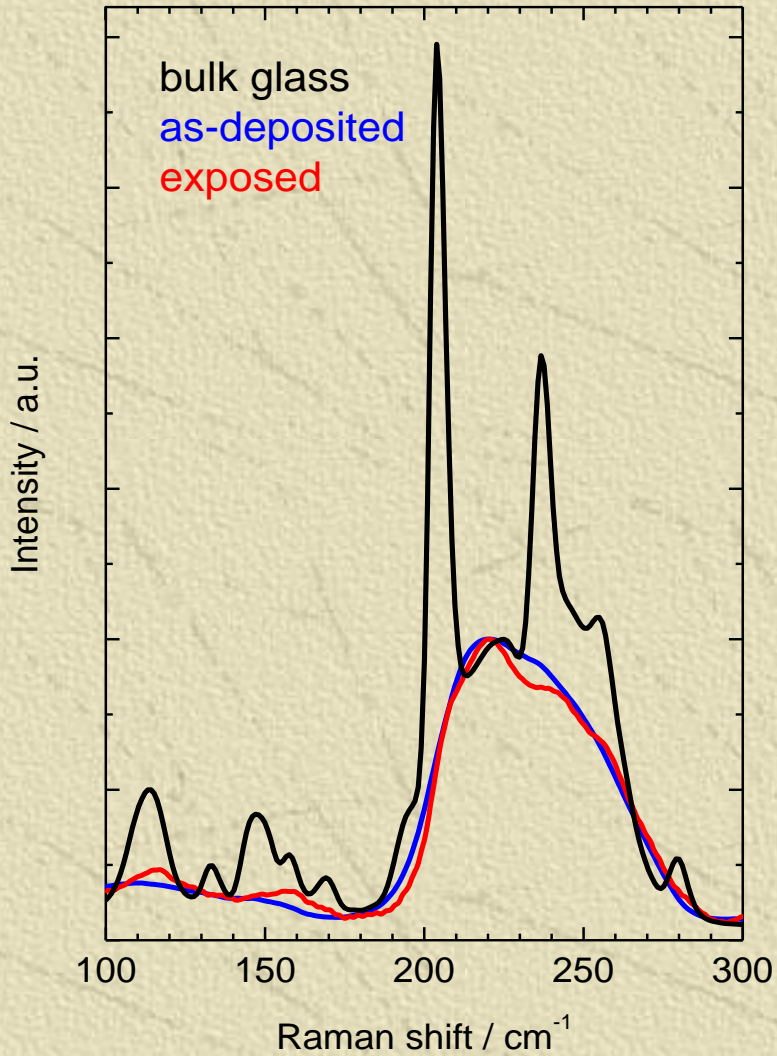




Raman spectra of bulk  $\text{As}_{50}\text{Se}_{50}$  glass (full line), as-deposited (dashed line), and exposed (dotted line) PLD  $\text{As}_{50}\text{Se}_{50}$  thin films



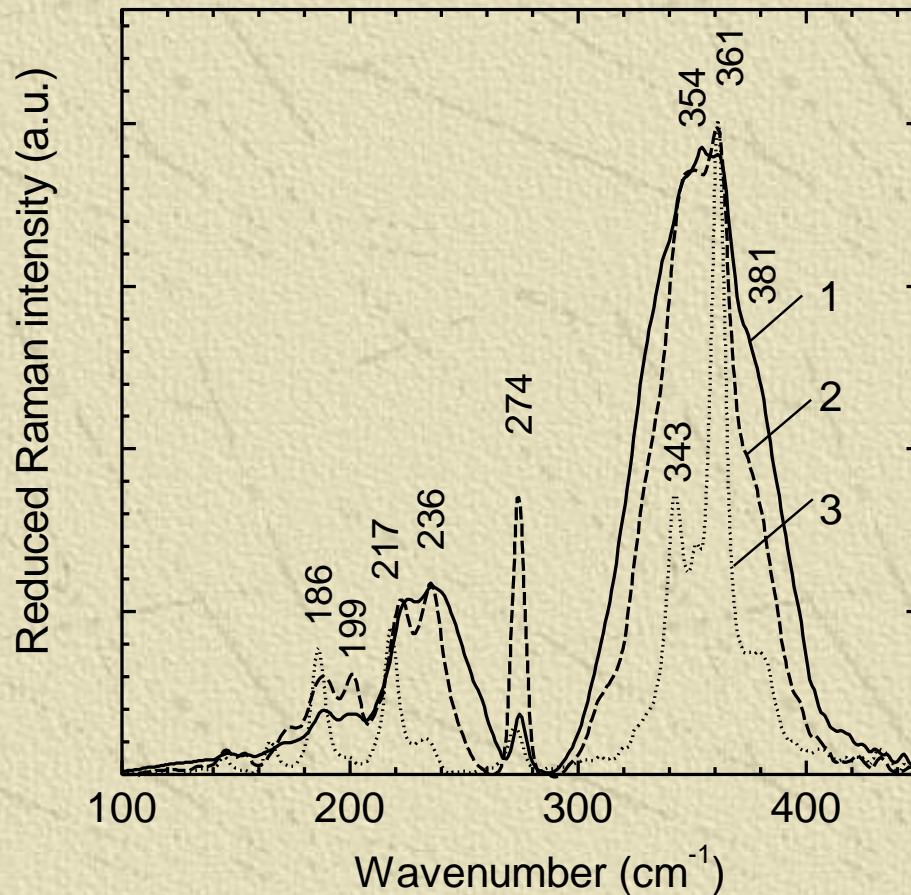
Raman spectra of bulk  $\text{As}_{57.14}\text{Se}_{42.86}$  ( $\text{As}_4\text{Se}_3$ ) glass (full line), as-deposited (dashed line), and exposed (dotted line) PLD  $\text{As}_4\text{Se}_3$  thin films



Raman spectra of bulk  $\text{As}_{60}\text{Se}_{40}$  glass (full line), as-deposited (dashed line), and exposed (dotted line) PLD  $\text{As}_{60}\text{Se}_{40}$  thin films

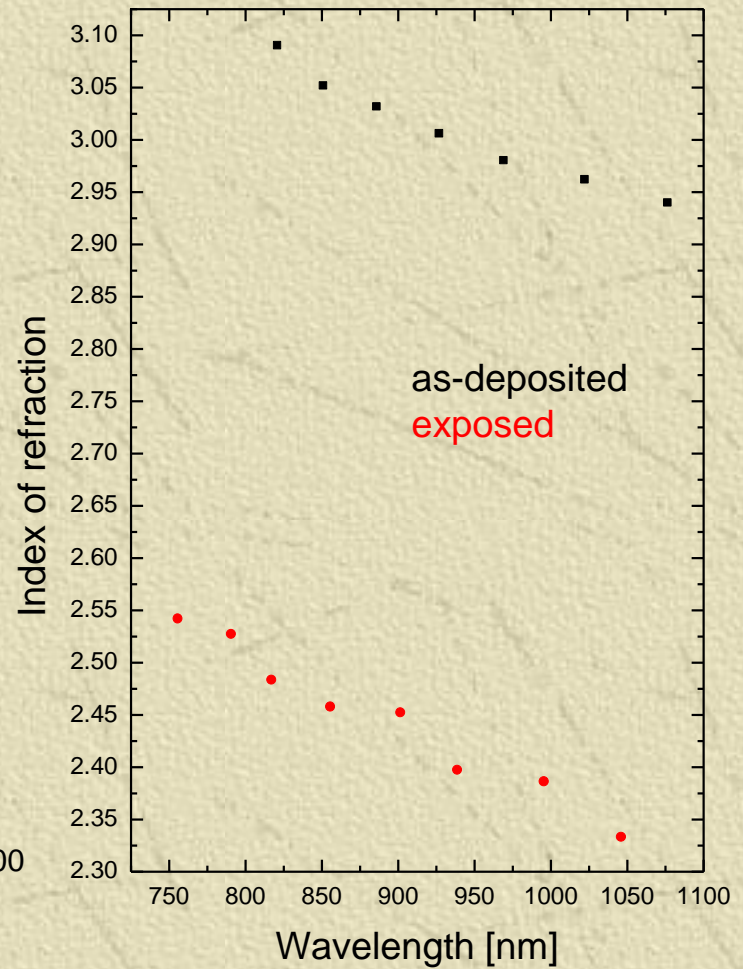
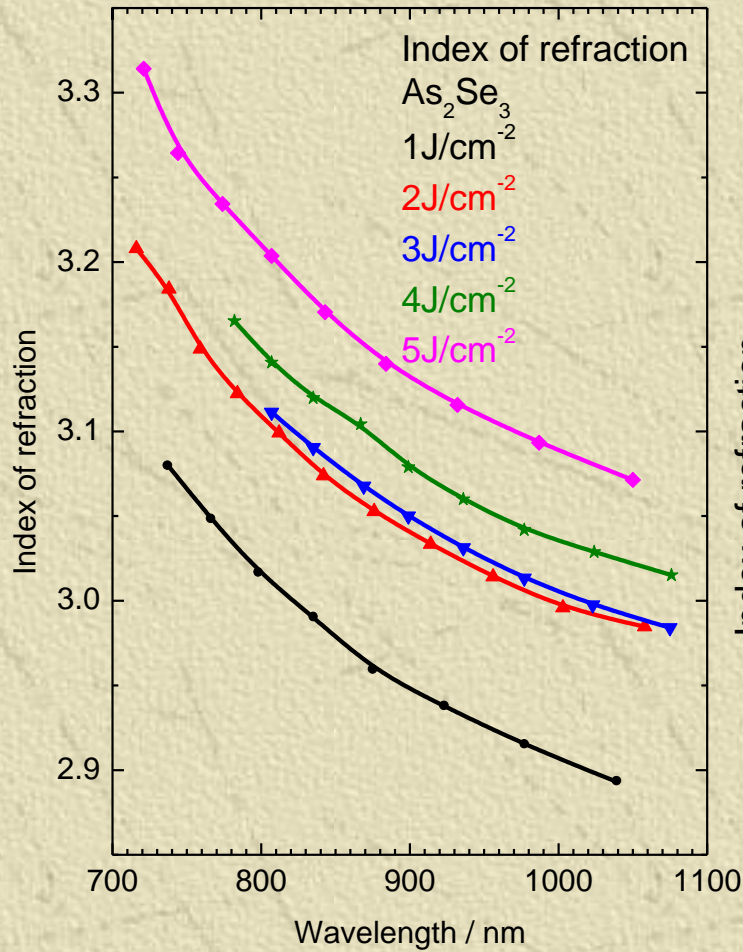
In **As-S** system: thermal dissociation  
 $2\text{As}_2\text{S}_3 = \text{As}_4\text{S}_4 + \text{S}_2 \Rightarrow$  change of composition

para-realgar,  $\text{As}_4\text{S}_4$ , is formed only at high temperatures



$\text{As}_{50}\text{S}_{50}$  from  $\text{As}_2\text{S}_3$

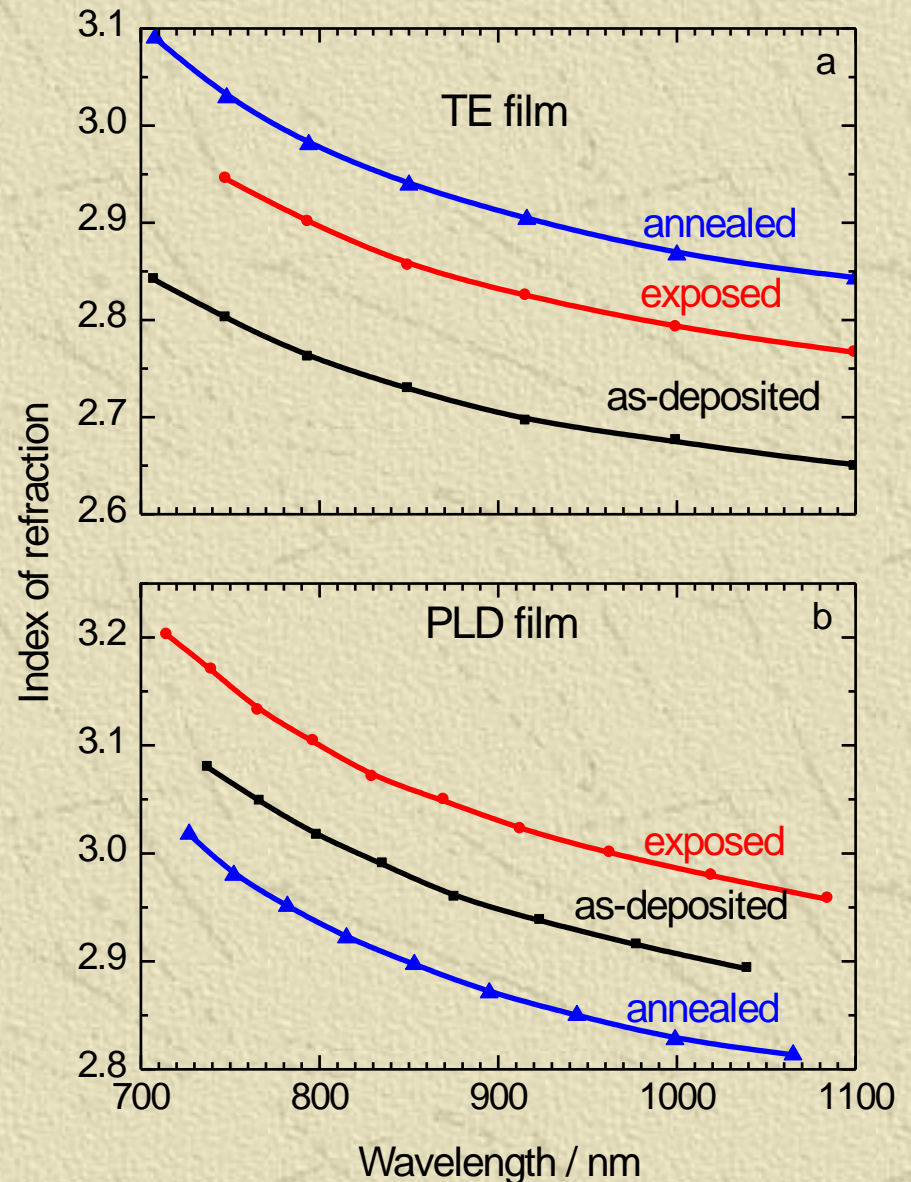
- 1 as-evaporated
- 2 exposed
- 3 annealed



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,  $\Delta n$  can  
be much larger



## In PLD films:

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

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

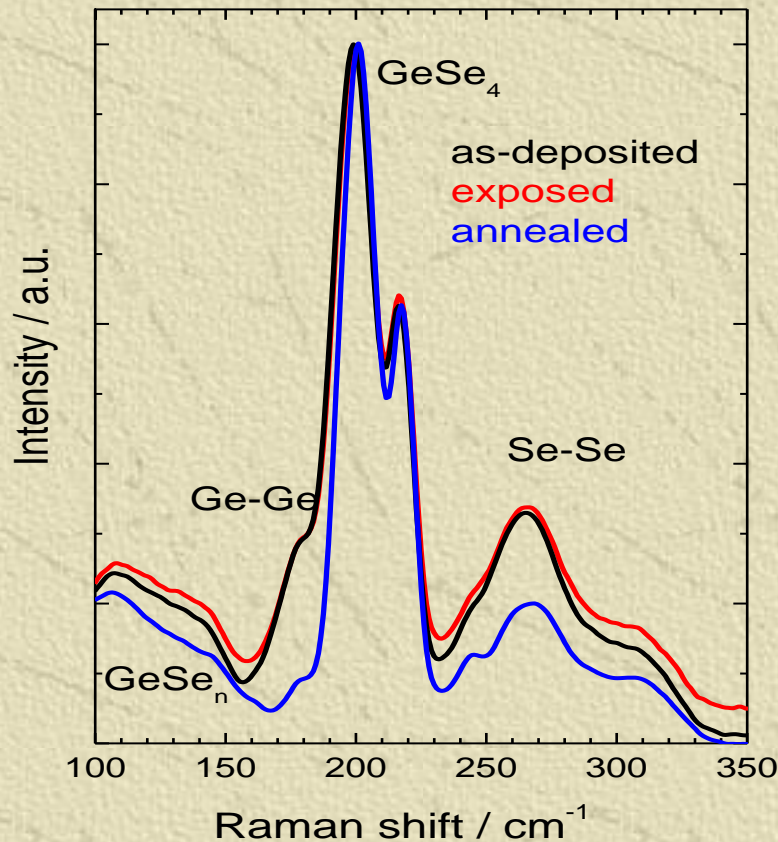
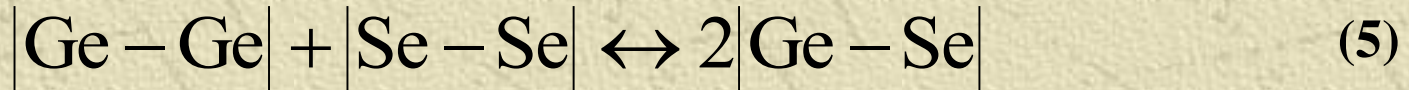
The values of **n** are significantly higher in PLD films in comparison with TE films-

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

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

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



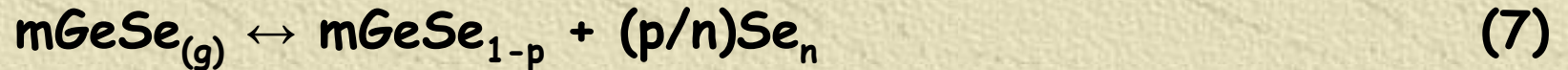
*Raman spectra  $Ge_xSe_{1-x}$ ,  
 $x = 0.24$  thin films*

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

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



At  $T > 500^\circ\text{C}$ ,  $\text{GeSe}$  becomes  $\text{Se}$  deficient (Chizhikov and Schastlivyi 1964):



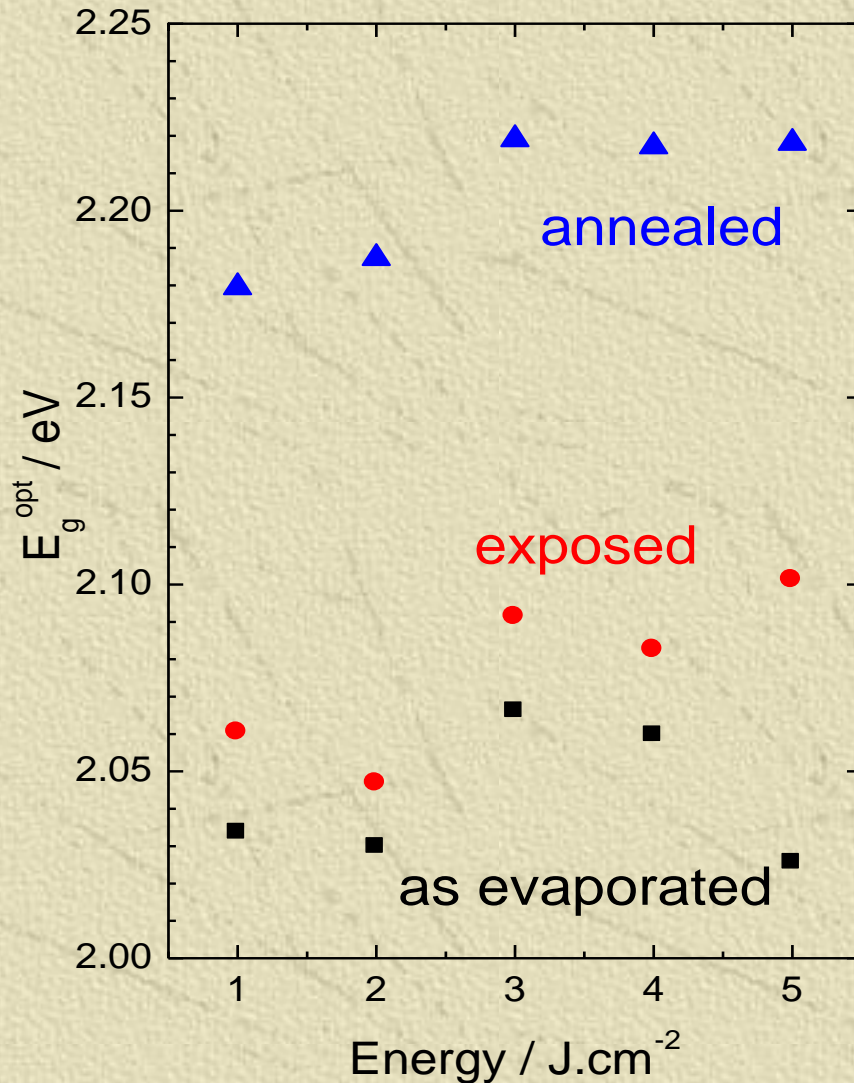
Due to high energy of the particles ( $\text{GeSe}_2$ ,  $\text{GeSe}$ ,  $\text{GeSe}_{1-p}$ ,  $\text{Se}_n$ , and other fragments of  $\text{GeSe}_2$ ) in the plume,

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

$$E_g^{\text{opt}}, \text{Ge}_{28}\text{Se}_{72}$$

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:

$\text{Sn}_{16}\text{Te}_{84}$ ,  $\text{In}_{13}\text{Te}_{87}$ ,  $\text{Sb}_{11}\text{Te}_{89}$ .

Melting  $t \cong 400\text{-}420^\circ\text{C}$

⇒ Bulk samples - crystalline

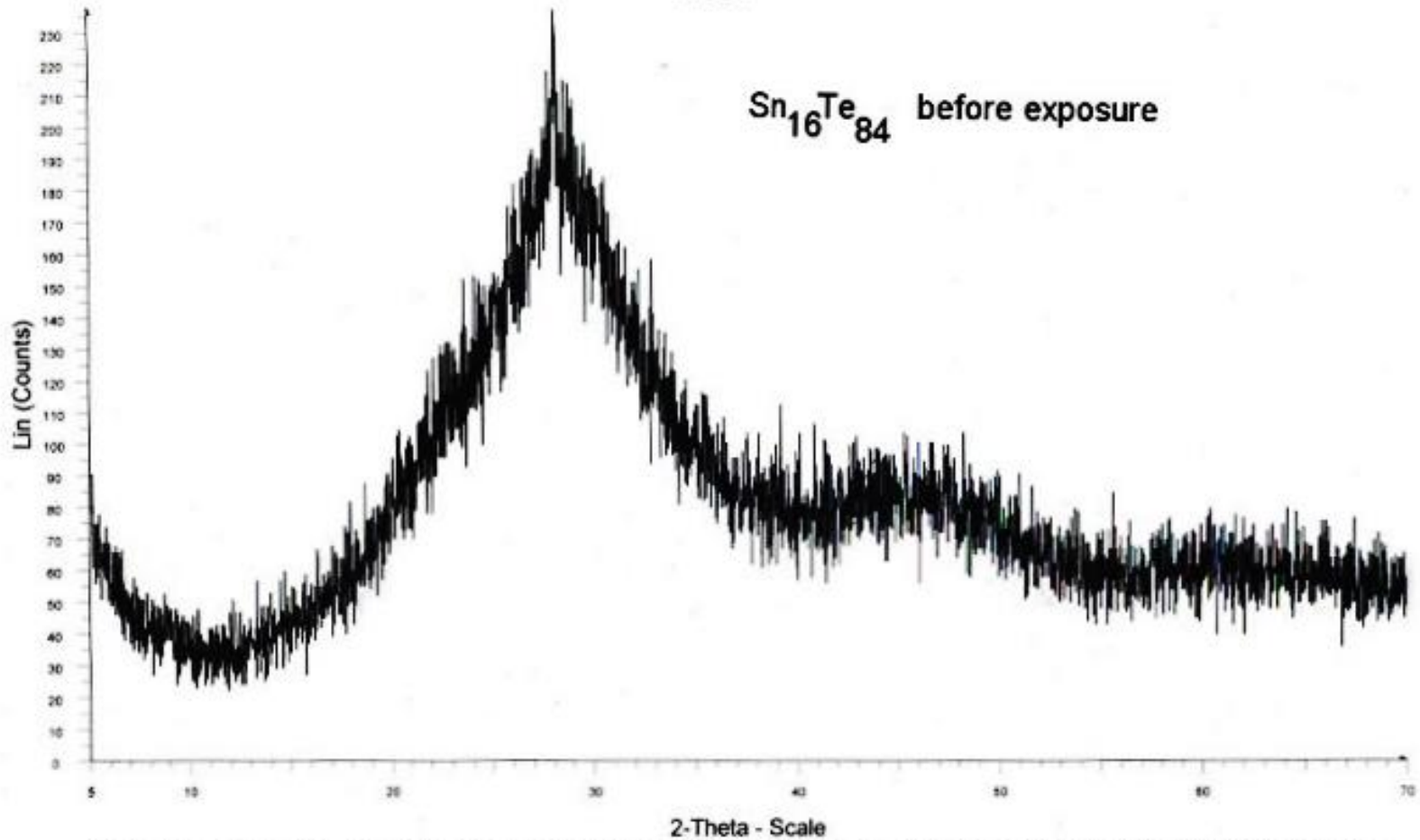
ablated films - amorphous, good optical transmittance up to 18  $\mu\text{m}$ , until now - many droplets

Exposure high pressure Hg lamp ( $\sim 14\text{mW}/\text{cm}^2$ ) - nearly no changes

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

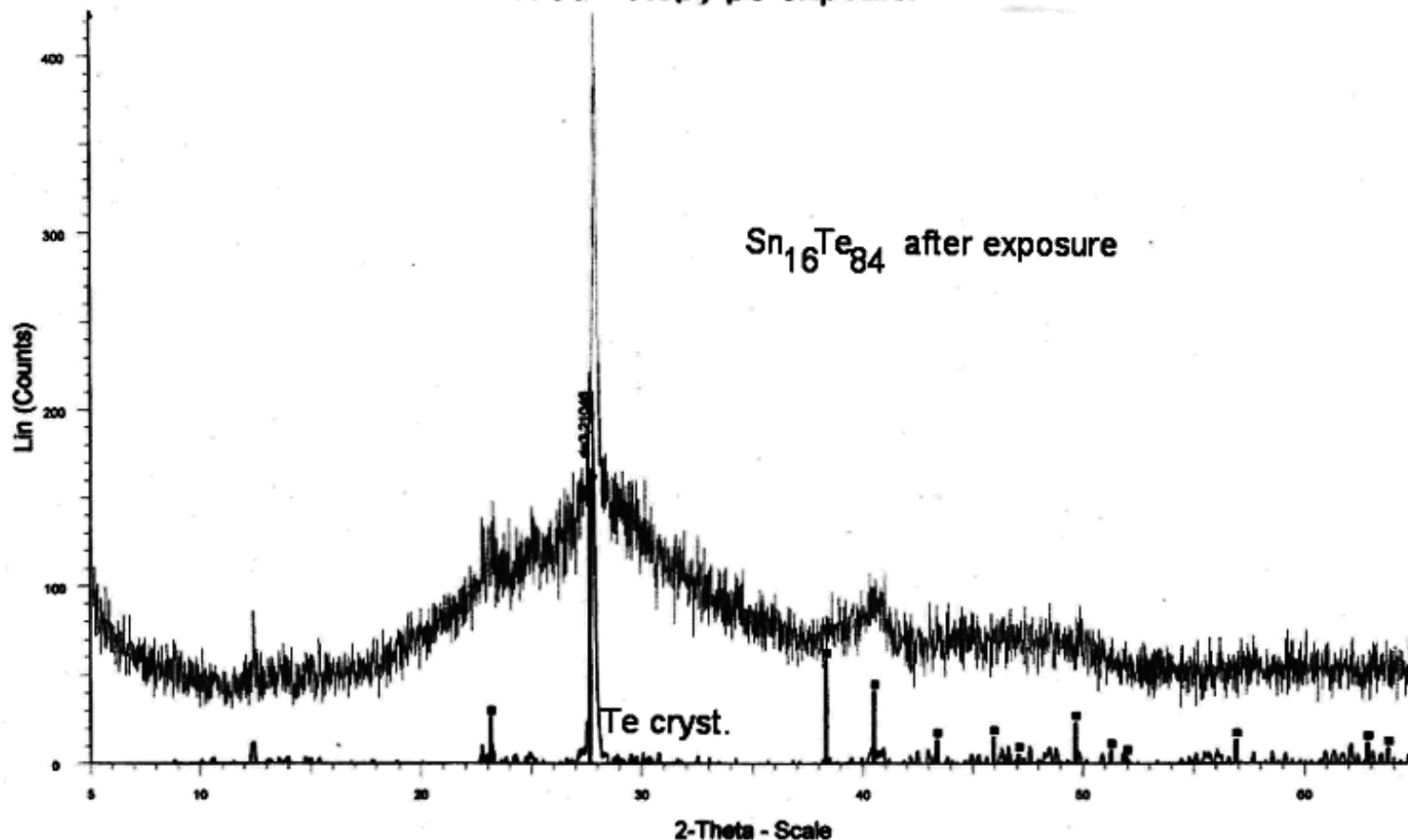
179a

$\text{Sn}_{16}\text{Te}_{84}$  before exposure



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

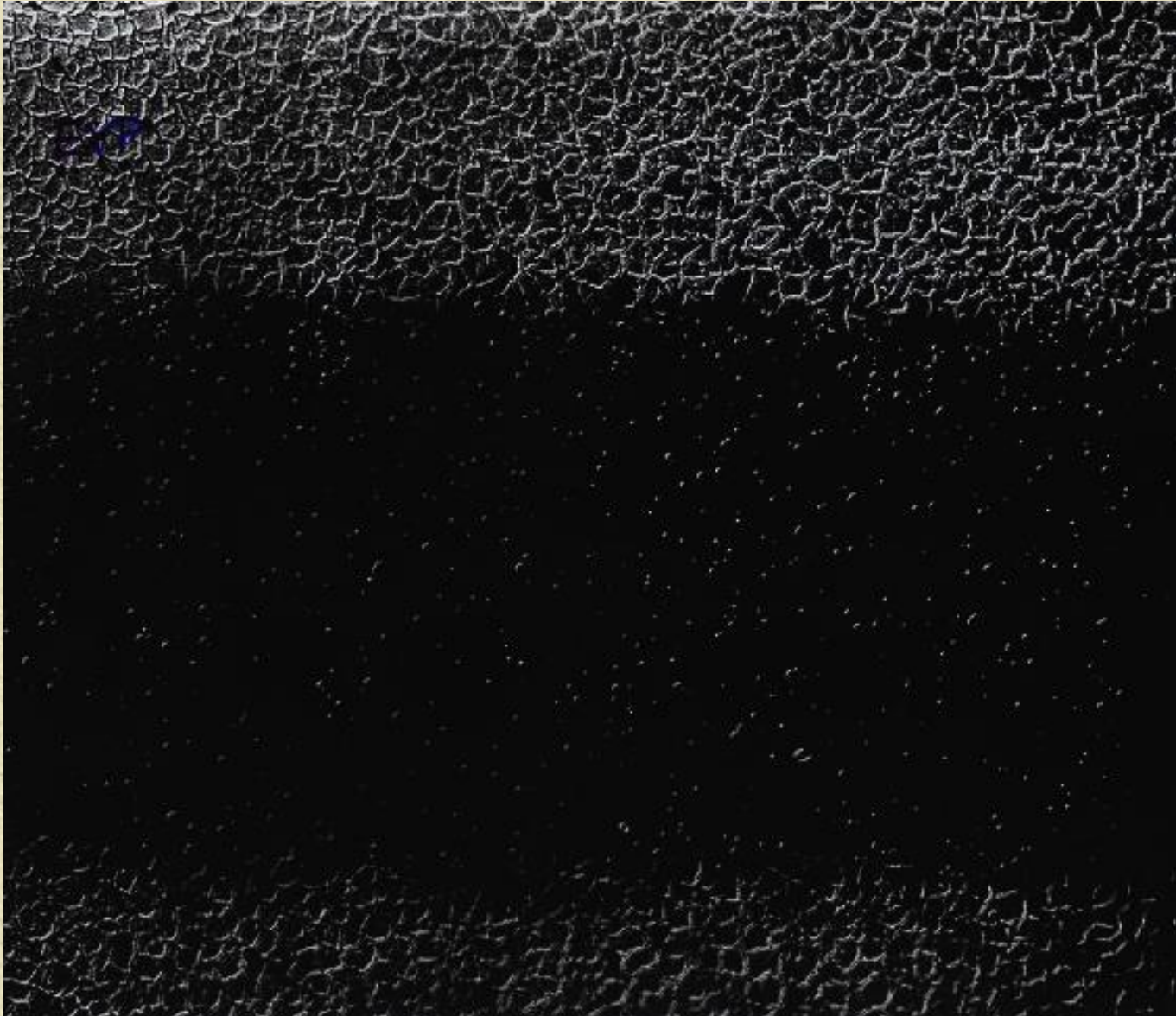
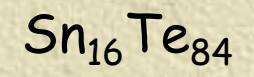


179d - stopy po expozici - File: 1658-Fru-179d.PAW - Type: 2Th/Th locked - Start: 5.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 11. s - Temp.: 25 °C (Room) - Time Started: 16 s - 2-Theta: 5.0  
Operations: Import

179d - stopy po expozici - File: 1658-Fru-179d.PAW - 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 | Step hAlpha2 0.500 | Import

35-1452 (\*) - Tellurium, syn - Te - Y: 37.50 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 4.4679 - b 4.46790 - c 5.9270 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P3121 (152) - 3 - 102





## 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 promising.

5. The photoinduced effects are different - in some cases - higher changes of  $n$ ,  $T$ ,  $R$ ,  $E_g^{\text{opt}}$

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**

The support of Ministry of Education of the Czech Republic under the projects LC 523, 002167501, and GA CR 203/05/0524 are highly acknowledged.

**Thank you for your kind invitation  
and for your attention**