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INSTITUTE OF ELECTROCHEMISTRY AND ENERGY SYSTEMS

Physicochemical and optical characterization of As-Se-Ag glassy materials

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Multicomponent chalcogenide glasses

disordered structure → **Unique properties** ← **modification in their behaviors by composition variation**

↓

Application

optical storage media
optical elements
electrolytes for solid state batteries
sensitive media in sensor systems

← ***Glassy electrolyte*:**

- **isotropic properties (ionic conductivity);**
- **absence of grain boundaries;**
- **near the Tg improved electrode/material contact;**
- **disordered structure, providing better ionic conductivity;**
- **easy film formation.**

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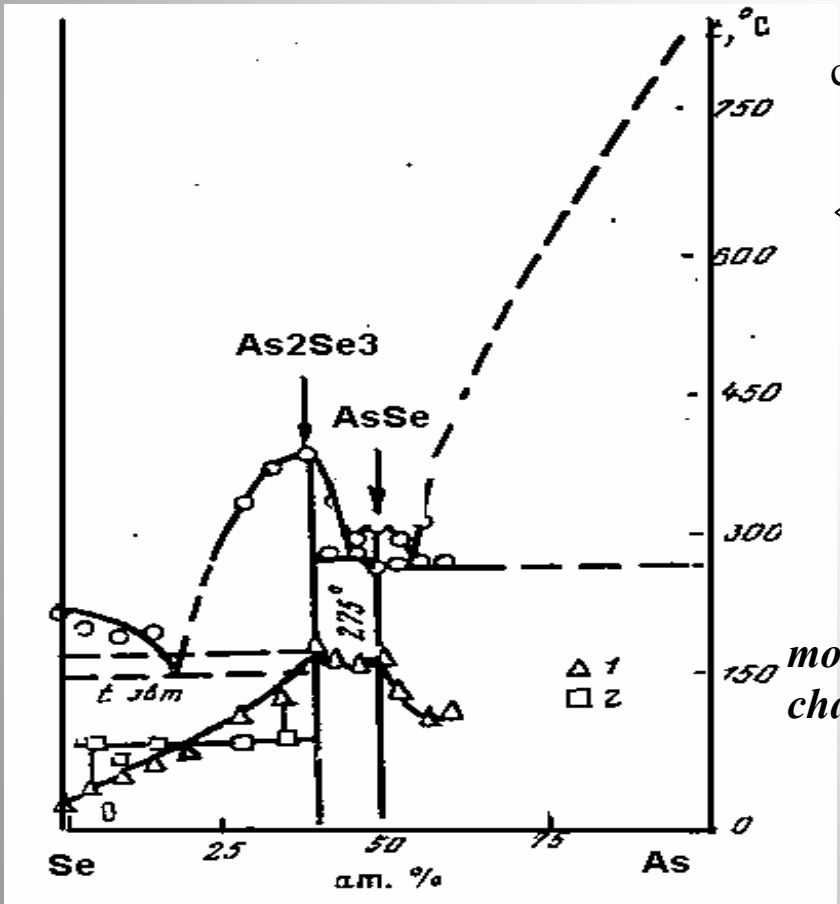
Glasses based on As and Se → interesting electrical and optical properties

Selenium-based chalcogenide glasses - promising materials for optical applications → **high refractive index**

Fabrication of optical fibers for infrared region

good transparency in the infrared region



Stable and homogeneous As_xSe_{100-x} glasses can be prepared in As–Se system in a large compositional region.

⇐ **Phase diagram of the binary As-Se system is simple with two compounds, easy prepared in glassy form and stable with time.**

Ag-chalcogenide glasses

Ag

modify basic physicochemical characteristics of the material

causes substantial changes in the optical and electrical properties

Objective of investigation:

- *Study of compositional dependence of basic physicochemical parameters in As-Se-Ag chalcogenide glasses.*
- *Study of optical characteristics of thin $(AsSe)_{100-x}Ag_x$ films, deposited by two different methods, VTE and PLD, from the corresponding bulk materials. Evaluation of their dependence on composition, namely on silver amount added to the amorphous glassy matrix.*

Scheme of the experiment

Glass preparation

↓

Structural study

↓

Study of physicochemical behaviors

- **Density**
- **Microhardness**
- **Molar volume**
- **Compactness**

↓

Deposition of thin films

↓

Optical characterization

Compositions

AsSe

with 0, 5, 10, 15, 20, 25 mol.% Ag

Preparation of glasses: Melt quenching technique

Heating the material to (or above) the melting point (Tm)

↓

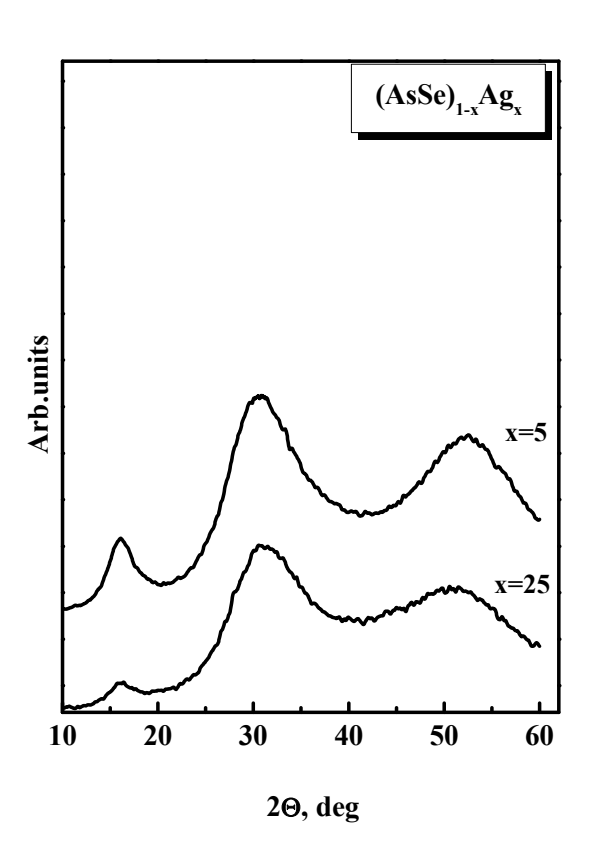
cooling the molten form sufficiently quickly.

- **Cooling media: mixture of cool water, ice and NaCl.**
- **Selection of cooling mode depends on structure, type, and volume of the material.**
- **The main feature of the melt-quenching process is that the amorphous solids are formed by continuous hardening (i.e. increase in viscosity) of the melt.**

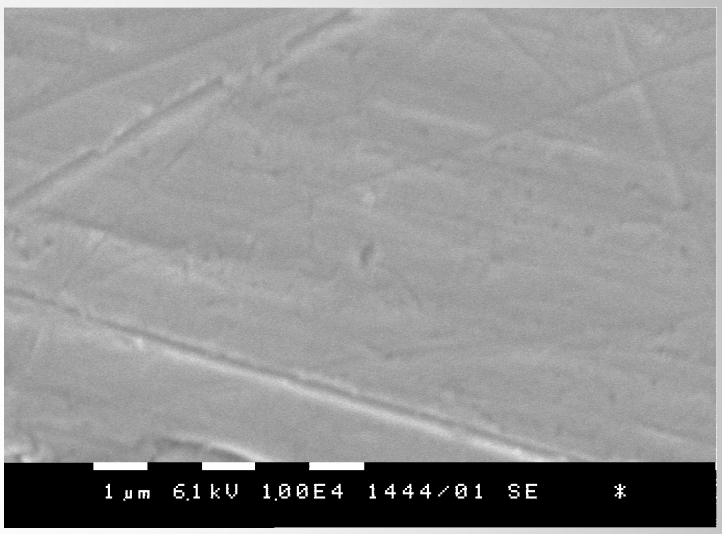
Synthesis of As-Se-Ag glasses:

- **First step: Preparation of binary AsSe glass in quartz ampoules evacuated down to ~10^{-3} Pa and heated in a rotary furnace up to melting temperature of As. After a few hours the melt was quenched in a mixture of ice and water.**
- **Second step: Preparation of silver containing glasses from AsSe and silver at heating up to 900ºC and quenching in a mixture of ice and water.**

XRD

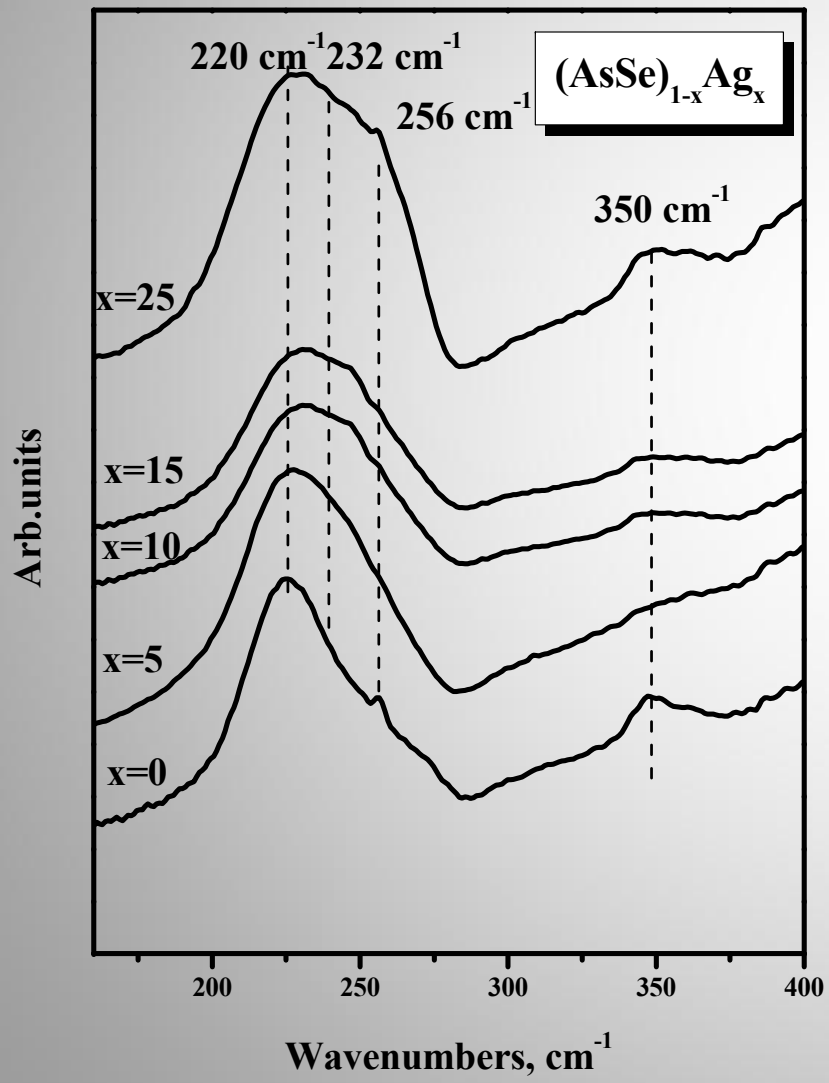


SEM



Smooth and homogeneous structure of the samples. Samples with 25 mol% Ag do not show any silver clusters concentrated into the glassy matrix.

IR spectra



basic bands

$220\ cm^{-1} \longrightarrow AsSe_3$

$232\ cm^{-1} \longrightarrow Ag_3AsSe_3$

$256\ cm^{-1} \longrightarrow$ Se – Se chains

$350\ cm^{-1} \longrightarrow Se_8$ rings

Structural units with very closed vibrational modes.

The main reason for the strong overlap of the vibrational modes is proximity in the masses of As and Se atoms and similar bond strengths of the As-Se and Se-Se bonds.

Physicochemical parameters - experimentally derived

➢ Density (ρ)

$$\rho = \frac{m}{m - m_1}\rho_1$$

→ m – weight of the sample on air; m_1 – weight of the sample in the liquid; ρ – density of the liquid

➢ Molar volume (V_m)

$$V_m = \frac{1}{\rho}\sum_i x_i A_i$$

→ x_i – atomic fraction of the i-th component of a glass;;
ρ – experimental density; x_i – atomic fraction of the components;
A_i – atomic weight of the components;

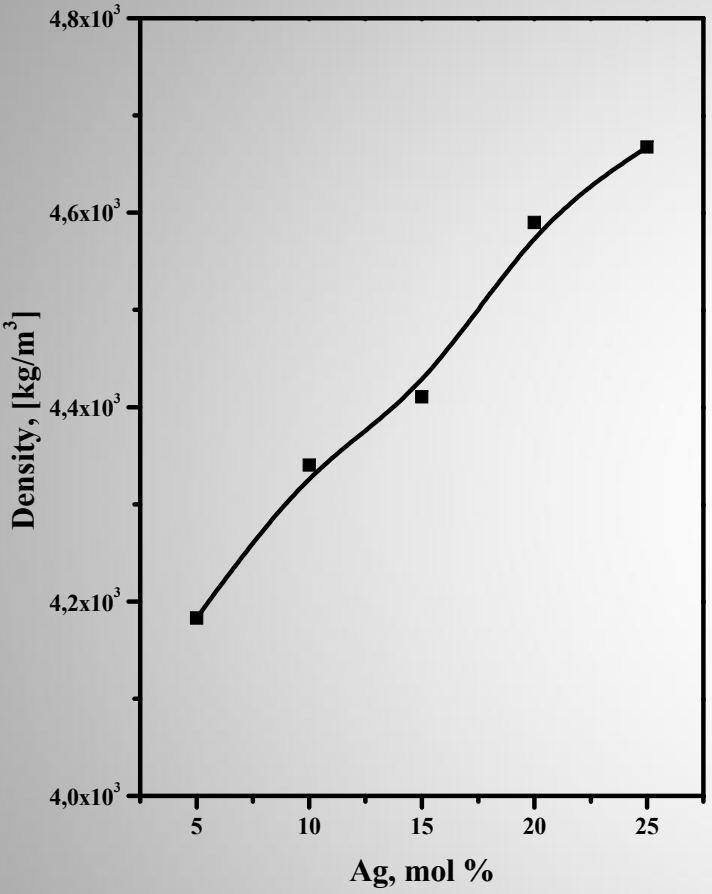
➢ Compactness (δ)

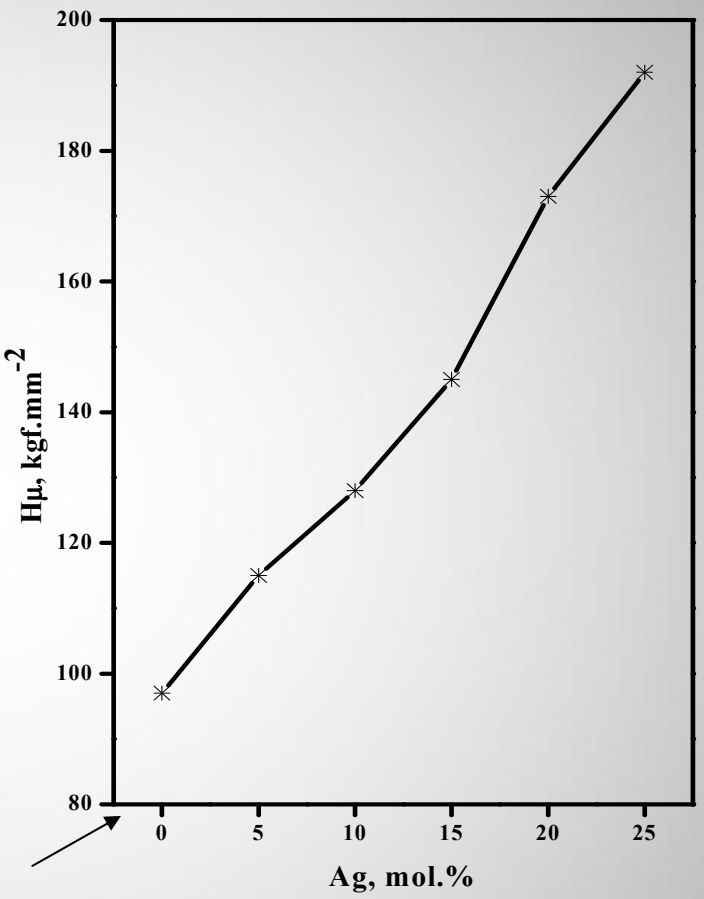
$$\delta = \left(\sum_i \frac{x_i A_i}{\rho_i} - \sum_i \frac{x_i A_i}{\rho}\right) \cdot \left(\sum_i \frac{x_i A_i}{\rho}\right)^{-1}$$

➢ Microhardness (Hμ)

$$H\mu = P/Ad^2$$

→ P is applied load, kgf; d [mm] – the length of the longer diagonal imprint;
A-technological parameter equal to 0.07028





absence of any deflections in ρ and Hμ — silver is well incorporated in the chalcogenide matrix and uniformly distributed.

Introduction of silver atoms leads to formation of Ag-containing structural configurations (IR spectra), changing the glass structure. As a result, the network stability of the glasses is improved, and the structure gets more dense and compact.

Physicochemical parameters - theoretically calculated

➢ **Average coordination number <Z>** - average number of bonds/atom, which must be broken to obtain fluidity.

<Z> =f (nearest neighbour atoms for As, Se and Ag); ZAg= 3; ZAs = 3; ZSe = 2;

$< Z > = \sum_i x_i Z_i$ x_i – atomic fraction of the i-th component of a glass; Z_1 – coordination number of the i-th atom;

Z > 2.4 → **Phillips and Thorpe theory:**

When Z > 2.40, the solid has continuously connected rigid regions with floppy regions inter-dispersed and may be termed as 'amorphous' solid.

Composition	Z	N_{CO}	<E>, eV
$As_{50}Se_{50}$	2.5	3.25	2.65
$As_{47,5}Se_{47,5}Ag_5$	2.525	3.3	2.73
$As_{45}Se_{45}Ag_{10}$	2.55	3.38	2.81
$As_{42,5}Se_{42,5}Ag_{15}$	2.575	3.44	2.89
$As_{40}Se_{40}Ag_{20}$	2.6	3.5	2.97
$As_{37,5}Se_{37,5}Ag_{25}$	2.625	3.56	3.04

➢ **Number of constrains per atom (Nco)**

Nco = Na + Nb = Z/2 + (2Z – 3) - Thorpe equation

Na and Nb are the radial and the axial bond strengths;

For the ideal glass, Nco=Nd=3,
where the mechanical stability of the network is optimized.

As-Se-Ag glasses → **Nco ≈ 3**

➢ **Overall mean bond energy**

<E> =Ec + Erm – Tichy equation

Ec - mean bond energy of the average cross-linking/atom (heteropolar bond energy);

Erm - average bond energy per atom of the 'remaining matrix' (homopolar bond energy)

<E> = f (<Z>, the type and energy of bonds-heteropolar and homopolar)

<E>↑ with Ag addition, due to formation of stronger heteropolar bonds. As a result, the network stability of the system increases, confirming the tendency of compositional dependence of experimentally derived physico-chemical parameters.

Amorphous chalcogenide films

Unique properties → **transparent in the infrared region of the spectrum**

Unique properties → **photo-induced structural changes under action of light with photon energy greater than band gaps of the materials.**

Opportunity for application

optical waveguides with different geometry, applicable in mid-IR fiber-optic sensing.

changes in the optical constants (Δn, Δk) and physicochemical properties (microhardness, density, solubility).

Planar waveguide

$N_{core\ layer} \neq N_{cladding\ layer}$ ***- obtained by direct writing with light on the surface of the material.***

Preparation of thin amorphous chalcogenide films:

- Vacuum thermal evaporation
- Pulsed laser deposition

Results:

- Transmission spectra recorded within the spectral range (400–2500 nm)
- Refractive index (n) - Swanepoel method.
- Determination of Eg from absorption coefficient data by Tauc procedure.
- Influence of the Ag content on the optical band gap of the films prepared by PLD and VTE.
- Spectral dispersion of the refractive index of the films with different Ag contents, prepared by PLD and VTE.

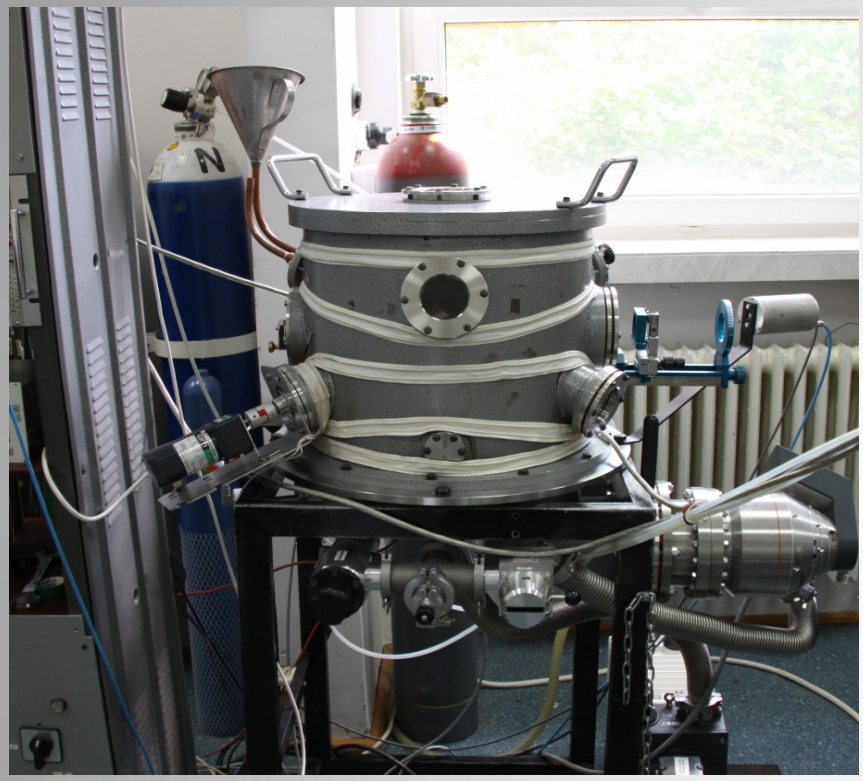
Preparation of thin As-Se-Ag films: Vacuum thermal evaporation

CONDITIONS OF VTE PROCESS

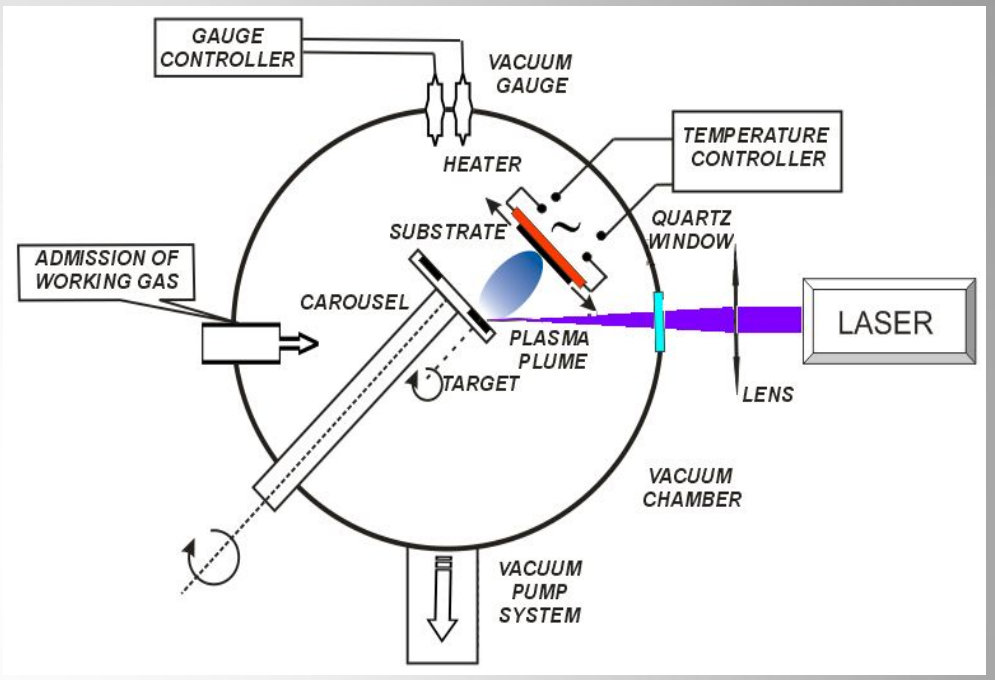
- source-substrate distance 0.12 m
- temperature of evaporation source 700–800 K
- temperature of the substrates 300 K
- residual gas pressure of 10^{-5} Torr

Thin films for optical measurements:

deposited on glass substrates **d ~ 800–900 nm**



PLD



Advantages of PLD:

- relative simplicity of the process
- nearly stoichiometric transfer of target material to the films
- easy control of the process by laser operating parameters and possibility to prepare films of unusual compositions

CONDITIONS OF THE PLD PROCESS

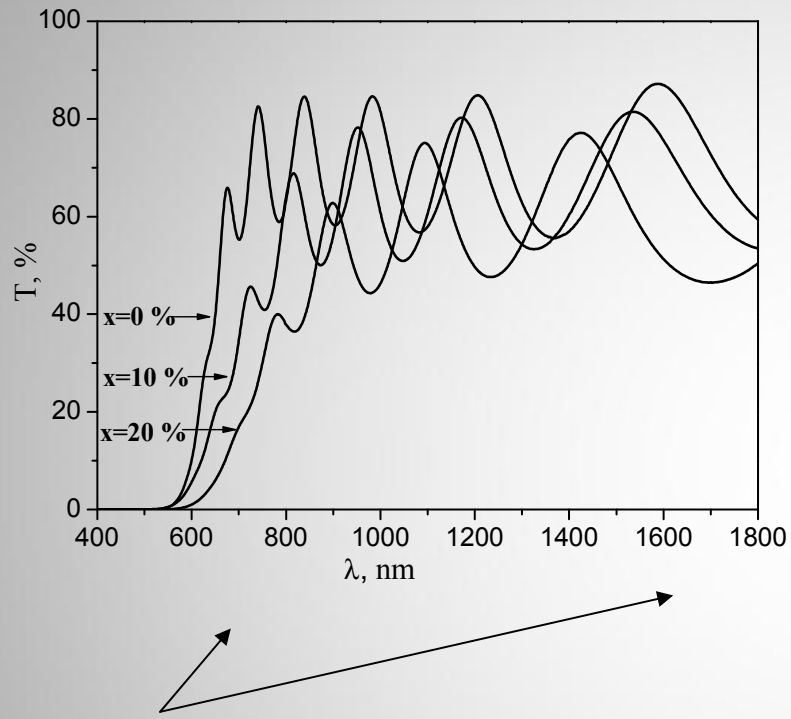
$P = 10^{-4}$ Pa

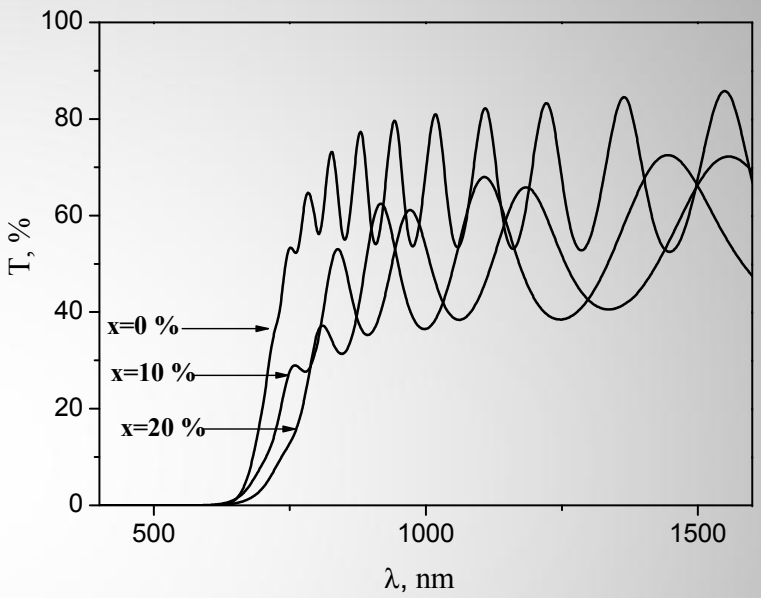
KrF* excimer laser, $\lambda = 248$ nm;

$\tau = 25$ ns; F = 1.6 J/cm2, N = 3000

deposition rate = 1.5–3.0 Å/pulse

VTE





PLD

The red shift of the abs. edge after addition of silver is caused by formation of additional defect states, localized just above the valence band.

Transmission spectra recorded within the spectral range 400–2500 nm

Absorption coefficient α:

$$\alpha = 1/d \, [\ln (1-R)^2 / T]$$

d – thickness of the film

R – reflectivity of the film

Absorption coefficient of amorphous semiconductors:

$$(\alpha h\nu) = B\{h\nu - Eg\}^m$$

Determination of the Eg values → Tauc procedure: plotting a graph of $(\alpha h\nu)^{1/2}$ versus hν → extrapolation of the straight line part to the energy axis of zero absorption coefficient

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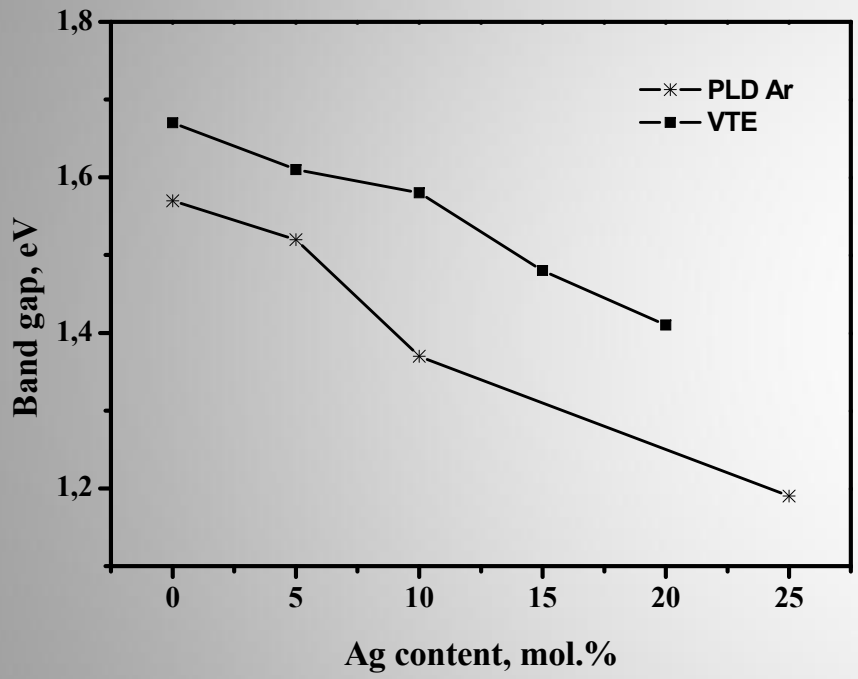
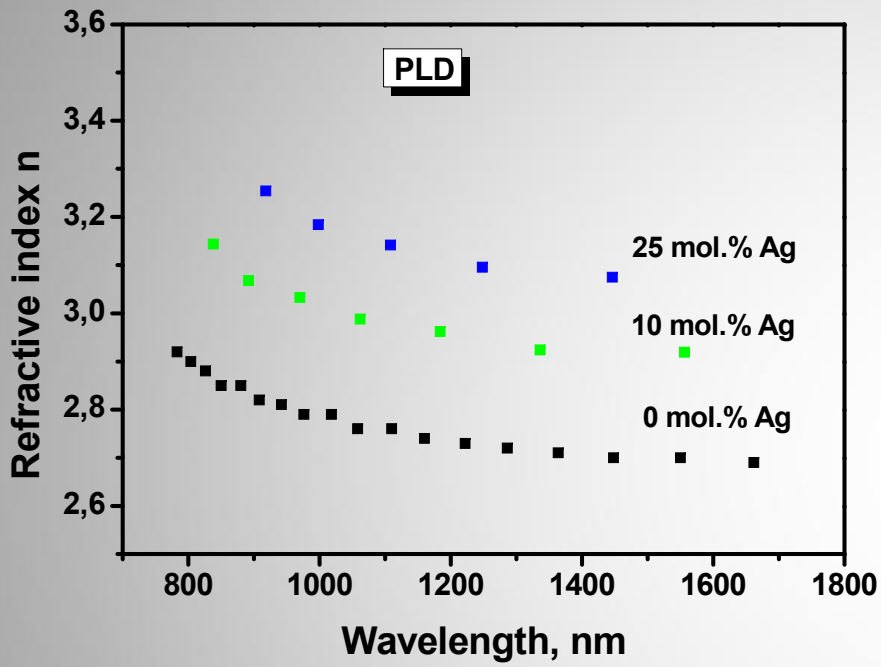
Influence of the Ag content on the optical band gap of amorphous $(AsSe)_{100-x}Ag_x$ films prepared by PLD and VTE.



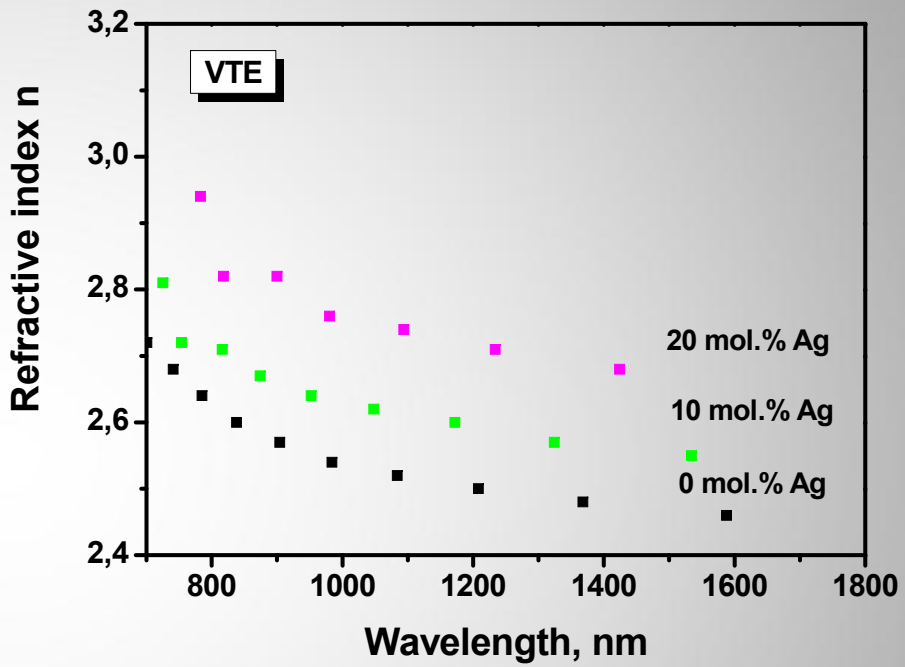
Eg↓ with increase of Ag - structural transformation and bond rearrangement in the films.
The atomic substitution of As by Ag probably causes an increase in disorder and the amount of defects present in amorphous structure, resulting in optical band gap decrease.

Eg(VTE) > Eg(PLD) due to the preparation technique, providing difference in the structure of the obtained films: Due to higher temperature and energy of the particles in the plume, the structure of PLD films can be closer to statistically disordered model of amorphous solids ***(P. Neˇmec et al. / Thin Solid Films 484 (2005) 140–145).*** *This distortion in the structure leads to higher Eg values of VTE thin films.*

Refractive index (n) of $(AsSe)_{100-x}Ag_x$ films - Swanepoel method



PLD films: n = 2.7 to 3.4



VTE films: n = 2.5 to 3.0

- The increase of n is related to higher polarizability of larger Ag atoms, compared to Se atoms.
- The refractive index n of PLD films is slightly higher as compared to VTE films, due to the different structure.

Conclusions

- The obtained materials exhibit homogeneous and glassy structure in a wide range of composition.
- Density results show that the silver atoms are well incorporated in the chalcogenide matrix and uniformly distributed.
- Stability in the behaviors and silver dispersion provide good network stability of the obtained materials.
- Thin amorphous $(AsSe)_{100-x}Ag_x$ films were obtained by VTE and PLD techniques, and their optical properties were investigated.
- A red shift of the absorption edge is observed upon addition of Ag to the glassy matrix.
- The observed decrease in the optical band gap with the increase of Ag concentration was attributed to structural transformation and bond rearrangement in the films. The atomic substitution of As for Ag probably caused an increase in disorder and the amount of defects present in amorphous structure, thus decreasing the optical band gap.
- Refractive index calculations showed that PLD films have a slightly higher index of refraction as compared to the VTE films. The increase of the refractive index with Ag content in both types of films is probably related to the higher polarizability of the larger Ag atoms.

Thank you!

Why Ag – As – Se glasses?

- **Ag** ⟶ **additives in network glasses, such as chalcogenides and oxides, because the resulting glasses can show high electrical conductivities with potential applications for batteries, sensors and displays.**

- **Ag+ ions** ⟶ **two types of interaction: some of the Ag+ ions form strong bond with the glassy network, some interact weakly with the network. It has been proposed that the last types of Ag+ ions are highly mobile compared to other Ag+ ions giving rise to high conductivity.**

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$$< Z > = \sum_i x_i Z_i$$

x_i – atomic fraction of the i-th component of a glass; Z_1 – coordination number of the i-th atom;

N_i – number of electrons in the outer shell of the atom;

$$Z_i = 8\text{-}N$$

$$Z = Z_{Ag}x + Z_{As}y + Z_{Se}z$$

$Z > 2.4$ ⟶

Phillips and Thorpe theory:

➢ **Glasses with Z < 2.40 consist of rigid regions, immersed in a 'floppy' matrix.**

➢ **Glasses with Z = 2.40 are unique - the floppy and the rigid regions are individually connected with a maximum number of connections.**

➢ **When Z > 2.40, the solid has continuously connected rigid regions with floppy regions inter-dispersed and may be termed as 'amorphous' solid.**

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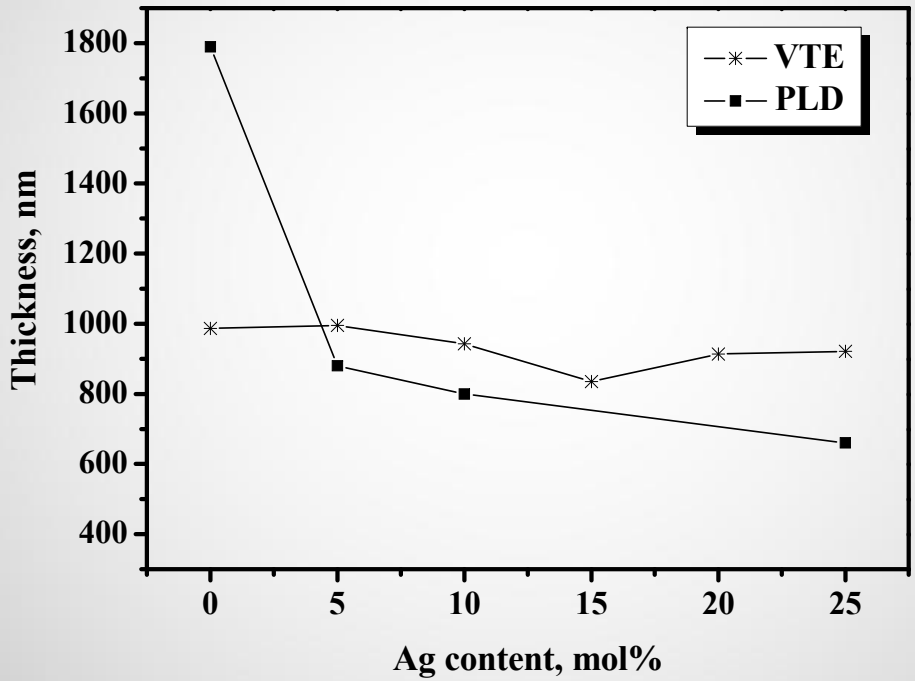
Thickness of As-Se-Ag films



PLD ⟶ d = f(x)

The thickness decrease with Ag percentage could be attributed to an increase of the reflectivity on addition of Ag, which makes the laser beam energy transfer to the target more difficult.