Silver containing chalcogenide glasses and their applications

V. Ilcheva, P. Petkov, T. Petkova, V. Boev

<u>Amorphous chalcogenides</u>

fundamental condensed matter research
technological applications

Chalcogenide glasses - (S, Se,Te) + **Ge, As, Sb, Ga (elements from IVth, Vth or VIth group)**

<u>Properties</u> ⟵ **disordered structure, compositional dependence of the properties**

↓

➢**optical, electrical**
➢**photosensitivity**

design of materials for specific requirements

photodarkening, photodoping, photocrystallization
and photoconductivity

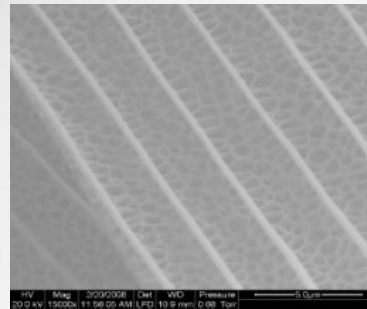## <u>Characteristics and Advantages</u>
1) Ability of composition variation -> Flexible structure -> Properties modification in   desired direction
2) Ability of doping with many different components (elements or compounds)
3) Absence of grain boundaries
4) Isotropic properties
5) High chemical and time stability, radiation durability and nontoxicity
8) Significant ionic conductivity
6) Easy to prepare in bulk and layered form
7)High refractive index (2.2 – 3.5) and good transparency to mid-infrared spectral region.
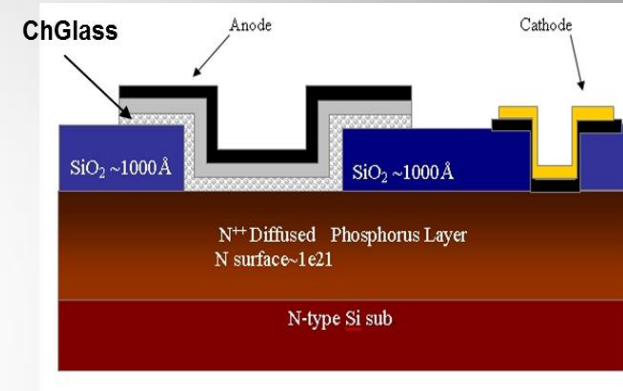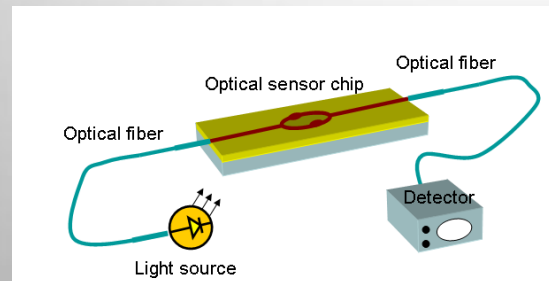
Application

➤ Waveguides

Fiber–optic communication

640 GB/s

Chalcogenide glass photonic chip
100 times faster than electronic
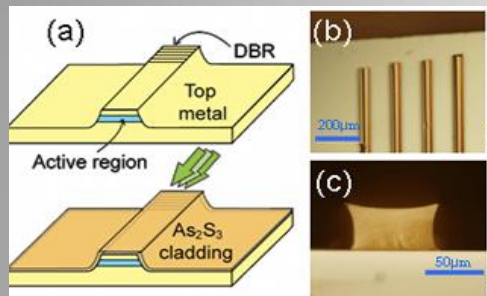
➤ Optical data storage

➤ sensor systems for liquid and gas analyzing

Fiber optic sensing

➤ Solid state electrolytes

Gas sensors based on optical detection
Classical sensors - the detection is related to the variation of the sensor material's electrical properties.
Gas sensors based on optical detection - based on the reversible alterations of sensor material's optical properties upon exposure to the gas environment.

PRAM 512 Samsung

Application

▶**Infrared optics**

proven phase change materials,
used in memory devices, based on
phase change transitions in these materials.

Glasses

Support many emerging energy – related technologies:
- glasses for SOFS;
- glass electrolytes for supercapacitors and other ES;
- glass mycrospheres for storing and transporting of hydrogen.

Specific characteristics of the
chalcogenide semiconductors
(single and mixed) → suitable material for solar energy systems

appropriate band gap, allowing to be used as a photon absorbers in thin film based solar cells
to generate electron-hole pairs → convert light energy to usable electrical energy.

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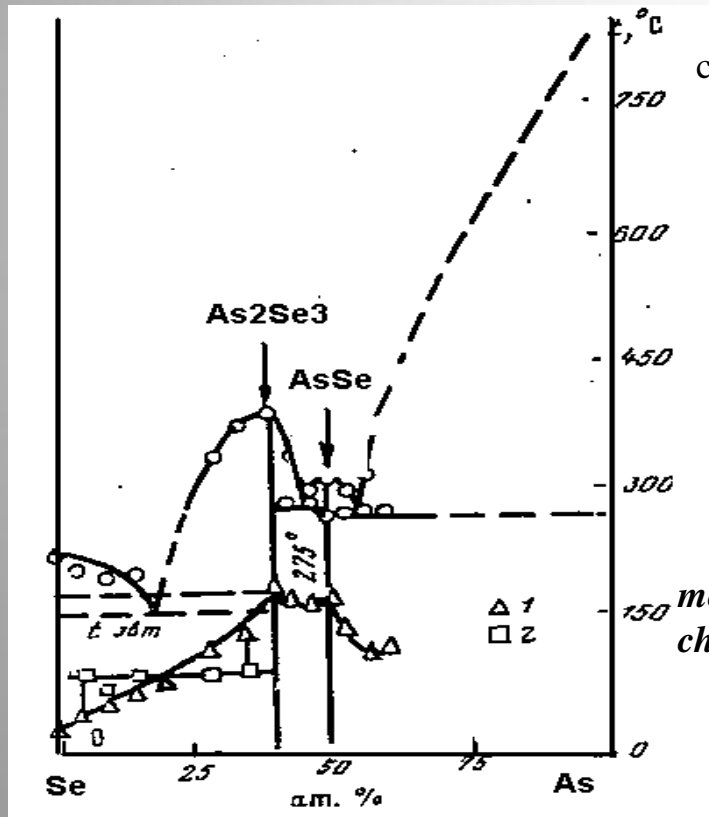
Stable and homogeneous As_xSe_{100-x} glasses
can be prepared in As–Se system in a large compositional region.

Phase diagram of the binary As-Se system is simple with two compounds.
Both can be easy prepared in glassy form and are stable with the time.

Ag-chalcogenide glasses

Ag

modify basic physico-chemical characteristics of the material

causes substantial changes in the optical and electrical properties

Objective of investigation:

➢ *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

melt quenching
technique

Structural study

➢**XRD**

➢**SEM**

➢**IR**

Deposition of thin films

Optical characterization

<u>Compositions</u>

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: might be used mixture of cool water, ice and NaCl.
➤Choosing of cooling mode depends on the structure, the type, volume of the material.
➤The main feature of the melt-quenching process is that the amorphous solids
are formed by the 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 900°C
and quenching in a mixture of ice and water.

XRD

SEM

$(AsSe)_{1-x}Ag_x$

x=5

x=25

Arb.units

2Θ, deg

1 µm   6.1kV   1.00E4   1444/01   SE   *
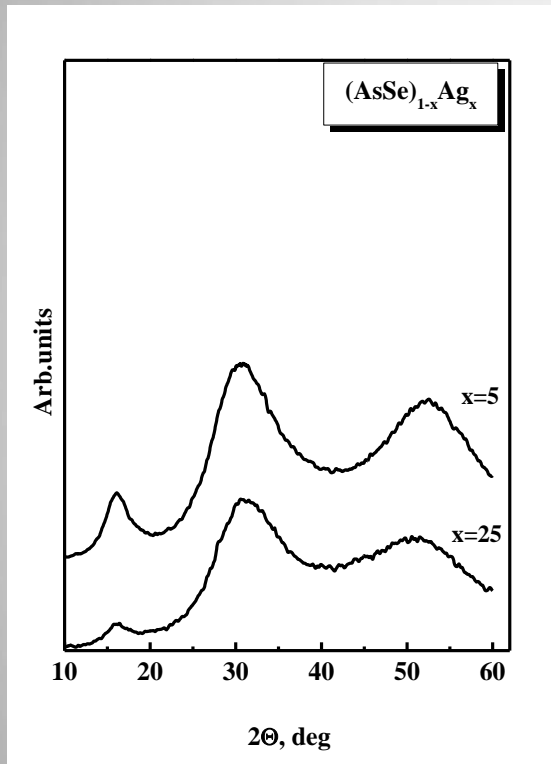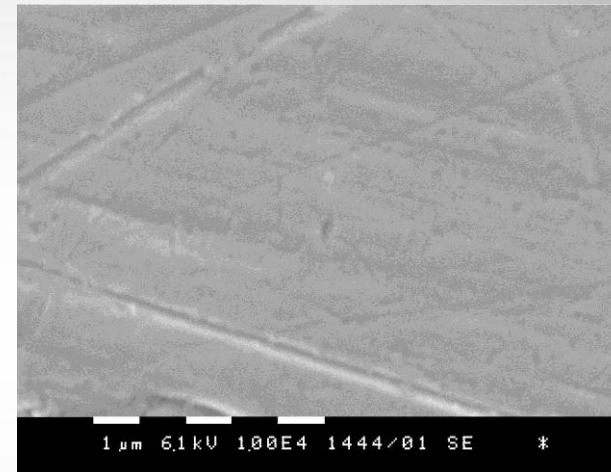
Smooth and homogeneous structure of the samples.
The samples with 25 mol% Ag doesn't show
some silver clusters concentrated into the glassy matrix.

<u>Preparation of thin amorphous chalcogenide films</u>:

➤ **Vacuum thermal evaporation**
➤ **Pulsed laser deposition**

<u>Results:</u>

➢ **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.**

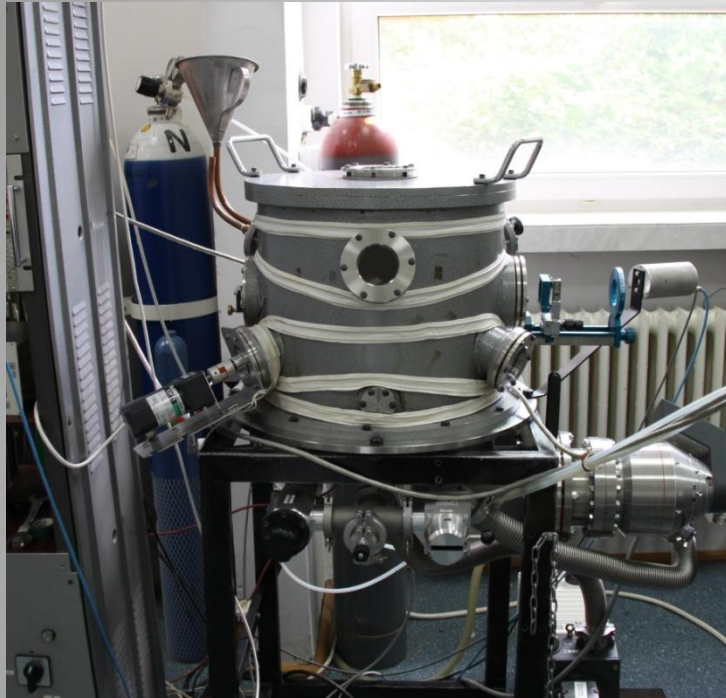# Preparation of thin As-Se-Ag films: Vacuum thermal evaporation

CONDITIONS OF VTE PROCESS

➢ **source-substrate distance - 0.12 m**
➢ **temperature of the substrates - 300 K**
➢ **residual gas pressure of 10^{-5} Torr**

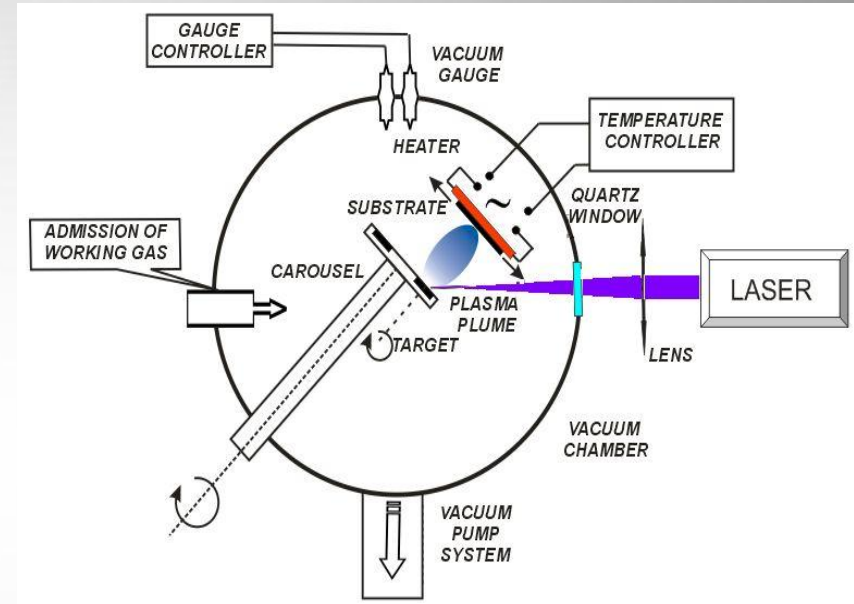## Thin films for optical measurements:

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
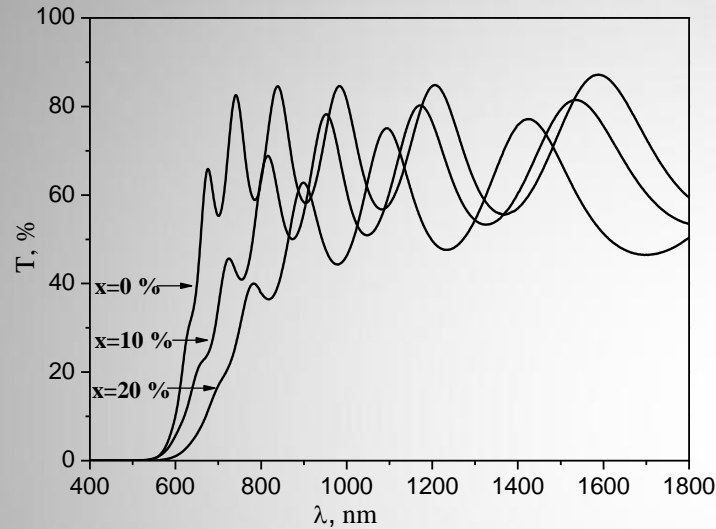
CONDITIONS OF PLD PROCESS

$P = 10^{-4}$ Pa
KrF* excimer laser, $\lambda = 248$ nm;
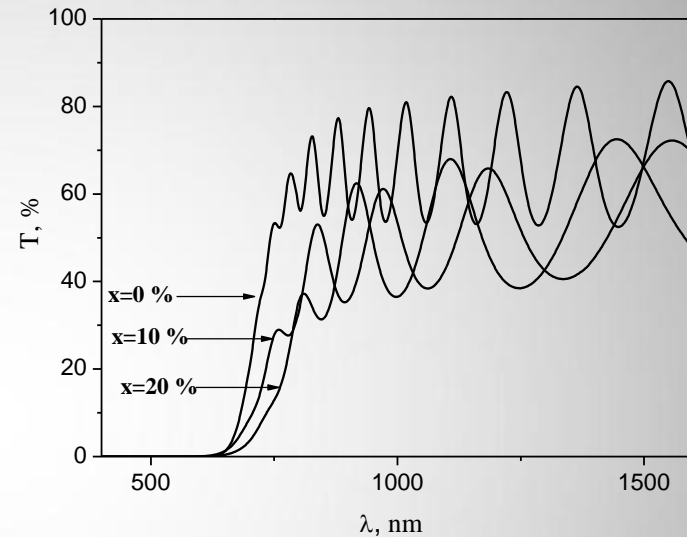$\tau = 25$ ns; $F = 1.6$ J/cm2 ; $N = 3000$
Deposition rate = 1.5 – 3.0 Å/pulse

VTE

PLD

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

# Influence of the Ag content on the optical band gap of amorphous $(AsSe)_{100-x}Ag_x$ films prepared by PLD and VTE.
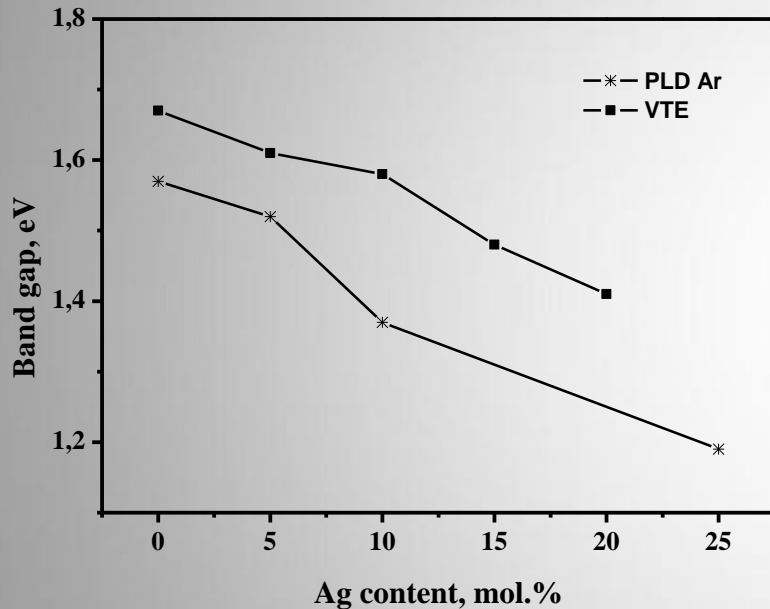
Eg↓ with increase of Ag - structural transformation and bond rearrangement in the films.
The atomic substitution of As by Ag probably causes an increase in disorder and the amount of defects present in amorphous structure, resulting in optical band gap decrease.

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
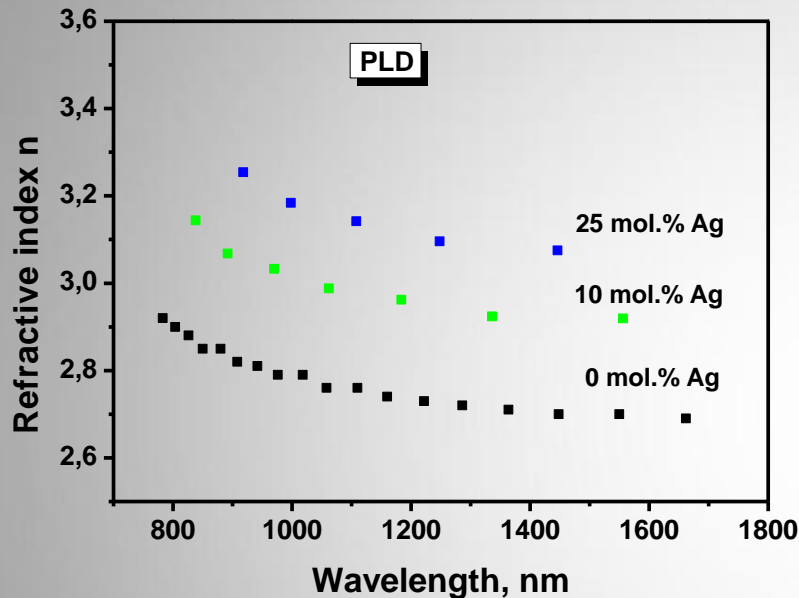
PLD films: n = 2.7 to 3.4
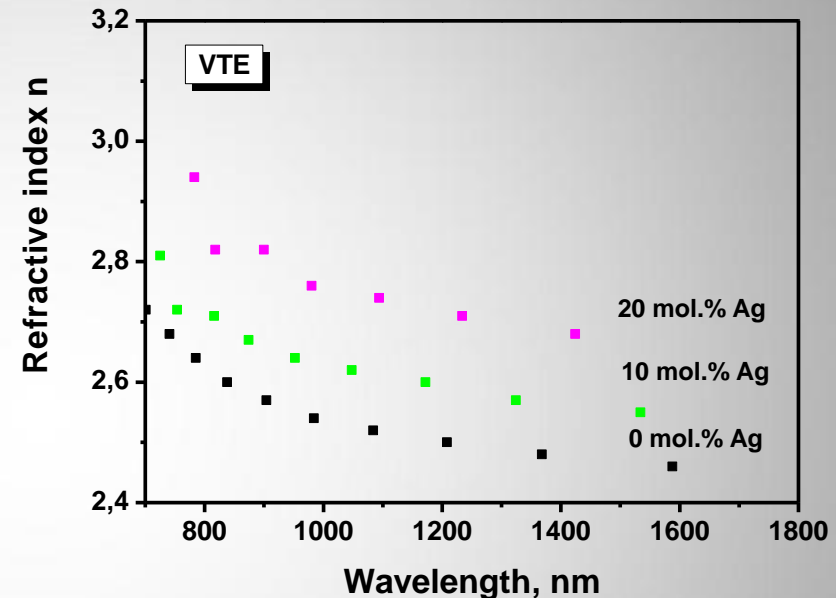
VTE films: n = 2.5 to 3.0

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.

Spectral dispersion of the refractive index *n* of amorphous $(AsSe)_{100-x}Ag_x$ films with different Ag contents prepared by PLD and VTE

Conclusions

➤ Thin amorphous $(AsSe)_{100-x}Ag_x$ films were obtained by VTE and PLD from the corresponding bulk glassy materials, and their optical properties were investigated.

➤ The obtained materials exhibit homogeneous and glassy structure in wide compositional region.

➤ A red shift of the absorption edge is observed after the addition of Ag to the glassy matrix.

➤ The observed decrease in the optical band gap with increase of Ag concentration was attributed to the structural transformation and bond rearrangement in the films. The atomic substitution of As by Ag probably caused an increase in disorder and the amount of defects present in amorphous structure, thus decreasing the optical band gap.

➤ Addition of silver leads to increase of the refractive index, related probably to higher polarisability of larger Ag atoms.

➤ The obtained results demonstrate, that the amorphous thin As-Se-Ag films have a long transmission window. Their optical characteristics could be gradually changed with the addition of third component into chalcogenide matrix, which enables to obtain desired parameters and to enlarge the possibility for their application.

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 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.

Thickness of As-Se-Ag films
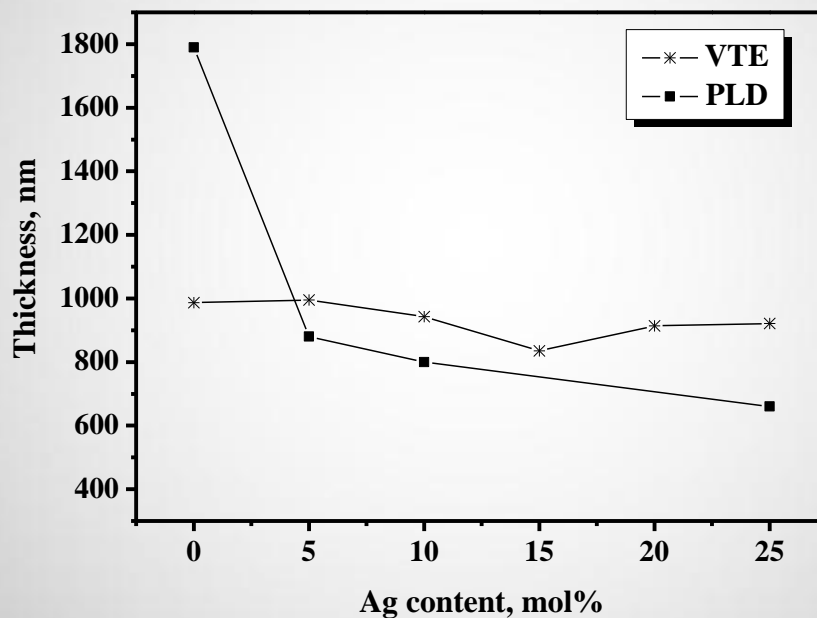
PLD $\longrightarrow$ **d = f(x)**

The thickness decrease with the percentage of Ag could be attributed to increase of reflectivity with addition of Ag, which makes the laser beam energy transfer to the target more difficult.
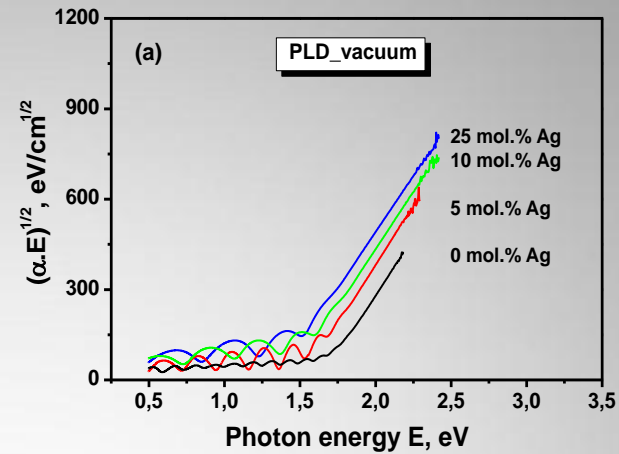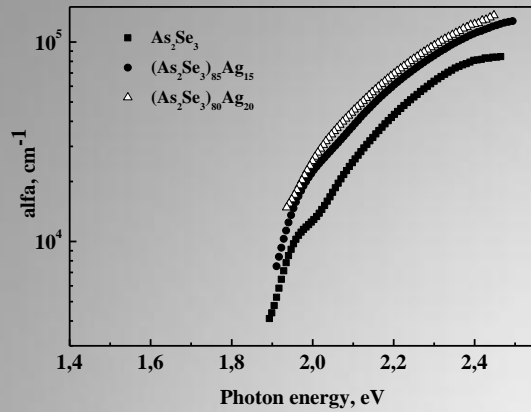
The absorption coefficient α for all investigated films was determined in the region of strong absorption ($\alpha \geq 10^4$ cm^{-1}), which involves optical transitions between the valence and conduction bands [5]. For that purpose, the obtained values of *n* were extrapolated in the high absorption region and α was estimated using an equation given in Ref.4.

The high absorption region ($\alpha \geq 10^4$ cm^{-1}) corresponds to transitions between extended states in both valence and conduction bands where the Tauc law [9] is valid. Thus, above exponential tail, the absorption coefficient of amorphous semiconductors can be described by the relation $\alpha h\nu = B(h\nu - Eg)^m$, where *hν* is the photon energy; *Eg* - the optical band gap; *B* - constant that depends on the transition probability; *m*- index, depending on the nature of electronic transitions. For amorphous materials non-direct optical transitions (m = 2) are observed.

Optical band gap *Eg opt* was determined from intercept on the energy axis of linear fit of high absorbing region ($\alpha \geq 10^4$ cm^{-1}) in plot *$(\alpha h\nu)^{1/2}$* versus *hν* (where α is absorption coefficient and hν is energy of incident photons) known as Tauc extrapolation [9].

Chalcogenides as optical fibers:

These can be essentially divided into two groups, namely "passive" and "active" applications:

(a) Passive Applications: The fibers are used as a light conduit from one location to another without interacting with the light, other than that due to scattering, absorption and end face reflection losses associated with the fiber.

(b) Active Applications: The light propagating through the fiber is modified by a process other than that due to scattering, absorption and end face reflection losses associated with the fiber. Examples of these include fiber lasers, amplifiers, bright sources, gratings and non-linear effects.

Gas sensors based on optical detection have focused significant attention

because in contrast with the classical sensors where the detection is related to the variation of the sensor material's electrical properties, the new class of miniaturized gas sensors is based on the reversible alterations of sensor material's optical properties upon exposure to the gas environment.

The main advantages of optical detection over the classical methods a re very high accuracy, fast response time, advanced sensitivity, and possibility to operate at room temperature [9].

Phase change materials

This material changes phases, reversibly and quickly, between an amorphous state that is electrically high in resistance, and a polycrystalline state that is highly reflective and low in resistance. The two phases of the chalcogenide alloy have important differences in electrical properties due to the change in free electron density. The resistivity of the polycrystalline state has been shown to be up to four orders of magnitude lower than that of the amorphous state. The storage of each memory bit information is a result of discrete transition between low and high resistance state (as a result of phase change transition of the materials, due to the change in the free electron density).

Physico-chemical 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); $Z_{Ag}= 3$; $Z_{As} = 3$; $Z_{Se} = 2$;

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

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

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

$Z_i = 8-N$

$Z = Z_{Ag}x + Z_{As}y + Z_{Se}z$ $Z > 2.4$

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.

➤**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**

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

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

<E> =Ec + Erm – Tichy equation   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.