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

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

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

- vapors in plume are very hot (\( \sim X.10^3 \text{K}, \) 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
The kinetic energy (temperature) of the particles in the plume is high (up to keV) ⇒

chemical reactions among particles (fragments) during or after condensation are quicker (easier, self-annealing) ⇒ 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 $\rightarrow$ 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 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 $\text{As}_2\text{Se}_3$ films contain (in comparison with TE films) less ‘wrong’ As-As and Se-Se bonds and less $\text{As}_4\text{Se}_4$, $\text{As}_4\text{Se}_3$, $\text{Se}_8$ or $\text{Se}_n$ particles.

- **High kinetic energy** of plasma-plume particles enables their interaction $\Rightarrow$ (Eqs. 1-3), densities of $\text{As}_4\text{Se}_4$, $\text{As}_4\text{Se}_3$, $\text{Se}_n$ are lowered, e.g.

$$\text{As}_4\text{Se}_4 + \frac{2}{n} \text{Se}_n = 2 \text{As}_2\text{Se}_3 \quad (1)$$

$$\text{As}_4\text{Se}_3 + \frac{3}{n} \text{Se}_n = 2 \text{As}_2\text{Se}_3, \quad (2)$$

or just

$$|\text{As-As}| + |\text{Se-Se}| = 2|\text{As-Se}| \quad (3)$$
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 $\text{As}_{60}\text{Se}_{40}$ 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
\[ 2\text{As}_2\text{S}_3 = \text{As}_4\text{S}_4 + \text{S}_2 \implies \text{change of composition} \]

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

\[ \text{As}_{50}\text{S}_{50} \text{ from As}_2\text{S}_3 \]

1 as-evaporated
2 exposed
3 annealed
Spectral dependence of index of refraction values for As$_4$Se$_3$ PLD thin films
Index of refraction, $n$, of $\text{As}_2\text{Se}_3$ 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 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.

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

(4)
In $\text{Ge}_x\text{Se}_{1-x}$:

exposure and annealing - decrease of the density of Ge-Ge and Se-Se bonds in $\text{Ge}_2(\text{Se}_{1/2})_6$ structural units

$$\text{Ge} - \text{Ge} + \text{Se} - \text{Se} \leftrightarrow 2\text{Ge} - \text{Se}$$  \hspace{1cm} (5)

Raman spectra $\text{Ge}_x\text{Se}_{1-x}$, $x = 0.24$ thin films

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

By annealing - decrease of Raman bands of Ge-Ge and Se-Se bonds → more chemically ordered system → higher $E_g$
\[ x\text{GeSe}_2(s) \leftrightarrow (x-y)\text{GeSe}_2(g) + y\text{GeSe}_2(g) + y/n\text{Se}_n(g), \]  

(6)

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

\[ m\text{GeSe}_2(g) \leftrightarrow m\text{GeSe}_{1-p} + (p/n)\text{Se}_n \]  

(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).
Slight photobleaching, larger bleaching by annealing

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

$E_g^{\text{opt}}$, Ge$_{28}$Se$_{72}$
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 $t \approx 400-420^\circ\text{C}$

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

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

Excimer laser pulses - crystallization, prevailing Te crystals
The Raman spectra of very low intensity, only small changes
179d - stopy po expozici

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

Te cryst.
$\text{Sn}_{16} \text{Te}_{84}$
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 promising.
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
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Thank you for your kind invitation and for your attention