

ROMANIAN ACADEMY "ILIE MURGULESCU" INSTITUTE OF PHYSICAL CHEMISTRY



THESIS SUMMARY

Correlation of optical and morph-structural properties in chalcogenide compounds with applications in optoelectronics

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1.Introduction

Chalcogenide compounds are the combinations of Group VI elements of the Periodic Table, especially the sulfur, selenium, and tellurium compounds. This name comes from the Greek language, showing that they occur in nature in the copper ores ($\chi\alpha\lambda\kappa\sigma\zeta$ - copper, $\gamma\epsilon\nu\nu\alpha\omega$ – to born şi ειδοζ - type) [1]. Chalcogenide is a chemical compound containing at least one chalcogen anion (S²⁻) and an electropositive element (Cd²⁺, Zn²⁺). Chalcogenides are known as amorphous, quasi-amorphous and crystalline materials with applications in several fields: thermoelectric, nonlinear optics, medicine, etc. The main objective of the thesis **is the study of obtaining, ternary** (GeSbSe) **and quaternary** [GeSb(As)STe] **chalcogenide systems with possible applications in IR.**

The second objective was to determine **the atomic structure** for binary and ternary chalcogenide films using X-ray diffraction and neutron diffraction measurements correlated with the Monte Carlo simulation method.

The third objective is given by **the IR study (Raman, FTIR, and IRSE)** to obtain information on chemical bonds. The positions of the vibration bands have been established and the related chemical bonds have been identified.

The final objective was to determine **the influence of the durability of the quaternary chalcogenide properties tested by MIL-C-48497**. One of the purposes of the quality standards is to assess the durability by subjecting covered surfaces to accelerated exposure, high and low temperatures, humidity and adhesion.

The thesis is structured in **5 Chapters** as follows:

- Chapter I contains general information on calcogenic materials, their classification, and applications.

- Chapter II gives a brief overview of methods for obtaining calcogenic materials, insisting on the method by which the calcogenic materials were obtained in the present thesis, namely the method of vacuum evaporation.

- Chapter III presents the methods used in the thesis for the characterization of calcogenic materials.

- Chapter IV contains the most important results obtained in the thesis for ternary calcogenides.

-Chapter V contains important results obtained for quaternary chalcogenides and contains: the production and characterization methods also durability tests.

The conclusions are presented at the end of this thesis.

2. ORIGINAL CONTRIBUTIONS 2.1 Obtaining binary (GeSe) and ternary (GeSbSe) calcogenide films

The binary $Ge_{40}Se_{60}$ and ternary $Ge_xSb_{40-x}Se_{60}$ glasses with x=15, 20, 25, 27, 32 and 35 at.% were prepared from elements of 99,999% purity. Appropriate quantities from elements were sealed into quartz ampoules to a pressure of 10^{-3} Pa. The bulk glasses were synthesized by the conventional melt-quenching method in a rotary furnace at 950 °C and after homogenization for 24 h, the melts were quenched in air. Part of the synthesized glasses was powdered serving as parent material for film preparation by vacuum thermal evaporation onto quartz substrates at a chamber residual pressure of 10^{-4} Pa. The other part was used for neutron diffraction (ND) and X-ray diffraction (XRD measurements. The thickness of the films was controlled in situ by MIKI FFV quartz sensor device.

2.2 GeSbSe - Neutron Diffraction (ND)

To investigate <u>the atomic structure of amorphous materials</u>, ND measurements were performed. From the experimental results we could evaluate the structural factors S (Q), but also the weighting factors, (wij), which are found in the partial structure factors, Sij (Q), defined after relations 1-3.The experimentally results obtained were overlapped with the theoretical simulation ones of the Reverse Monte Carlo model.

$$S(Q) = \sum_{i,j}^{k} w_{ij} S_{ij}(Q) , \qquad (1)$$

$$w_{ij}^{ND} = \frac{c_i c_j b_i b_j}{\left[\sum_{i,j}^k c_i b_j\right]^2},$$
(2)

$$w_{ij}^{XRD}(Q) = \frac{c_i c_j f_i(Q) f_j(Q)}{\left[\sum_{i,j}^k c_i f_i(Q)\right]^2}$$
(3)

where c_i , c_j are the molar fractions of the components, b_i , b_j are the coherent neutron and $f_i(Q)$, $f_j(Q)$ are the X-ray scattering amplitudes, and k is the number of elements in the sample. Figure 1 presents the S(Q) from neutron diffraction experiments, where the results of the Reverse Monte Carlo model calculation are also drawn.



Figure 1 - Neutron diffraction structure factor, S(Q), of the chalcogenide samples vs composition of GexSb40-xSe60 (x=40, 35, 32, 27, 20, 15 at.%) are displayed: experimental data (colour marks) and RMC simulation (solid lines).

2.3 GeSbSe - X-ray Diffraction (XRD)

In this study the XRD structure factors were obtained up to 18 Å⁻¹, as for higher *Q*-values the experimental data became rather noisy. Because the atomic parameters of the components are similar, the XRD structure factors were similar to ND ones. We consider here the XRD data for four samples which shows well the concentration dependence within the series. The XRD experimental *S*(*Q*) data together with the RMC simulation results are presented in Figure 2.



Figure 2 - X-ray diffraction structure factor, S(Q), of the ternary GexSb40-xSe60 with composition of x=35, 27, 15 at.% and the binary Ge40Se60 glass are displayed: experimental data (colour marks) and RMC simulation (solid lines).

To illustrate the differences, the comparison of the corresponding weighting factors, w_{ij} , for the two radiations is shown in Table 1, where and at Q=1.05 Å⁻¹ are given for the Ge₁₅Sb₂₅Se₆₀ sample. It can be seen that the Ge-Se and Se-Se atom pairs have a significant contribution to the neutron experiment, while the Sb-Sb and Sb-Se atom pairs have a dominant weight in the X-ray experiment. On the other hand, the differences appeared for the Ge-Ge and Ge-Sb atom pairs, are not so significant. *Taking into consideration all these characteristics, we have concluded that the two radiations give complementary information and, both types of measurements are needed to obtain a real structure for the investigated samples.*

Ge15Sb25Se60						
Ge-Ge	Ge-Sb	Ge-Se	Sb-Sb	Sb-Se	Se-Se	
		ND weightin	ng factor (%)			
2.75	6.24	21.43	3.54	24.30	41.74	
	XRI) weighting fact	or (%) at Q=1.0	5 Å ⁻¹		
1.59	8.49	13.56	11.32	36.16	28.88	

Table 1. Neutron- and X-ray diffraction weighting factors, $w_{ij}(\%)$ at Q=1.05 Å⁻¹, in the Ge₁₅Sb₂₅Se₆₀ sample.

2.4 Influence of Sb content in GeSbSe sample from structural analysis

The results from X-ray and neutron diffraction (RMC) correlated with the Reverse Monte Carlo simulations in binary and ternary films indicate that Sb atoms incorporated in Ge₄₀Se₆₀ are covalently bonded to Se and form trigonal SbSe₃ units (Figure 3). The Se atoms are connected to Ge forming tetrahedral geometric units GeSe₄ (Figure 4).



Figure 3 - Ge-Se pair distribution functions and their 3D bonds in $Ge_{15}Sb_{25}Se_{60}(a)$ and $Ge_{35}Sb_5Se_{60}(b)$ cell units. The color represents the type of atoms: Ge-red and Se-blue colored.



Figure 4. – Sb - Se pair distribution functions and their 3D bonds in $Ge_{15}Sb_{25}Se_{60}(a)$ and $Ge_{35}Sb_{5}Se_{60}(b)$ cell units. The color represents the type of atoms: Sbgreen and Se-blue colored.

From the partial distribution functions, the number of neighboring atoms of Ge, Sb, and Se were calculated. From the literature, the coordination numbers for Ge (CN = 4), Sb (CN = 3) and Se (CN = 2) were known, so in order to obtain more information about the atomic structure, simulations were made in which Ge and Sb atoms were forced to have four and three neighbors respectively, as shown in Table 2.

	Numar de coordinare, CN _{ij}						
Perechi de atomi	Ge40Se60	Ge35Sb5Se60	Ge32Sb8Se60	Ge27Sb13Se60	Ge20Sb20Se60	Ge15Sb25Se60	
Ge-Se	2.97	3.10	3.22	3.45	3.63	3.84	
Ge-Sb	-	0.05	0.02	0.03	0.05	0.07	
Sb-Se	-	2.97	2.80	2.78	2.64	2.59	
Sb-Ge	-	0.03	0.05	0.04	0.09	0.11	
Se-Ge	1.98	1.81	1.72	1.55	1.21	0.96	
Se-Sb	-	0.21	0.31	0.58	0.88	1.08	
Ge-Ge	0.74	0.55	0.52	0.40	0.23	0.05	
Se-Sb	-	0.21	0.31	0.58	0.88	1.08	
Ge-Ge	0.74	0.55	0.52	0.40	0.23	0.05	

Tabelul 2 - Average coordination numbers, CN_{ij} , calculated from the RMC simulation. The error is ~5% for Ge-Se, Sb-Se, Se-Ge and ~10% for Ge-Sb, Sb-Ge, Se-Sb, Ge-Ge.

From the results presented, the coordinate number is below the expected number but has a good dependence on the Ge / Sb ratio. The results suggest the presence of two basic structural units, GeSe₄ tetrahedral and SbSe₃ pyramid units. The average number of coordinates is very close to 4, as proposed by the formation of tetrahedral units in the network, however, with the increase the Sb content the Ge-Se coordination number is slightly increased from 3.15 to 3.70.

Using the ultimate atomic configuration of the RMC algorithm, the distribution angles were calculated. Figure 5 shows the distribution angles for the Ge-Sb atoms and the Se-Ge-Se, Se-Sb-bonds in relation to both: $\cos(\theta)$ and θ (θ -real binding angle).



Figura 5 - Bond-angle distributions of Se-Ge-Se (a), and Se-Sb-Se (b) configurations for the corresponding compositions of $Ge_{40}Se_{60}$ (black square), $Ge_{35}Sb_5Se_{60}$ (red circle), $Ge_{32}Sb_8Se_{60}$ (blue triangle), $Ge_{27}Sb_{13}Se_{60}$ (green crosses), $Ge_{20}Sb_{20}Se_{60}$ (orange square) and $Ge_{15}Sb_{25}Se_{60}$ (purple reverse triangle).

The Se-Ge-Se bonding angles are maximum at $107 \pm 3^{\circ}$ for ternary films and at $109.6 \pm 2^{\circ}$ for the binary film. The values are very close to the tetrahedral angle (109.47°). It can be seen that the distribution is asymmetric and very similar for all the studied samples. A shift occurs with increasing Sb concentration, suggesting the destruction of tetrahedral network. The Se-Sb-Se binding angle distributions exhibit similar characteristics for all samples, the maximum being 118 $\pm 3^{\circ}$ and $111 \pm 5^{\circ}$. With the increase of the concentration of Sb there is a displacement which involves considerable distortions in the pyramid network's flat geometry.

3 GeSbSe - Optical Properties Studies

3.1 Spectroscopic ellipsometry (SE) and transmission measurements

The influence of composition and optical constants was studied by ellipsometric measurements in spectral range 193-1000 nm, at incidence angles 60°, 65°, and 70°.

From the analysis of ellipsometry data, the optical constants (n and k), Eg and the film thickness are determined. The pattern contains 2 layers on the glass substrate, namely: roughness / calcogenic layer/substrate. The calcogenic film layer was simulated by the General Oscillator method involving the Gauss and Lorentz oscillators, and good Ψ and Δ spectra (Figure 6) with a mean square error (MSE) of less than 10 were obtained.



Figure. 6 - Spectra Ψ :(*a*) and Δ : (*b*) obtained from the experimental data together with the simulated ones for the ternary system Ge₃₅Sb₅Se₆₀.



From the best fit, the optical and dielectric constants were determined (Figure 7).

Figure 7 - The dispersion curves: n(a) și k(b) for films $Ge_xSb_{40-x}Se_{60-x$

The optical constants for both quantities show a tendency to decrease with the increasing of the Ge content and, correspondingly, decreasing the Sb content.

The value of E_g (Table 3) was determined with Tauc's expression [4] for indirect electron transitions, using linear extrapolation. Figure 8 indicates the value of E_g according to the content of Ge and the coordinate Z number of the thin film compared to the bulk. The coordinate number (Z) is calculated by the formula:

$$Z = [4X + 3 (40-X) + 2x60] / 100$$
(4)

Table 4. – Calculating the average coordinate number of covalent bonds according to the content of Ge (X).

Z
2.55
2.6
2.65
2.67
2.72
2.75



Figure 8 - *The value of* E_g *depending on the coordinate number* Z *and the content of* G*e*.

The spectroscopic ellipsometry in Mid-IR (IRSE) measurements were performed at 50° and 70° angle of incidence, 16cm^{-1} resolution, in spectral range 250-4000 cm⁻¹.



Figure. 9 - Dispersion curves of n(a) and k(b) for the $Ge_xSb_{40-x}Se_{60}$ films in the middle IR range.

Layer modeling was the same as for those measured in the UV-VIS-NIR domain. The obtained optical constants show a decreasing tendency (Figure 9), with the increase of the content of Ge and respectively the lowering of the Sb content.

The transmission measurements (Figure 10) show that in the spectral range UV (200-400nm) all the films are opaque and only around 700nm the films become transparent. Transmission values are in the range 40-85%, and with increasing the Ge content, transmission in the IR region bis shifted to high wavelengths. The reflectance spectra of the films were calculated using the relations:

$$A = \alpha d / 2.303$$
 (5)

$$\mathbf{A} + \mathbf{T} + \mathbf{R} = 1 \tag{6}$$

where d - is the film thickness and R - is the reflectance.

In Figure 10b, the R spectra are exemplified for the compositions $Ge_{20}Sb_{20}Se_{60}$ and $Ge_{35}Sb_5Se_{60}$. As the absorbance values are negligibly small (k \rightarrow 0) in the (0.85–3.4) µm spectral region, R_{min} of ~ 20% corresponds to a T_{max} of ~ 80%.



Figure. 10 - SE transmittance spectra (a) and reflectance spectra (b), exemplified for the $Ge_{20}Sb_{20}Se_{60}$ and $Ge_{35}Sb_5Se_{60}$ films.

In Figure 10 the wavelength values $\lambda_{T50\%}$ at which the transmission increases to T=50% are given as a function of Ge content. As can be seen, with adding Ge up to 32 at.%, the value of $\lambda_{T50\%}$ slightly decreases, moves to shorter wavelengths, while at maximal Ge of 35 at.% $\lambda_{T50\%}$ moves back toward longer wavelengths. Thus, by increasing the Ge at.%, respectively decreasing the Sb at.%, a wider spectral region (0.72–3.65) µm can be achieved, where T values are larger than 50%, that is important for use in the infrared-transmitting lens and infrared imaging sensors application.



Figure 11 - Wavelengths value of $\lambda_{T50\%}$ for T=50% in dependence on Ge content in the GexSb40-xSe60 films.

Considering the IRSE dispersion spectra of the quantities ε_2 and Im $(-1/\varepsilon)$ being representatives for absorption and dielectric loss in the material respectively, we identified the IR active vibrational modes attributed to impurity atoms and complexes in the chalcogenide films present in Table 4.



Figure 12 - Imaginary part ε_2 of the dielectric function ε of the $Ge_xSb_{40-x}Se_{60}$ films in the middle-IR range.

Figure 13 - The dielectric loss function $Im(-1/\varepsilon)$ of the $Ge_xSb_{40-x}Se_{60}$.

Table 5 - IR vibrational bands and the corresponding assignation of the chemical bonds in the $Ge_xSb_{40-x}Se_{60}$ films.

Assignation of chemical bonds	Ge15Sb25Se60	Ge20Sb20Se60	Ge ₂₅ Sb ₁₅ Se ₆₀	Ge ₂₇ Sb ₁₃ Se ₆₀	Ge ₃₂ Sb ₈ Se ₆₀	Ge ₃₅ Sb ₅ Se ₆₀	Literature
Se-Se	486	500	510		506	495	[5]
Ge-O		580		550			[6]
Ge-O NO ₂ NO ₂		650 860	679 855	700		630 760	[6] [7] [7]
Ge-O Ge-O	1130		1053	1040	1060	1048	[5] [5]
NO ₂ C-H		1357	1360	1355	1344	1345 2853	[7] [7]
С-Н О-Н			3044 3412		3718	3773	[5] [5]

3.2 GeSSe - Infrared Fourier Transform Spectroscopy (FTIR)

The spectra were measured in the 400-4000 cm⁻¹ spectral range with a resolution of 4 cm⁻¹ and 64 scans. The transformation of Kubelka Munk was applied to convert the reflection spectrum into absorption units. The IR (FTIR) spectra (Figure 14a) and IRSE (Figure 14b) of GeSbSe films highlighted the vibrational modes and highlighted the presence of metal-oxygen bonds and impurities, as well as water linkages on the film surface. The assignment of the vibrational band positions of the chemical bonds with the literature data, are presented in Table 5.



Figure 14 – The comparison of the two methods: FTIR and IRSE (a)Spectra FTIR for $Ge_xSb_{40-x}Se_{60}$; (b)Spectrals IRSE for $Ge_xSb_{40-x}Se_{60}$.

Tabelul 5 - IR vibrational bands and the corresponding assignation of the chemical bonds in the $Ge_xSb_{40-x}Se_{60}$ films.

Ge15	Ge ₂₀	Ge25	Ge ₂₇	Ge ₃₂	Ge35	v (cm ⁻¹)	Lit.
491.73	492.90	493.92	493.92	497.41	494.74	Se-Se	485-490[5]
807.03	808.27	810.88	808.38	830.77	810.78	Ge-O	700-800[8-9]
1034.73	1030.79	1036.27	1050.88	1069.37	1067.58	Ge-O	1048[9]
1120.56	1119.79	1122.20	1122.84	1128.45	1122.97	Ge-O	1118 [5]
1270.72	1269.76	1272.43	1270.47	1257.58	1270.68	Se-H -S-O-	1280 [5] 1270-1315 [11]
1547.91	1563.33	1661.05	1639.66	-	1634.79	-OH,-S-O-	1597 [10] 1639[9]
2546.24	2587.40	2678.36	2628.82	2280.96	2668.87	Se-H,S-H, H ₂ O	2439 [5]
3538.04	3634.76	3858.97	3708.33	3831.36	3755.50	-OH	3737[11]

3.3 GeSbSe - FT-Raman Spectroscopy Measurements (Fourier Transform Raman Spectroscopy)

The FT-Raman spectra for the $Ge_xSb_{40-x}Se_{60}$ films were considered in the wavelength range of 50–350 cm⁻¹ (figure 15), where the vibrational modes of main heteropolar chemical bonds are active.



Figure 15 - Raman spectra for Ge_xSb_{40-x}Se₆₀ samples

The small peaks around 64, 75, 95 and 110 cm⁻¹ are connected with the vibration of Sb atoms in the pyramidal units. Their intensity decreases as the concentration of Sb in the films decreases [12]. The peak around 121 cm⁻¹ can be associated with the Sb-Se bonds vibration and the peak at 170 cm⁻¹ with the Ge-Ge bonds. Other low-intensity bands were observed in the 250-350 cm⁻¹ region due to increasing the Ge content and can be attributed to Se-Se Ge-Ge, Ge-Sb bonds in the GeSe₄ structural unit. The absence of the 150 cm⁻¹ bonds indicates the absence of Sb-Sb bonds in the structural units Se₂Sb-SbSe₂ [13], which is consistent with the decrease in Sb concentration in the investigated films.

3.4 Topographic Studies - AFM Measurements

To evaluate the morphology and roughness of GeSbSe films, AFM measurements were performed in non-contact mode at room temperature. The 2D AFM surface images of the Ge_xSb_{40x}Se₆₀ films, taken from a 1 μ m×1 μ m scanned surface area, are presented in Figure 16. As it can be seen, the surface is covered with nanometric grains; depending on the composition, some particularities could be noticed regarding the spatial distribution of the constituting grains. By increasing the Ge content to 25 at.% (Figure 16c) the surface particles tend to create cauliflowerlike patterns, thus increasing the surface roughness due to their corrugation, created by the bunching of the grains in form of cauliflowers. Further increase in the Ge content leads to slightly disordered surfaces and decreased roughness values.



Figure 16 - 2D AFM topographical image of the $Ge_xSb_{40-x}Se_{60}$ films surface taken at $1 \ \mu m \times 1 \ \mu m$ scan: x=15 at.% (a); x=20 at.% (b); x=25 at.% (c); x=27 at.% (d); x=32 at.% (e) and x=35 at.% (f).

The microstructural changes evidenced by the RMS roughness variation according to the Ge content increase are shown in Figure 17.



Figure 17- RMS roughness dependence on the Ge content in the chalcogenide films at different scanning scales as indicated in the legend.

It can be seen from Figure 17 that at a concentration of 25 at% Ge content, there is a steep increase in roughness due to the spatial distribution of the surface particles (such as the cauliflower aggregate grains). At Ge concentrations of 27 and 32 at.%, the granules become less pronounced, resulting a decrease in surface roughness, while at a concentration of 35 at% Ge, the superficial surface granules become separate with a slight increase in roughness. Thus GeSbSe films have smooth surfaces with RMS roughness values in the range of 1.0-2.4 nm at a scale of $(1x1) \mu m^2$. Even on a bigger scale, the roughness does not exceed 4.5 nm.

4. Quaternary films GeSb(As)STe

GeSb(As)STe quaternary films were obtained under the same conditions as the ternary films by vacuum deposition using the 5N purity synthesis method.

4.1 Optical properties studies

4.1.1. Spectroscopic ellipsometry measurements (SE)

Quaternary films of $Ge_xSb(As)_{40-x}S_{50}Te_{10}$ with x = 10, 20, 27 at.% were measured by ellipsometry in the NIR spectral range with a resolution of 2 nm at an incidence angle of 50⁰. The model used to simulate experimental data was the same as for the ternary films. The values of optical constants were obtained (Figure 18) from the best fit. In both calcogenic systems, the values of n and k decrease as the concentration of Ge increases; after 700 nm, all the films are completely transparent (k = 0) [14].



Figure 18 - Dispersion curves of the refractive index n (a) and extinction coefficient k (b) of all quaternary chalcogenides.

The value of E_g (Figure 19a) was determined by Tauc expression [4] for indirect transitions using linear extrapolation. Analyzing E_g values we can observe that the values increase with Ge content (Figure 19b).



Figure 19 - E_g determined by the Tauc formula for both quaternary systems)(a) and the variation of the Eg function of Ge content (b).

Mid-IR spectroscopic measurements (IRSE) were performed in the spectral range 280-8000 cm⁻¹ at a resolution of 16 cm⁻¹ at an incidence angle of 50-70°. From the best fit in the spectral range of 300-2000 cm⁻¹ (taking into account the film absorption area), obtained the dispersion of the dielectric constants of the films Figure 20.



Figure 20 - *Dispersion curves for the refractive index, n (a&c) and extinction coefficient k (b & d) for both systems.*

Values n and k tend to decrease with increasing Ge content. **Transmission measurements** are shown in Figure 21 for both quaternary chalcogenide systems. The films are completely opaque in the UV region and just around 700 nm, the films become transparent. Each system becomes more transparent with increasing the Ge content or decreasing the concentration of As and Sb. Transmission values range from 40% to 85%. By increasing the Ge content in the quaternary chalcogenide systems, the transmission in the IR region is shifted to shorter wavelengths.



Figure 21 - Transmission spectra for quaternary chalcogenide systems.

The IR-SE spectral dependence of the real ε_1 and the imaginary ε_2 of the dielectric functions was determined from the best fit performed in the spectral range of 300-2000 cm⁻¹. Most vibrational bands related to the base chemical bonds are below the measurement limit of 300 cm⁻¹, so they can not be detected. The peculiarities observed are related to the vibrational modes of the impurity atoms or complexes in the films. The lack of characteristic peaks related to the vibration modes of the hydrogen-related species in the spectral range over 1400 cm⁻¹ indicates that the evaporated films do not contain water-related impurities. The absorption bands related to the Ge-O and Te-O chemical bonds were detected due to the oxidation of the film surface.



Figure 22 - IR-SE spectral dependence for the dielectric functions: the imaginary part ε_2 : (a) for Ge_xAs_{40-x}S₅₀Te₁₀, (b) for Ge_xSb_{40-x}S₅₀Te₁₀.



Figure 23 - $Im(-1/\varepsilon)$ for $Ge_xAs_{40-x}S_{50}Te_{10}$ with composition (x = 10, 20, 27 at.%).

Figure 24 - $Im(-1/\varepsilon)$ for $Ge_xSb_{40-x}S_{50}Te_{10}$ with composition (x = 10, 20, 27 at.%).

The values corresponding to the transversal $\omega(TO)$ and longitudinal $\omega(LO)$ vibration modes of Ge_xAs(Sb)_{40-x}S₅₀Te₁₀ films are shown in Table 6 and Table 7 [15].

Sample	Vibrational modes $\omega_{(TO)} (cm^{-1})$					
	V GeS4/2	v Ge-O or v Te-O	V S-O-			
Ge10As30S50Te10	357.64	-	1256.62			
Ge20As20S50Te10	354.35	-	1269.79			
Ge27As13S50Te10	377.82	-	1243.03			
Ge10Sb30S50Te10	337.42	525.23	1234.09			
Ge20Sb20S50Te10	359.30	514.52	1241.88			
Ge27Sb13S50Te10	362.76	523.42	1242.28			
Literature	377 [7],	529 [10]	1270-1315[6,9],			
	361-397 [10].					

Table 6 - Vibration mode positions given by the $\omega_{(TO)}$ for Ge_xAs(Sb)_{40-x}S₅₀Te₁₀ films.

Sample	Vibrational modes $\omega_{(LO)}(cm^{-1})$							
	V GeS4/2	V Ge-O Or V Te-O	V S-O-					
Ge10As30S50Te10	389.56	517.43	1249.11					
Ge20As20S50Te10	394.46	517.40	1272.80					
Ge27As13S50Te10	411.62	520.69	1225.01					
Ge10Sb30S50Te10	338.19	525.71	1232.17					
Ge20Sb20S50Te10	380.25	515.68	1242.21					
Ge27Sb13S50Te10	399.54	522.24	1239.12					
Literature	415 [7],	529 [10]	1270-1315[6,7],					
	361-397 [10].							

Table 7 - Vibration mode positions given by the $\omega_{(LO)}$ for Ge_xAs(Sb)_{40-x}S₅₀Te₁₀ films.

4.3 Topographic studies

4.3.1 Atomic Force Microscopy (AFM)

The surface morphology of the films was studied by recording AFM images in intermittent contact mode (Easy Scan2 from Nanosurf) using sharp tips (NCLR type) with a radius of curvature of less than 10 nm (typically 7 nm).

Figure 25 and Figure 26 presents the 2-dimensional topographic and 3-dimensional topographic AFM images taken from a $8\mu m \times 8\mu m$ scanning area for Ge_xSb(As)_{40-x}S₅₀Te₁₀ (x=10, 20, 27 at.%) films.





Figure 25 - 2D&3D AFM images at the scale of $(8\mu m \times 8\mu m)$ for $Ge_xSb_{40-x}S_{50}Te_{10}$ films.



Figure 26 - 2D&3D AFM images at the scale of $(8\mu m \times 8\mu m)$ for $Ge_x A_{40-x} S_{50} Te_{10}$ films.

The surfaces of all samples (Figure 25 and Figure 26) are free of cracks, without exfoliations. The films with Sb content are completely coated with a uniform distribution of granules originating from the film structure, influenced by the deposition conditions (material evaporation phase). For films with As content, the substrate is completely covered with a non-uniform grain structure, forming a bimodal distribution of large and small superficial particles [14].

4.4 Stability Studies of Optical Properties MIL-C-48497

In accordance with MIL-C-48497 [15] for optical coatings, quaternary calcogenides were tested at:

<u>Humidity:</u> both chalcogenide systems were exposed to +49°C and relative humidity 95-100% for 24 hours.

<u>Temperature</u>: All films were exposed to temperatures of $-62^{\circ}C + 72^{\circ}C$ for 2 hours, the temperature increase being 1°C per minute.

<u>Adhesion:</u> An adhesive tape (scotch tape) is firmly pressed onto the surface and quickly removed from the surface.

The samples were wiped with the cloth dipped in acetone and inspected with a magnifying glass and found to be free of peeling marks. After performing the "quality standard" test, all quaternary films were measured and characterized by ellipsometry under the same experimental conditions as the original [16]. Based on the ellipsometric analysis, the effect of quality tests on quaternary chalcogenide films showed that the thickness of the film slightly decreased after the quality tests while the roughness of the surface was strongly affected by the tests. For films with Sb content the surface roughness increases; and for As-containing films, the surface roughness decreases. Refractive indices have different behaviors depending on the film composition. Thus, the refractive indices of As-containing films are not influenced by the tests performed or by the Ge content. The refractive index for Sb-containing films increases as a result of the quality test results.

Surface morphology was checked before and after **MIL-C-48497** test. Two examples are presented in the Figures 27 and 28 for $Ge_{27}(As)Sb_{13}S_{50}Te_{10}$ surface topology investigation.



Figure 27 - Surface morphology for $Ge_{27}Sb_{13}S_{50}Te_{10}$ before performing the quality standard tests investigated by AFM and SEM: (A) - AFM image on a $(2x2 \ \mu m^2)$ scale; (B) - identification of the particle size; (C) - Film surface at a 20 μ m scale; (D) - surface of the film at a 2 μ m scale.

The AFM image on the scale of $(2x2) \ \mu m^2$ (Figure 27A) showed the presence of both large particles (greater than 160 nm) and small particles (approximately 60 nm), and SEM analysis revealed the formation of a superficial layer with many protuberances, and some fissures around them (Figure 27C), which in some places lead to the detachment of parts of the film [15]. The surface morphology of the As-containing film prior to the "quality test" investigated by SEM revealed a compact, continuous and polycrystalline film of approximately 1 μ m thickness. Due to the deposition technique used, splashes from the evaporation material form hemispherical protuberances of the same composition as the deposited material covering the surface of the film (Figure 28A). Most semi-spheres on the surface have diameters smaller than film thickness and no cracks, and around the largest protuberances, surface circular cracks with a diameter of approximately 2-3 μ m have been observed. The AFM image (Figure 28B) for the As-containing film before the "quality tests" showed the presence of large particles (greater than 100 nm), result which is consistent with SEM results, and after the quality, tests revealed the presence of a smooth surface with evenly distributed granules.



Figure 28 - Surface morphology for $Ge_{27}As_{13}S_{50}Te_{10}$ before and after the quality standard tests investigated by AFM and SEM; (A) - the film surface at 5 μ m scale before the quality standard test; (C) - after the quality standard test; (B) - The AFM image before the quality test; (D) - after the quality test on a scale of $(2x2 \ \mu m^2)$ and identifying the particle size.

Following the quality standard test performed on the As-containing film, the protrusions on the surface of the film disappear and corrugated films appear in many areas (Figure 28C). AFM investigations have shown the existence of a fine granulation structure on the surface of the film. The surface area of the film correlated with the SEM information has improved characteristics compared to the original SEM, this must be caused by removing impurities (dust, etc.) from the surface of the film [15].

Conclusions

The chalcogenide systems, binary, ternary and quaternary have been synthesized from elements with 99.999% purity. Films with the same composition were obtained using the vacuum evaporation method at room temperature deposited on the quartz substrates.

The structural properties of ternary films were investigated by **XRD** and **ND** coupled with simulation procedure **Reverse Monte Carlo** (RMC). It has been found that the addition of the Sb atom initially does not modify the Ge-tetrahedral basic structural units, but the Sb concentration increases or the well-defined Sb-pyramid units are formed.

The **RMC simulations** have shown that with increasing Ge concentration, the interatomic distances in the Ge-Se bonds increase, while the interatomic distances in the Sb-S bonds remain unchanged; thus at a higher concentration value of 25 at. % Ge was established the crosslinking of Ge atoms in the Ge-Se bond chains resulting in a structural rearrangement in the films. *The films go through a topological phase transition around the average coordinate number* $Z \sim 2.67$ where the two-dimensional structure (2D) transforms into a three-dimensional network (3D) which contributes to changes in all the properties (chemical, morphological, structural and optical) systems studied.

The optical properties of the ternary and quaternary systems were analyzed by ellipsometry in the UV-VIS-NIR domain. The thickness obtained is in accordance with the desired thickness (~ 1.5μ m) and the values of the optical constants (n and k) show a decreasing tendency with the increase of the Ge content for all calcogenic materials. From the obtained optical constants, we determined the value of E_g, which increases with the content of Ge.

The ellipsometric IR study was performed to determine the information on chemical bonds; thus the vibration band positions have been established and the related chemical bonds have been identified, confirming that the evaporated films do not contain water. However, defects related to the appearance of oxygen bonds (Ge-O and Te-O) were present in films, most likely due to surface oxidation over time. All the spectral analyzes (Raman, FTIR, and IRSE) investigated on ternary films showed the existence of organic impurities after 1100 cm⁻¹. Raman's analysis highlighted the vibration modes of Sb in the spectral range of 50-350 cm⁻¹. The absence of the 150 cm⁻¹ bands indicates the absence of Sb-Sb bonds in the Se₂Sb-SbSe₂ structural units, which is consistent with the decrease in Sb concentration in the investigated films.

Transmission measurements for ternary and quaternary chalcogenic systems have shown that the films are transparent from 700 nm to around 3000 nm.

AFM images for all chalcogenic systems have revealed a completely coated surface with evenly distributed granules and having a particular structure depending on the film composition. The RMS does not exceed 5 nm.

Standard tests (MIL-C-48497) on durability properties for quaternary systems showed that: film thickness drops slightly after quality tests, while surface roughness is strongly affected by tests, a more noticeable effect being observed on films with the content of Sb. Refractive indices have different behavior depending on the sample composition, so refractive indices of As-

containing films are not influenced by the tests performed or by the content of Ge, in contrast to the films containing Sb, where the refractive index increases as a result of quality tests.

Morphological analyzes of samples before and after quality tests revealed the stability of quaternary films containing As, while quaternary films containing Sb are less resistant. Moreover, the quality tests have led to better relief surfaces due to the removal of a superficial layer (including surface contaminants).

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