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CORRELATION BETWEEN MECHANICAL PARAMETERS FOR AMORPHOUS CHALCOGENIDE FILMS

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Young's modulus, linear thermal expansion coefficient, stress, microhardness, wear resistance, adhesion and cohesion strength for thin films of As_2S_3 , As_2Se_3 , $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$, $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ and $\text{Ge}_{36}\text{As}_4\text{S}_{60}$ chalcogenide glasses thermally deposited onto unheated zinc selenide substrates have been determined. The interrelationship between mechanical parameters of the films has been studied. Wear resistance of chalcogenide films has been found to be related to the adhesive force and mechanical parameters used in the formal theory of glass strength. The effect of the additional stress arising in result of the temperature increase under friction on the wear resistance of the films has been shown.

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1. Introduction

Thin films deposited from chalcogenide glasses, are applicable in opto- and microelectronics for different purposes: protective, passivating and optical coatings [1], electrical switches [2], heterojunctions [3], data recording, etc. Mechanical strength determination is of great importance for the application of the films. The main mechanical properties of special interest are microhardness, wear resistance, adhesion and shear strength, which are related to the Young's modulus and linear thermal expansion coefficient. Mechanical properties for the films of this type of materials have been studied episodically. The available papers as a rule give information on the one of the named characteristics only and for the certain film material (see, e.g., [4 - 7]).

In this work the combined studies of the mechanical properties for thin chalcogenide films aimed to define the correlation between wear resistance and basic mechanical parameters of the films have been performed. The following glass compositions that are used for IR optical components, design of multilayer film structures for varied applications, and available from different manufacturers [2, 8] have been picked up for the studies: As_2S_3 , As_2Se_3 , $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$, $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ and $\text{Ge}_{36}\text{As}_4\text{S}_{60}$.

2. Experimental

Deposition of thin films has been performed by thermal evaporation of the bulk glasses from the effusion cells onto unheated ZnSe [9] and Si (111) substrates in vacuum deposition unit of VUP-5 type (Sumy, Ukraine) at pressure of 10^{-4} Pa and deposition rate of about (6.0 ± 0.1) nm/s. The bulk glass samples were prepared by the melting of As, Se and Ge high-purity components mixture (99.999 %) in evacuated ampoules with the subsequent quenching of the melt. Thickness of thin films under investigation was about 1.5 μm . Microhardness has been measured on the films of at least 4 μm thick. Optical thickness monitoring for thin film during the deposition process has been conducted by the interference technique.

The Young's moduli and linear thermal expansion coefficients have been determined from the results of the measurement of thermal constituent of the stress, arisen under heating in the films

deposited onto the substrates measured $25.0 \times 5.0 \times 0.2 \text{ mm}^3$ with different linear thermal expansion coefficients (ZnSe and Si).

Stress in thin films has been determined from the measurement of the deflection of free edge of the substrate supported as a cantilever during film deposition or heating of film - substrate system. Substrate deflection and linear thermal expansion coefficient measurements have been conducted by laser dilatometer ($\lambda = 0.63 \text{ }\mu\text{m}$) with the accuracy of $\pm \lambda/4$ [10].

The linear thermal expansion coefficient values for thin films have been calculated from the equations:

$$\alpha_f = \frac{\alpha_{s1} - \alpha_{s2} A}{1 - A}, \quad (1)$$

$$A = k \frac{E_{s1} (1 - \nu_{s2}) \delta_2}{E_{s2} (1 - \nu_{s1}) \delta_1}, \quad (2)$$

where k is geometrical factor close to the unit; $\alpha_{s1} = 8.52 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{s2} = 2.51 \times 10^{-6} \text{ K}^{-1}$ for ZnSe and Si, respectively; $E_{s1} = 6.49 \times 10^{10} \text{ Pa}$ and $E_{s2} = 18.0 \times 10^{10} \text{ Pa}$, $\nu_{s1} = 0.28$ and $\nu_{s2} = 0.262$ - corresponding Young's modulus and Poisson's ratio values; δ_1 and δ_2 - substrate deflection of the film - substrate system under heating from $T_1 = 303 \text{ K}$, to $T_2 = 363 \text{ K}$ ($\Delta T = T_2 - T_1 = 60.0 \pm 0.3$) K.

The value of the substrate Young's modulus has been defined from the measurement of the deflection of the loaded substrate edge [11]. Poisson's ratio values were taken from literature [12]. The error of the linear thermal expansion coefficient determination for thin films was not higher than 5 %.

Thin film Young's modulus has been computed from the equation

$$E_f = \frac{E_{s1} d_s^2 \delta_1 (1 - \nu_f)}{3(1 - \nu_{s1}) l^2 d_f \Delta T (\alpha_f - \alpha_{s1})}, \quad (3)$$

where $d_s = 2.0 \times 10^{-4} \text{ m}$ - substrate thickness; $d_f = 1.5 \times 10^{-6} \text{ m}$ - film thickness; l - the length of the deformed portion of the substrate (the gauge length); ν_f - Poisson's ratio of film material.

For the selected film and substrate thicknesses the corrections for the equations (1) - (3), accounting for the film and substrate Young's modulus and thickness ratio have been not higher than 0.5 % (see [13]). Young's modulus determination error was not higher than 7 %.

Microhardness for thin films ($H_{\mu f}$) has been measured on PMT-3 device (Minsk, Belarus) with the accuracy better than 5 % at indentation depth not higher than 2/3 of the film thickness. The microhardness number has been derived from 9 microhardness indentations. The coefficient of variation was not higher than ± 10 %.

Wear resistance measurements have been performed with the help of the device described in [14]. Samples have been rubbed by application of the force of about $(2.00 \pm 0.01) \text{ N}$ to the film via the rubbing tip at a distance of $r_0 = 5 \times 10^{-3} \text{ m}$ from the rotational axis of the sample rotating at an angular speed of 500 RPM. Thin films were rubbed by the batiste cloth moving at a speed of $5.0 \times 10^{-4} \text{ m/s}$. The device provides removal of the wear products from the zone of friction and allows determination of revolutions number of stood by the sample up to the moment when the scratch cuts through the film. To determine the relative wear resistance for the films the experimental data have been rated to the wear resistance for $\text{Ge}_{16}\text{Sb}_{24}\text{Se}_{60}$ film taken for a unit. Wear resistance has been determined with the accuracy better than 3 %. The coefficient of variation was about ± 7 %.

Adhesion and shear strengths have been determined by the normal pull-off method [15]. Pins have been resin bonded to the films. The sum of the force breaking away the film from the substrate and the shearing force around the pin perimeter has been measured with the help of mechanical-to-electric transducer. Force values have been measured to an accuracy of 0.1 N [8]. The pins of two different radii have been used $r_1 = 2r_2 = 2 \times 10^{-3} \text{ m}$. For this case adhesion and shear strengths have been calculated from the equations:

$$\sigma_a = \frac{F_1 - 2F_2}{2\pi r_2^2}, \quad (4)$$

$$\sigma_{sh} = \frac{4F_2 - F_1}{4\pi r_2 d_f}, \quad (5)$$

where F_1 and F_2 - the sum of the breaking and shearing forces for the pins with r_1 and r_2 face radius, respectively. Adhesion and shear strengths have been estimated from the data of 5 measurements for each film, coefficient of variation being not higher than $\pm 5\%$.

3. Results and discussion

Tables 1 - 3 present the mechanical parameters for thin films and the data from literature for the corresponding chalcogenide glasses. The following correlation between film and bulk glass parameters has been found:

$$E_f = 0.92E_s, \quad (6)$$

$$\alpha_f = 1.12\alpha_s, \quad (7)$$

$$H_{\mu f} = 0.29H_{\mu s}. \quad (8)$$

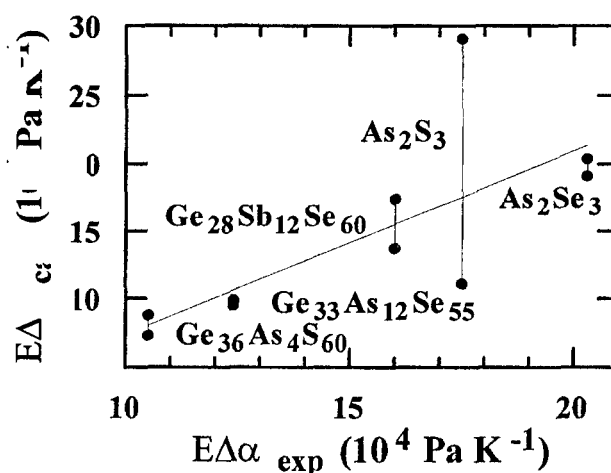


Fig. 1. Theoretical $E\Delta\alpha$ value ($E\Delta\alpha_{calc}$) versus experimental ($E\Delta\alpha_{exp}$). The line corresponds to the proportionality factor equal to the unit.

These relationships between bulk material and film mechanical parameters closely coincide with the ones observed for SiO_2 , SiN and Si_3N_4 thin films. The authors of the reference [23] have attributed the decrease in the $E_f/(1 - \nu_f)$ value for thin films against the bulk material to the packing density that is the ratio between film density ρ_f and density of bulk material ρ_b (ρ_f/ρ_b).

The higher linear thermal expansion coefficient values for the films with respect to bulk materials and their dependence on the substrate material for ZnS , ZnSe , SrF_2 and BaF_2 films ascribed to the structural peculiarities of the films have been observed earlier [24]. Substantially lower thin film microhardness as opposed to that for bulk glass and its dependence on the annealing temperature has been reported for As_2S_3 [25] and SiO_2 films [26].

Table 1. The Young's moduli (E) and linear thermal expansion coefficients (α) for chalcogenide glasses and thin films on their base.

Compound	E, 10^{10} Pa			α , 10^{-6} K $^{-1}$		
	Bulk glass	References	Film	Bulk glass	References	Film
As ₂ S ₃	1.62	[2]	1.0	22.4	[5]	26.0
	1.38	[13]		23.7	[2]	
	0.8	[5]		26	[6]	
As ₂ Se ₃	1.83	[17]	1.5	19	[13, 5]	22.0
Ge ₂₈ Sb ₁₂ Se ₆₀	2.14	[5]	2.0	15.0	[5, 6]	16.5
	2.07	[13]		15.8	[18]	
	2.18	[17]				
Ge ₃₃ As ₁₂ Se ₅₅	2.07	[13]	1.8	13.3	[6]	15.0
				13	[13]	
Ge ₃₆ As ₄ S ₆₀	2.10	[17]	1.9	12.0	[17]	14.0

Table 2. Poisson's ratio (ν) and microhardness (H_μ) for chalcogenide bulk glasses and thin films.

Compound	ν		H_μ , 10^7 Pa		
	Bulk glass	References	Bulk glass	References	Film
As ₂ S ₃	0.305	[18]	09	[16; 19]	33
			134	[22]	
As ₂ Se ₃	0.289	[20]	140-156	[22]	34
	0.297	[18]	114	[19]	
Ge ₂₈ Sb ₁₂ Se ₆₀	0.265	[20]	150	[19]	45
Ge ₃₃ As ₁₂ Se ₅₅	0.266	[20]	171	[19]	50
Ge ₃₆ As ₄ S ₆₀	0.250	[20]	200	[20]	58

Table 3. Relative wear resistance (ϵ), initial stress (σ_0), adhesion and shear strengths (σ_a and σ_{sh}) for chalcogenide thin films.

Compound	ϵ , relative units	σ_0 , MPa	σ_a , GPa	σ_{sh} , MPa
ZnSe	6.2	8.2	4.8	29 - 49
As ₂ S ₃	3.1	-1.3	1.8	26
As ₂ Se ₃	3.5	2.1	2.6	30
Ge ₂₈ Sb ₁₂ Se ₆₀	1.0	-4.2	1.5	33
Ge ₃₃ As ₁₂ Se ₅₅	4.5	12.0	4.0	35
Ge ₃₆ As ₄ S ₆₀	4.9	11.4	3.5	39

Information on the Young's modulus and linear thermal expansion coefficient is necessary for computation of thermal stress in thin films. Fig. 1 shows the interrelation between the value of the $E\Delta\alpha$ product determined experimentally for thin films deposited onto ZnSe substrates and calculated from the literature data.

Data from different references on the ZnSe crystal parameters ($E_s = 4.1 \times 10^{10}$ Pa [19] and $E_s = 7.1 \times 10^{10}$ Pa [27]; $\alpha_s = 7.8 \times 10^{-6}$ K⁻¹ [28] and $\alpha_{s2} = 8.5 \times 10^{-6}$ K⁻¹ [17]) have been used in calculations for comparison. The discordance in ZnSe parameters is related to anisotropy and the difference in crystal perfection. For the glasses, the discrepancies between parameters given in Tables 1 and 2, as a rule, are attributed to the peculiarities in glass preparation technique.

As it is seen from Fig. 1, there is substantial difference between experimental and computed $E\Delta\alpha$ values.

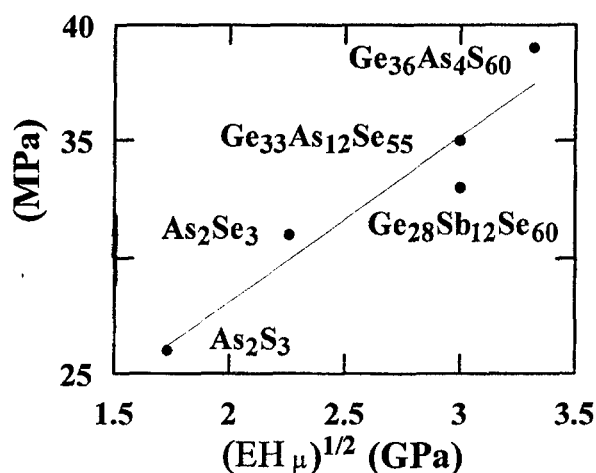


Fig. 2. Shear strength, σ_{sh} (MPa), versus $\sqrt{EH_\mu}$ (GPa) for thin chalcogenide films.

It is known that the adhesive and cohesive forces define mechanical strength of thin film. According to the formal theory of the glass strength [29], the strength of the glass is described by the equation:

$$\sigma_{sh} = C_0 \sqrt{EH_\mu}, \quad (9)$$

where $C_0 = 1.1 \times 10^{-2}$ is a constant, determined from the experiment.

Fig. 2 shows the dependence of the shear strength for thin films on the $\sqrt{EH_\mu}$ value. From this dependence the constant C_0 in eq. (9) for thin films under investigation has been found to be about 7.5×10^{-3} . In view of the found relationships (6) and (8) this constant is equal to 5.8×10^{-3} that is in agreement with experimental results with the accuracy of 23 %.

The dependences of the relative wear resistance for the films on the adhesion strength and $\sqrt{EH_\mu}$ value are given in Fig. 3 and 4, respectively. The highest deviation from the straight line in Fig. 3 has been found to be over ± 45 %.

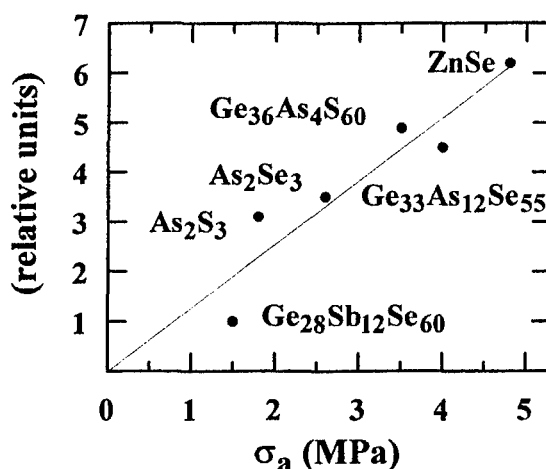


Fig. 3. Relative wear resistance, ϵ , for chalcogenide films versus adhesion strength, σ_a . The line is drawn by the least-squares technique.

Experimental data shown in Fig. 4 (with the exception of $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ films) can be described by the linear dependence with a slope of $1.2 \times 10^{-9} \text{ Pa}^{-1}$. The significant deviation from the linear dependence given in Fig. 4 of the relative wear resistance for $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ films can be associated with the thermal stress resulting from thermal spike under the work done by frictional forces.

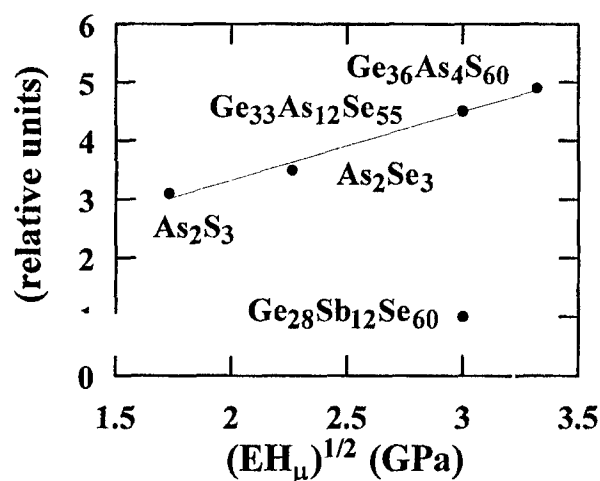


Fig. 4. Relative wear resistance, ϵ (relative units), versus $\sqrt{EH_\mu}$ (GPa) for chalcogenide films.

The computations of the contact temperature under rubbing of the films (carried out following the equations of ref. [30]) gave the temperature increase possible in the near-surface region of the sample of about $\Delta T_c = 40 - 60$ K. Fig. 5 shows theoretical dependence of the relative wear resistance on the total stress, that can arise in thin films under investigation with temperature increase in 60 K. It is seen that in result of the heating the highest compressive stress arises in $Ge_{28}Sb_{12}Se_{60}$ films.

The calculations have revealed that for the above-mentioned conditions of the experiment the wear resistance of the films is additionally affected by an external compressive stress of about 1.0×10^7 Pa grown up in the zone of friction. Thus the origination of the high compressive stress $\sigma_T = E \alpha \Delta T_c$ exceeding the flow limit, reducing the adhesion strength and the wear resistance is characteristic of $Ge_{28}Sb_{12}Se_{60}$ films.

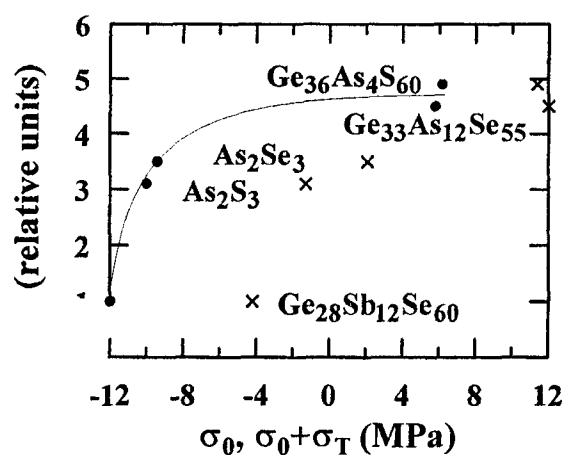


Fig. 5. Calculated dependence of the relative wear resistance, ϵ , for chalcogenide films on the value of the total stress $\sigma_0 + \sigma_T$. Crosses show the initial stress σ_0 .

4. Conclusions

The interrelation between mechanical properties of As_2S_3 , As_2Se_3 , $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$, $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ and $\text{Ge}_{36}\text{As}_4\text{S}_{60}$ chalcogenide glasses and thin films on their base has been determined. The necessity of the combined studies of the mechanical properties for the prediction of the wear resistance has been shown. The effect of the additional stress originating under friction should be taken into account in the explanation of the deviations from the found relationships between wear resistance and mechanical parameters.

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