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Modeling of the As₂(S, Se)₃Sn₀.₁ Planar Waveguides Before and After Illumination

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Is studied the influence of the illumination to characteristics of the structure of the thin films of As_2S_3 and As_2Se_3 doped with 2% of tin. As a result of photostructural transformation under illumination the tin atoms change their valence from IV to II. In a like manner the illumination changes the coordination number of the tin atoms and that make the structure of the doped thin films more stable.

I. Introduction

A great interest for vitreous materials is the appearance of new possibilities for its application as optical and photoelectric media, planar waveguides, active and passive elements for optoelectronics.

The interaction of laser radiation with vitreous chalcogenide semiconductor leads both irreversible and reversible changes of the atomic and the electronic structures. These changes are manifesting in the experiment through changes of mechanical, thermal, optical, photoelectcical and other characteristics [1].

Under the laser illumination the structure of the chalcogenide thin waveguides is changes, new defects appear, film crystallization or amorphization take place, phase transition or transition from one unstable state to another unstable state are observed[1]. However there are several conception with something in view not understanding of their microstructure mechanism, mainly in the case of irreversible and reversible photostructural changes. This position is greatly caused by the difficulties of direct observation of local atomic structure transformation in disordered solids using ordinary techniques for vitreous structure.

In difference with the crystalline state distinguish by *long range order* (LRO), i.e. by the existence of correlation between the position of every two atoms situated as far as possible one from another, the vitreous states of chalcogenide glasses is distinguish by the absence of the *long range order* (LRO). The chalcogenide glasses are not a total disorder but a certain limited order called *shot range order* (SRO) defined by the inter-atomic correlation in the first coordination spheres of an arbitrary atom, i.e. up to the maximum distance were the bonding forces are acting. In vitreous chalcogenide glasses the order extends up to larger inter-atomic distances and a new type of order are defined as the medium range order (MRO) [2].

In this article we submit that an analyse of the composition of condensed molecules by means of mass spectrometry may harvest complementary information important in

Table

Results of the mass spectrometric analysis of vaporization from thin films of As_2S_3
and As_2Se_3 doped with 2 % of Sn.
Ionizing electron energy V=70 eV and vaporization temperature 453K for As_2S_3.
Ionizing electron energy V=70 eV and vaporization temperature 543K for As_2Se_3.

Ion for As-S-Sn	m/z	I, before	I, after	Ion for As-Se-Sn	m/z	I, before	I, after
S	32	5	10	As	75	80	90
S_2	64	16	26	Se	80	78	85
As	75	36	49	As_2	150	64	75
S_3	96	-	1	AsSe	155	100	100
AsS	107	100	100	Se_2	160	32	50
S_4	128	-	41	SnSe	200	-	2
AsS_2	139	11	13	As_3	225	22	33
As_2	150	19	42	As_2Se	230	40	25
SnS	152	-	2	$AsSe_2$	235	9	4
S_5	160	-	1	$SnSe_2$	280	5	-
AsS_3	171	2	11	As_4	300	10	20
As_2S	182	29	17	As_3Se	305	68	34
SnS_2	184	2	-	As_2Se_2	310	28	15
S_6	192	-	1	$AsSe_3$	315	2	1
As_2S_2	214	34	16	Se_4	320	2	2
S_7	224	-	8	As_3Se_2	385	10	5
As_3	225	14	24	As_2Se_3	390	5	-
As_2S_3	246	17	-	As_4Se_2	460	5	3
S_8	256	-	30	As_3Se_3	465	8	5
As_3S	257	19	23	As_4Se_3	540	14	20
As_2S_4	278	18	-	As_5Se_3	615	8	20
As_3S_2	289	16	12	As_4Se_4	620	3	25
As_4	300	6	21				
As_2S_5	310	9	-				
As_3S_3	321	30	19				
As_2S_6	342	-	5				
As_3S_4	353	80	4				
As_4S_3	396	8	37				
As_4S_4	428	29	19				
As_4S_5	460	19	5				

Chart 1. Mass spectrum of the As-S-Sn semiconductor system before Ar-laser radiation.
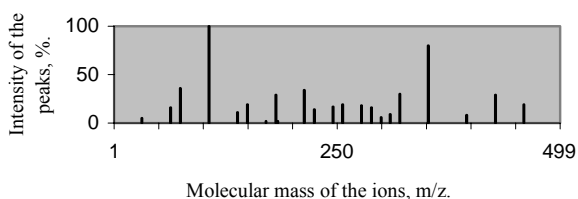

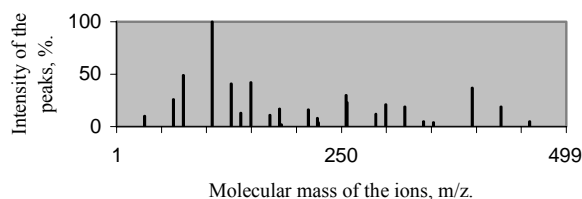Chart 2. Mass spectrum of the As-S-Sn semiconductor system after Ar-laser radiation.

Chart 3. Mass spectrum of the As-Se-Sn semiconductor system before Ar-laser radiation.`
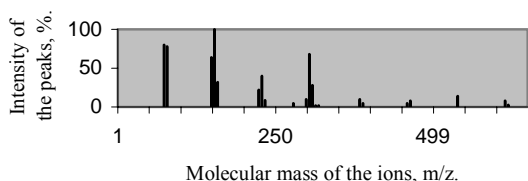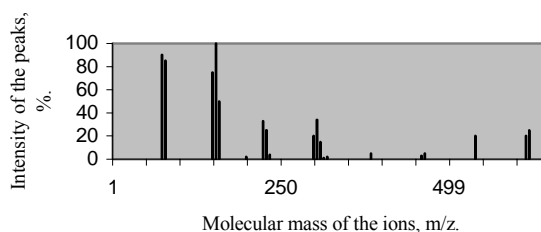

` Chart 4. Mass spectrum of the As-Se-Sn semiconductor system after Ar-laser radiation.

building structural models in SRO and MRO and gives additional experimental materials, which may explain the mechanism of the photostructural changes in vitreous semiconductors[3-6].

II. Experiments

The bulk samples of As_2S_3 and As_2Se_3 doped with tin were synthesized using elementary As, S, Se and Sn of high purity. Thin films were obtained by thermal deposition (vaporization of the bulk samples) in a vacuum on the preliminary cleaned oxide glass substrates and on the oxide glass capillaries (for mass spectroscopy analysis of thin films obtained in the same condition).

Mass spectrums were registered using MX-1320 mass spectrometry. The measurements were made at ionising electron energy 70eV and vaporization temperature 453 K for As_2S_3 and 543 K for As_2Se_3.

The identification of the species was made according to the relative abundance of the sulfur isotopes they contain. The intensity of peaks were measured with an error of $\not\subset 1\%$.

For the illumination of the thin films Ar-laser (λ=514 nm) was used. Data of mass spectrometric analysis of As_2S_3 and As_2Se_3 doped with tin chalcogenide glasses before and after illumination shows us the perceptible difference in quota of $As_m S_n$ and $As_m Se_n$ molecular units[4].

Using HyperChem Computational Chemistry Program we realized 3D structures, with minimum potential energy (Kcal/mol) conformation for the molecules: As_4[3.47]; S_8[4.44]; As_4S_3[11.87]; As_2S_5[14.36]; As_2S_4[17.62]; As_2S_6[19.11]; As_4S_4[21.88]; As_4S_5[24.98]; As_2S_3[25.81]; As_4S_6[43.13]; As_4Se_3 [80, 26]; As_4Se_4[177, 29]; As_4Se_5[150, 07]; As_4Se_6[184, 33]; As_2Se_3[97, 18]; As_2Se_4[115, 42]; As_2Se_5[148, 03]; As_2Se_6 [191,09].

The total energy of the molecule configurations we obtained using Single Point Calculation of the HyperChem Computational Chemistry Program. A single point calculation performs the static properties of a molecule.

The properties include potential energy, derivatives of the potential energy, molecular orbital energies, and the coefficients of molecular orbitals for excited states. The molecular structure data for a single point calculation usually reflects the coordinates of a stationary point on the potential energy surface, typically a minimum or transition state.

As regards a geometry optimisation, HyperChem starts with a set of Cartesian coordinates for a molecule and tries to find a new set of coordinates with minimum potential energy.

The potential energy is very complex, even for a molecule containing only a few dihedral angles. Since minimization calculations can't cross or enter potential energy barriers, the molecular structure found during an optimisation may be a local and not a global minimum. The minimum represents the potential energy closest to the starting structure of a molecule. Frequently are using minimizations to generate a structure at a stationary point for a subsequent single point calculation or to remove extreme force in a molecule, preparing it for a molecular dynamics simulation.

III. Results

The table presented bellow shows the results of the mass spectrometric analysis of gases state above the thin As_2S_3 and As_2Se_3 films doped with 2% of tin before and after Ar-laser illumination.

Mass spectrums of the thin films of As_2S_3 doped with 2% of Sn before and after Ar-laser illumination are presented on Chart 1 (before illumination) and Chart 2 (after illumination). There are also perceptible visible differences in the intensity of the ion currents. For such thin films before illumination we registered the following ions: $As_m S_n^+$ (m=1-4; n=1-5), As_m^+(m=1-4), S_n^+(n=1-2) and SnS_2^+. After illumination the following new kinds of ions are present on the mass spectrum S_n^+ (n=3-8), As_2S_6 and SnS^+ and also increasing of the intensity of the As_m^+ was detected.

Mass spectrums of the thin films of As_2Se_3 doped with 2% of Sn before and after Ar-laser illumination are presented on Chart 3 (before

illumination) and Chart 4 (after illumination). We registered before illumination of the films the following ions: $As_mSe_n^+$ (m=1-5; n=1-4), As_m^+(m=1-4), Se_n^+(n=1-2) and $SnSe_2^+$. After illumination, the new kind of $SnSe^+$ ion and increasing of the intensity of the As_m^+ ions are present on the mass spectrum.

IV. Discussion

Taking into account that molecules have tendency to formed evidently with minimum of the potential energy may be explained the appearance after illumination molecules that contain homogeneous As-As, S-S or Se-Se bonds. That fact influents the physical proprieties of the thin films.

The observed changes in the mass spectra may be explained in view of some re-arrangement of the component atoms in the shot-range order. After the illumination the fragments of the form $[As_mS_n]^+$ & $[As_mSe_n]^+$ differ from the same before illumination. Illumination increases the intensities of the peaks, corresponding to the particles that contain As-As, S-S and Se-Se homogeneous bonds (As_4, S_8, As_4S_3, As_4Se_3).

Molecules As_2S_3 and As_4S_6 contain only heterogeneous bonds As-S, but molecules As_2Se_3 and As_4Se_6 contain only heterogeneous bonds As-Se. Molecules As_4, S_8, Se_4 contain only homogeneous As-As, S-S and Se-Se bonds. Molecules As_2S_4, As_2S_5, As_2S_6 contain respectively one, two and three homogeneous S-S bonds. Molecules As_4S_5, As_4S_4, As_4S_3 contain respectively one, two and three homogeneous As-As bonds.

The As_2Se_4, As_2Se_5, As_2Se_6 molecules contain respectively one, two and three homogeneous Se-Se bonds. The As_4Se_5, As_4Se_4, As_4Se_3 molecules contain respectively one, two and three homogeneous As-As bonds.

Molecules that contain only homogeneous As-As or S-S bonds have got a minimum of the potential energy. Thus, As_4 molecule has got the potential energy 3,47 Kcal/mol and S_8 molecule has got the potential energy 4,44 Kal/mol.

If the molecules contain homogeneous bonds As-As their have got a loss potential energy, for example As_4S_3, As_4S_4, and As_4S_5 have got respectively the potential energy 11,87 Kcal/mol; 21,88 Kcal/mol; 24,98 Kcal/mol. But the molecules As_4S_6, that contain only heterogeneous As-S bonds have got respectively potential energy 43,13 Kcal/mol.

Modelling based on the mass spectroscopy data suggest the appearance for As_2S_3 thin films after illumination the homogeneous As-As & S-S bonds and for As_2Se_3 thin films As-As & Se-Se homogeneous bonds. That fact leads to more compact packing of the component atoms. As result this fact caused the increase of the density of the films.

V. Conclusions

That behaviour under the illumination may be connected with the characteristic of the structure of the thin films of As2S3 and As2Se3 doped with 2% of tin. For that reason, as a result of photostructural transformation under illumination the tin atoms change their valence from IV to II. In a like manner the illumination changes the coordination number of the tin atoms and that make the structure of the doped thin films more stable. That one permit us to conclude that the As2S3 and As2Se3 doped with tin alloys are more perspective for holographic and optical recording than the chalcogenide glass alloys without tin.

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Моделювання $As_2(S, Se)_3Sn_{0.1}$ плоских хвильоводів до та після освітлення

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Розглядається вплив освітлення на характеристики структури тонких плівок As_2S_3 и As_2Se_3 легованих оловом 2 %. В результаті фотоструктурного перетворення під дією освітлення атоми олова міняють валентність з IV а II. Аналогично, освітлення змінює координаційне число атомів олова, що робить структуру легованих тонких плівок більш стійкою.