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THE COMPUTER SIMULATION OF THE MOLECULAR STRUCTURE OF SELENIUM ELECTROPHOTOGRAPHIC LAYER

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Abstract

The modern selenium electrophotographic photosensor is a multilayer system in which different properties of various layers are attained by changes in the material molecular structure without any changes in its chemical composition. The models of the selenium molecular structure at different distances from the surface of the electrophotographic layer are considered. The changes of the bond length, the bond angle and the dihedral angle distributions are analysed for various parts of the layer. The correlation between the form of the third peak of RDF and the short range order parameters of selenium is defined.

Keywords: amorphous semiconductors, photosensors.

Introduction

Non-crystalline semiconductors are used in various fields of electronics for fabrication of thin-film transistors, photovoltaic devices, threshold and memory switches, imaging devices, photosensors, optical modulators, and for litographic application as high resolution photo and electron resists. The important feature of non-crystalline semiconductors in comparison with crystals is the possibility of changing the molecular structure and properties of the material without changing the composition. However, this possibility calls for detailed investigation of the molecular structure of non-crystalline semiconductors. In the present work the way of this problem solution is given for the case of non-crystalline selenium.

Non-crystalline selenium (a-Se) is most widely used as photosensitive material in modern electrophotographic apparatus.

A selenium electrophotographic layer (SEL) is a multilayer system the required properties of which are supplied mostly by changes in molecular structure along the thickness of the layer at constant chemical composition of the material. For studying the molecular structure of various parts of SEL the following procedure was adopted: method of sequential removal of ultrathin cuttings with the help of microtom technique combined with diffractive experiment carried out with an electron microscope

UEMV–100 K (VASILEVA, 1986). Electrophotographic layers 50–55 μm thick, prepared by selenium sublimation method, were studied. With the help of UMTP–3 microtom cuts-off 20–40 nm (200–400 Å) thick were successively taken off the selenium layer. Each hundred of cuts-off was the object of electron diffraction experiment. The study showed (VASILEVA, 1986: AVILOV, 1982) that the molecular structure of selenium in electrophotographic layers of high quality differs in the regions adjacent to both SEL surfaces and in the central part of the layer. Changes in the structure essentially influence the physical properties of the material. Thus, the 5–10 μm thick part of SEL adjacent to the free surface possesses bigger microhardness as compared to the layer thickness (AVILOV, 1982).

However, the radial distribution function (RDF) obtained by experiment in SEL at different distances from the substrate makes it possible to draw only qualitative conclusions concerning changes in the degree of order of the molecular structure. Complete information on space positions of the atoms in different parts of a SEL can be obtained by simulation of the structure.

The molecular structure of selenium in the cuts-off obtained from the two surface-adjacent and one central regions of a SEL was the object of modelling in the present paper. Thereby, we choose the cuts-off with typical RDF for the given region. These were the cuts–off situated at the following distances from the surface of the substrate: 2.7 μm — sample No. 1; 22 μm — sample No. 2; 49 μm — sample No. 3. The total thickness of the electrophotographic layer was 52 μm. The experimental RDF of these cuts-off, shown in *Fig.1a.* by full lines, were taken for computer memory as initial data for constructing models of the selenium molecular structure.

2. Construction of the models

The relaxation method of mathematical simulation was used for constructing atomic models in different parts of SEL. The modelling process of the selenium structure included the following main stages: choice of initial atom positions distributed by chance in the volume of a sphere 2.9 nm (29 Å) in diameter (the number of atoms in the volume of such a sphere was calculated on the basis of the experimental density and was equal to 420) — 1st stage; further directed displacement of atoms in order to obtain the required similarity of RDF model and experimental RDF — 2nd stage; formation of atoms in molecules (existence of ring and chain molecules was allowed) — 3rd stage; relaxation of the model for minimizing the total energy of the system of the atoms — 4th stage.

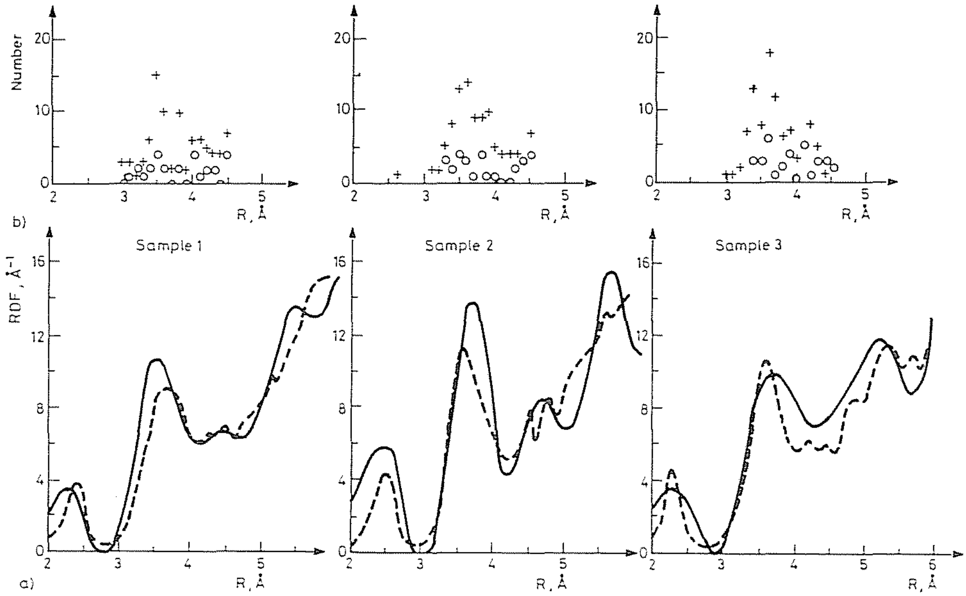

Fig. 1. RDF for models (dashed lines) compared with experiment (solid lines) (a); distributions of model distances to 2nd (+) and 3rd (o) neighbours (b).

At the second stage of modelling the subgradient, and at the fourth stage the gradient methods were used to locate directions of the atomic displacements. The search for the optimum positions of the atoms in both cases was done with the help of a specially developed algorithm, allowing to cut down considerably the computer time in comparison with the Monte-Carlo procedure (VASILEVA, 1982).

When calculating the RDF model the effects of the finite size of the model were minimized with the aid of a correction factor (MASON, 1986).

In order to decrease the influence of the finite size of the model on the results, displacements of atoms at the 4th stage of the model construction were effected for the atoms, situated in the inner part of the model 2.2 nm (22 Å) in diameter, whereby the core 2 nm (20 Å) in diameter actually served as a model of the structure, all atoms of which, including those at the boundary, had normal environment within 0.45 nm (4.5 Å) radius (outmost distance at which Van-der-Waals interaction was observed). The necessity of atomic displacement at the 4th stage in the volume larger than that of the core was dictated by the fact that the boundary part, separating the volume in which atoms were displaced, from the part of immobile atoms, became depleted of the atoms as a result of relaxation, that is, had lesser atom density as compared to the mean atom density. It is explained by the fact, as a result of the search for the atomic positions corresponding to the minimum of their total energy, some of the atoms are displaced from the inner part of the model to the outer part, while no displacements occur in the reverse direction. The layer of the depletion, as calculations show, has a thickness equal to 1 nm (10 Å).

It was supposed that the total energy of atoms consisted of four components:

a.) Bond-stretching energy between the given atom and its covalently bonded nearest neighbours:

$$U_s = 0.5\alpha(\Gamma_{l,i}^2 - d^2)^2, \tag{1}$$

where α — constant; $\Gamma_{l,i}$ — bond length between atoms l and i; d — most probable distance between nearest neighbours, determined by the position of the 1st peak of the experimental RDF;

b.) Bond-bending energy:

$$U_B = 0.5\beta[(\overline{\Gamma}_{l,i} \cdot \overline{\Gamma}_{l,j}) - c]^2, \tag{2}$$

where β — constant, $\overline{\Gamma}_{l,i}$ and $\overline{\Gamma}_{l,j}$ — vectors, binding atom l with atoms i and j; c — constant, which is selected in such a way as to make potential U_B equal to zero at bond angle 105 ° (bond angle for crystalline selenium);

c.) Energy of the Van-der-Waals interaction between the given atom and the atoms which have no covalent bond with it:

$$U_V = \sum_i U_{l,i},$$

$$U_{l,i} = \begin{cases} -\frac{A}{\Gamma_{l,i}^6} + \frac{B}{\Gamma_{l,i}^{12}}, & \Gamma_{l,i} \le \Gamma_c \\ O & \Gamma_{l,i} > \Gamma_c \end{cases} \tag{3}$$

where $\Gamma_{l,i}$ — distance between atoms l and i, Γ_c — cut-off distance of Van-der-Waals interaction (for Se 0.45 nm (4.5 Å)), A and B — constants, chosen in such a way as to make potential U_v minimum at $\Gamma_{l,i}$=0.37 nm (3.7 Å);

d.) Bond-twisting energy:

$$U_D = \gamma\left\{[\overline{\Gamma}_{i,j} \times \overline{\Gamma}_{j,k}] \cdot [\overline{\Gamma}_{j,k} \times \overline{\Gamma}_{k,l}] - K_o\right\}^2, \tag{4}$$

where γ — constant, i, j, k, l — indexes of sequentially bonded atoms in molecule Se, K_o — constant, which provides for minimum potential U_D at dihedral angle 102 °.

3. Optimization of relaxation parameters

In the process of modelling, for each sample constants $\alpha, \beta, A, B, \gamma$ expressed as (1–4) as well as the optimum number of relaxation cycles (cycle–single sequential displacement of all atoms in the system) were experimentally selected in the following way: first of all, at constant coefficient γ=0.0015, variations of coefficients α, β, A, B were taken to obtain best similarity of the 1st and 2nd maxima of experimental and model RDF. As a result, for all samples the values of the coefficients α, β, A, B proved to be identical: $\alpha = 1.0$, $\beta = 0.5$, $A = 5.0 \cdot 10^3$, $B = 6.41 \cdot 10^6$. The maximum number of relaxation cycles under examination (N) was equal to 15. Optimum, that is, the one which provides for the least mean square deviation (msd) of the model and experimental RDF, proved to be N=8. At $N \geq 12$ maxima of model RDF appeared too sharp and exceeding in height the peaks of experimental RDF.

Then, at constant coefficients α, β, A, B for each sample model structures with different values of coefficient γ (in the range of γ from 0.0015 to 1.0) were calculated. For all models the optimum number of relaxation cycles was determined. For different samples it occupied the interval from 7 to 9. The criterion for choosing one or another model type was a minimum msd value at the least value of the amount of three components of total energy (E): bond-stretching energy, bond-bending energy and energy of Van der Waals interaction (*Table 1*).

Table 1
Three components of the total energy

Parameter	Number of sample											
	1				2				3			
γ	0.0015	0.01	0.1	1.0	0.0015	0.01	0.1	1.0	0.0015	0.01	0.1	1.0
ν	8	8	8	7	8	9	8	9	8	9	9	8
MSD	0.45	0.59	0.54	1.47	1.23	1.30	1.38	2.19	0.94	0.83	0.72	1.63
E, arb.u.	3127	118	203	3248	−9.86	80	32	−13	168	188	80	368

On the basis of these criteria the value of γ=0.0015 was taken for sample 2, and γ=0.1 for sample 3. As regards sample 1 minimum msd (at γ=0.0015) did not correspond to minimum energy (at γ=0.01). Since the similarity of experimental and model RDF at $\gamma=0.01$ was quite satisfactory, the value γ was taken as optimum, because in that case the energy E was considerably smaller than that at $\gamma=0.0015$.

It should be noted that at $\gamma=1.0$ for all samples the dihedral angles distribution had an obvious maximum in the parts of angles 100–110°. But at that, a noticeable change for the worse was observed in the similarity of experimental and model RDF, especially in the first two maxima. Besides, at $\gamma=1.0$, for samples 1 and 2, the increase in number of relaxation cycles from 7 to 15 brought about an increase in the total energy of the system instead of a decrease. These facts helped to draw the conclusion that the value $\gamma=1.0$ is unacceptable for all samples as it does not reflect the real contribution of bond-twisting energy to the total energy of the system.

4. Results and discussion

The obtained structure models of different parts of SEL consisted of fragments of deformed chain molecules and also included several unbonded atoms. In sample 1 57% of the atoms forming molecules were in trans, 43% in cis configuration, in sample 2 48.5 and 51.5%, in sample 3 51 and 49%, respectively.

Fig. 2. shows the dependences of the mean density $\rho(R)$ of atoms in concentric layers 0.1 nm (1 Å) thick, the centre of which coincides with the centre of the model, depending on the distance from the centre. Most considerable fluctuations $\rho(R)$ at $R \leq 0.2$ nm (2 Å) are caused by the small number of atoms in the inner spherical layers. Maximum deviation $\rho(R)$ from the experimental density 0.033 Å^{-3} in models of diameter 2 nm (20 Å) at $R > 0.2$ nm (2 Å) comprised: in sample 1 27%, in sample 2 39%, in sample 3 24%. The boundary layer 1 nm (10 Å)$<R\leq$ 1.1 nm (11 Å) in all models had lower $\rho(R)$ on account of the effect described above.

RDF of the models (*Fig. 1.* — dashed lines) well reproduce the main features of the experimental RDF of samples 1–3.

Figs. 3–5. show the distribution of near–neighbour distances, bond angles and dihedral angles in the models, respectively. *Table 2* presents energy characteristics of the models: values of total energy of the system (U) as well as its components.

Analysis of the above data enables certain structural features of different parts of SEL to be revealed.

Bond length distributions are identical in appearance (*Fig. 3.*) for all samples, although, as the energy characteristics of the models show (*Table 2*), the degree of distortion of distances to the near-neighbours in

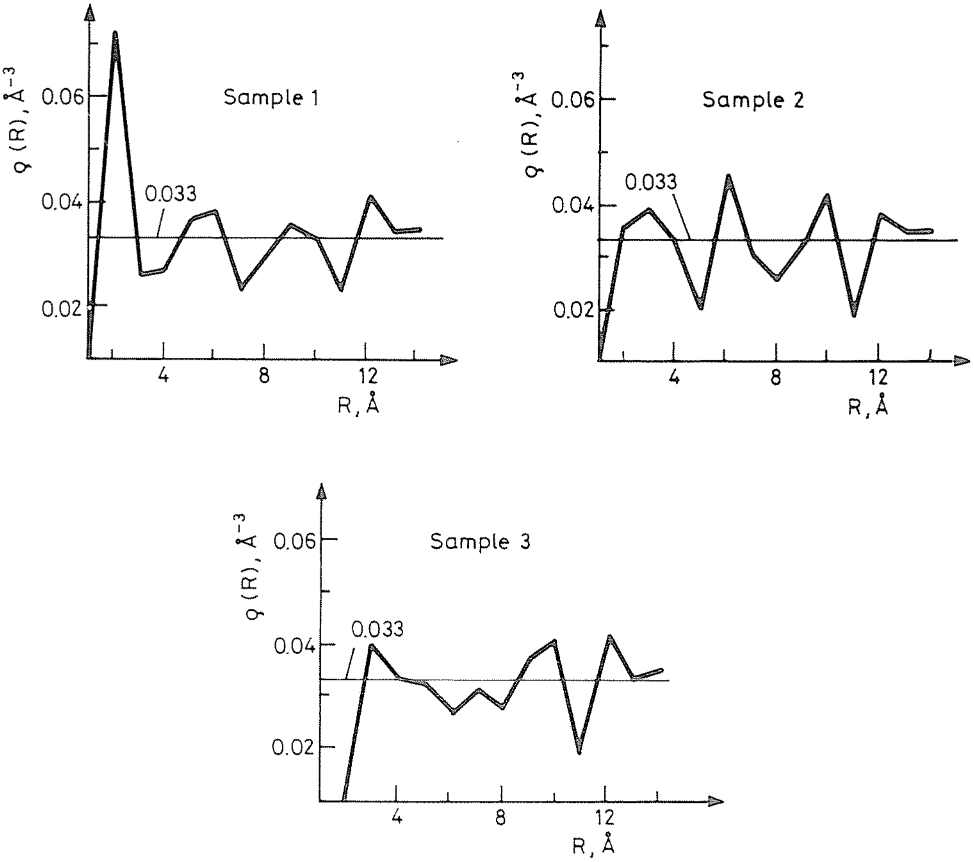

Fig. 2. Mean density of atoms in concentric layers

Table 2
Energy characteristics of the models

Number of sample	Number of atoms in the system	Number of un-bonded atoms	U_S, arb.u.	U_B, arb.u.	U_V, arb.u.	U_D, arb.u.	U_D^*, arb.u.	γ	U, arb.u.
1	130	6	214	136	−232	10.5	0.82	0.01	129
2	140	5	82	122	−214	2.2	0.97	0.0015	−7.7
2	-	-	-	-	-	668	0.49	1.0	-
3	138	1	245	109	−275	105.7	0.9	0.1	185

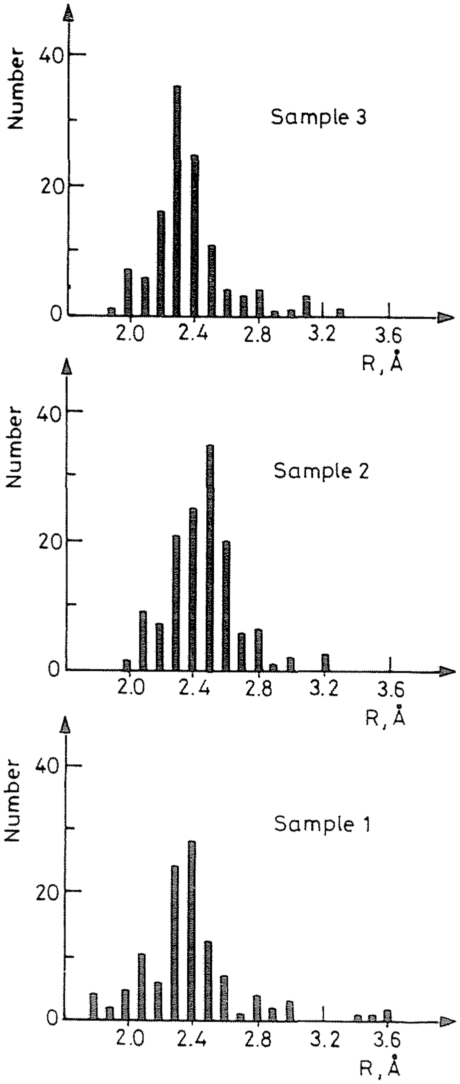

Fig. 3. Bond length distributions

the chain is the lowest in the central part of SEL (sample 2) and increases at both surfaces of the layer (sample 1 and 3).

Bond angles have the greatest deviations from the optimum value in the part of the layer next to the substrata (sample 1), which is confirmed by the most sloping distribution of bond angles in that sample (*Fig. 4.*), which is evidently the result of the influence of the substrate on the material structure.

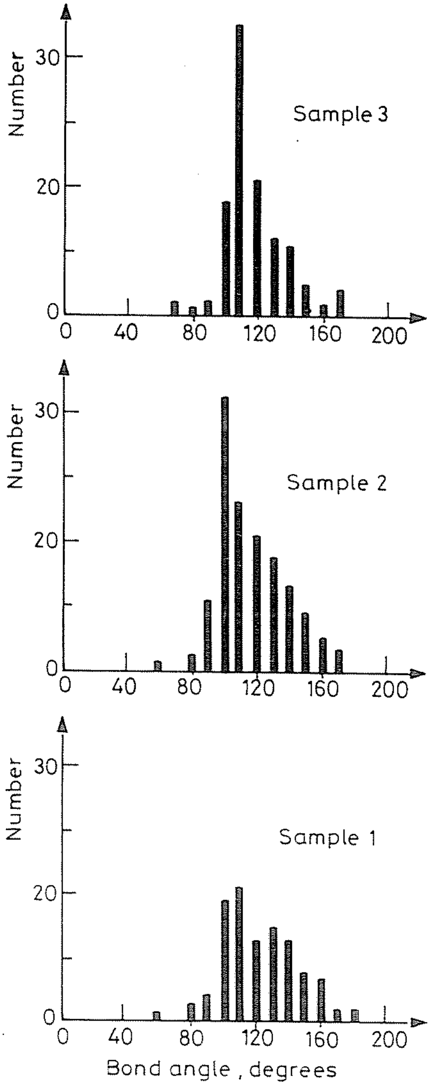

Fig. 4. Bond angle distributions

The degree of distortion of dihedral angles is characterized by U_D^*, a parameter representing a fraction of bond-twisting energy over one dihedral angle and is reduced to one value of the constant γ. Comparison of values U_D^* (*Table 2*, γ=0.1) showed that samples 1–3 differ by that parameter insignificantly: sample 1 — by 9%, sample 2 — by 8%, as compared to sample 3. It is also confirmed by the similar character of dihedral angles distribution in samples 1 — 3 (*Fig. 5*).

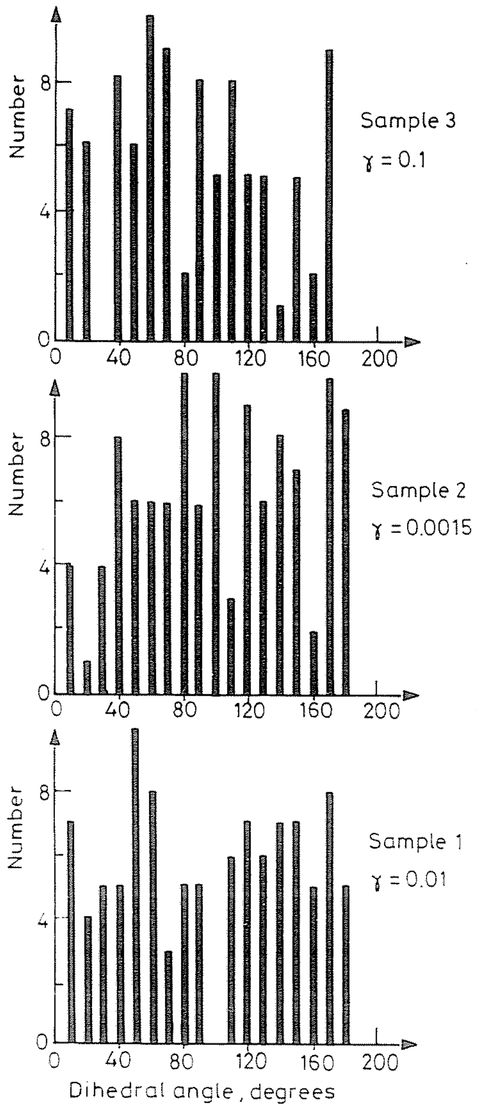

Fig. 5. Dihedral angle distributions

Parameter U_D^* values, being close to each other, evidently reflect the slight difference in distortion degree of dihedral angles in the models of the samples under observation which is confirmed by the fact that the variation of coefficient γ at construction of the model causes considerable changes in parameter U_D^* as well as in the character of distribution of dihedral angles in the model. Thus, the structural model of sample 2 at γ=1.0 is characterized by parameter U_D^* with differs by about 50% from the values of the above (*Table 2*). The character of distribution of dihedral angles, in this case, also differs from distribution shown in *Fig. 5.* and has a strongly marked maximum in the region of angles 100–110° (*Fig. 6.*).

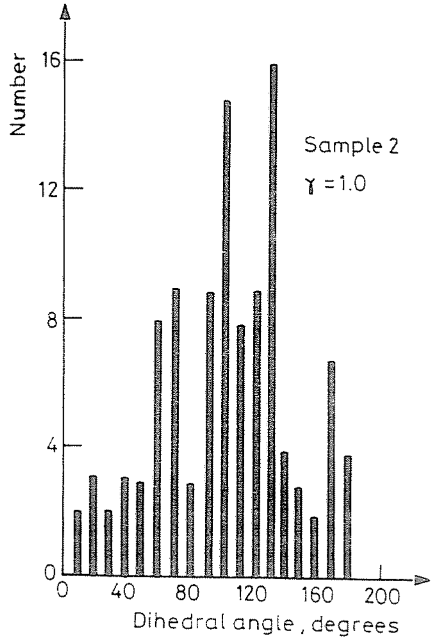

Fig. 6. Dihedral angle distribution

Thus, the best similarity of experimental and model RDF for the samples out of various regions of the SEL is reached at different values of constant γ, equation (4), which leads to differences in the contributions of bond-twisting energy to the total energy. Whereby, the distortion degree of dihedral angles (deformation value of dihedral angles) in samples 1–3 differs but slightly.

In our opinion, such a situation is possible due to the various local environment of atoms in the studied samples which is confirmed by differences in RDF sample in the region of the second, and, especially, of the third maxima, various contributions of bond-stretching and bond-bending energy to the total energy of the system (*Table 2*), as well as the results of detailed analysis of the contribution of different components to the energy of Van-der-Waals interaction (U_{V}) of the models, as stated below.

Since, in calculating U_{V} of the models we took into consideration the interaction of each atom with other atoms in the sphere of radius

Γ_c=0.45 nm (4.5 Å) and into that sphere the second and the third neighbours of the given atom (in the same molecule), mainly, find their way, as well as atoms from other molecules, we have to examine the following components of energy U_V: energy of interaction between neighbours of the 2nd order for a molecule (U_2), energy of interaction between neighbours of the 3rd order for a molecule (U_3) and energy of interaction between atoms of various molecules (U_{V-V}):

$$U_V = U_2 + U_3 + U_{V-V}.$$

For the calculation of U_2 and U_3 we used, as obtained out of models, distributions of distances up to the 2nd and the 3rd neighbours in molecules shown in *Fig. 1b.*

The total energy of these two components U_V was:

for sample 1 $U_2 + U_3 = -(30.5 + 8.4) = -38.9$ arb.u.
for sample 2 $U_2 + U_3 = -(7.7 + 18.8) = -26.5$ arb.u
for sample 3 $U_2 + U_3 = -(61.8 + 25.4) = -87.2$ arb.u.

Subtracting these values from the total energy U_V we obtained the energies of interaction between atoms of different molecules: U_{V-V}=−193 (sample 1);−187.5 (sample 2);−187.8 (sample 3) arb.u.

Thus, at slightly varied values of the energy of intermolecular interaction in the models we observe much more significant differences in Van-der-Waals component energy of intramolecular interaction. Whereby, as shown in the calculation of interaction forces between atoms inside molecules, the noted difference in energies of molecular interaction of the studied sample is due, mainly, to differences in interatomic interaction, having repulsive character. The obtained values of energy of intramolecular interaction is correlating with values of the bond-twisting energy (*Table 2*).

The least distortion energy of Van-der-Waals distances in sample 3 ($U_2 + U_3 = -87.2$) corresponds to the largest bond-twisting energy ($U_D = 105.7$) and vice versa: the least value $U_D = 2.2$ corresponds to the largest value $U_2 + U_3 = -26.5$ (sample 2).

Thus, structural modifications of selenium in various regions of SEL are characterized by a broad distribution of dihedral angles and by approximately equal degree of dihedral angles distortion. However, they possess different intramolecular Van-der-Waals interaction as well as different bond-twisting energy which provides, in considerable degree, for the difference in the total energy of the system. The causes for the said differences are, probably, connected with different material condensation conditions at forming SEL.

Whereby, the wide range of the values of dihedral angles in all regions of SEL (*Fig. 5.*), which is the necessary condition for good coincidence of experimental and model RDF indicates that the model of freely rotating chain (MALAURENT, 1977) is preferable to the model of disordered chain (SUZUKI, 1978) for selenium layers sputtered by sublimation method.

References

AVILOV, A. – VASILEVA, N. – KARALUNETZ, A. et al. (1982): Structure Investigation of Selenium Electrophotographic Layers. *Proc. of Moscow Power Eng. Inst.*, No. *586*, pp. 71–75. (in Russian)

MALAURENT, J. – DIXMIER, J. (1977): Random Chain Assembly Model for Amorphous Sulfur, Selenium and Tellurium. *Phys. Stat. Sol.* (a), Vol. *43*, pp. K61–K65.

MASON, J. (1968): Radial Distribution Functions from Small Packing of Spheres. *Nature*, Vol. *217*, pp. 733–735 .

SUZUKI, K. – MISAWA, M. (1978): Ring-Chain Transition in Liquid Selenium by a Disordered Chain Model. *J. Phys. Soc. Jap.*, Vol. *44*, No. 5, pp. 1612–1618.

VASILEVA, N. – POPOV, A. – KHALTURIN, V. (1982): Application of Subgradient Method for Simulation of the Structure of Non-crystalline Semiconductors. Proc. of the 'Intern. Conf. Amorphous Semiconductors-82'. Bucharest. pp. 50–52. (in Russian)

VASILEVA, N. – POPOV, A. – SHEMETOVA, V. (1968): Effect of Preparation Regimes on the Structure and Properties of Selenium Electrophotographic Layers. Abstracts of All-Union Scientific Conf. 'Achievements and Perspectives of Electrophotography'. Grozny. pp. 98–100. (in Russian)

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