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A MONTE-CARLO COMPUTER SIMULATION METHOD OF CONTINUOUS NETWORK MODELS OF AMORPHOUS GERMANIUM THIN FILMS

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A practical computer simulation of the network models of amorphous semiconductors, using the Monte-Carlo method, has been developed. A randomly chosen atom of the structure is slightly displaced by a random amount and in a random direction. After each move, the potential energy of the amorphous structure is calculated, and the new position is retained in the case of decrease of energy. The iterative procedure was stopped when the energy did not decrease any more. The model is tested by the radial distribution functions before and after the computation and compared to the experimental data from X-ray diffraction.

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1. Introduction

The experimental data obtained for vacuum-deposited semiconductor thin films indicate the following types of structures of these materials:

a) the non-crystalline (amorphous) structures,

b) the crystalline phases of higher or lower symmetry, and

c) the polycrystalline phases with crystallites of variable dimensions.

The vacuum deposition onto a low-temperature support mainly causes the formation of the amorphous phase. In an amorphous semiconductor, the covalent bonds determine the neighborhood order, which is lost at the increasing distance due to small radial and angular disturbances. Among the first simulations of amorphous semiconductor structure known in the literature, we can mention those of Kaplow, Rowe and Averbach [1] for amorphous selenium, and of Henderson and Herman [2] for germanium. They used mechanical models. The Monte-Carlo method is generally used for the computer simulation of the structures. A pseudo-random number generator can simulate the deposition of add-atoms onto a substrate, their migration in different directions, the creation of initial condensing centre, and rotation of these atoms for local bonds matching and for torsion reduction in bonds. In this method, the structure parameters in intermediate stages of the structure evolution are recorded in computer files. Finally, the new computer model is validated by comparing the initial and final radial distribution functions with the X-ray diffraction data.

In such a model, Shevchik and Paul [3] begin the calculations with an initial condensing centre, subsequently adds new atoms, and slightly distorts the bonds around a 20° wide solid angle. In the new variant of the model, the new add-atoms are rotated in order to reduce torsion energy of new bonds.

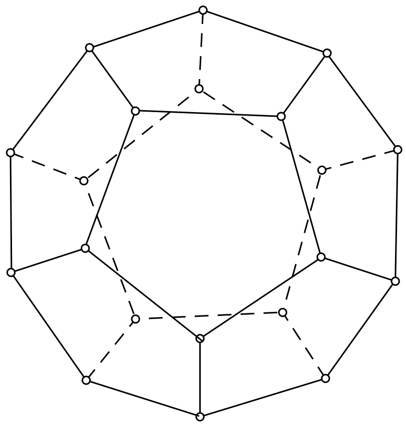
Duffy et al. [4] proposed a new procedure for the minimization of the structure deformation energy by acting simultaneously on bond lengths and angles. After every displacement of an atom, they have recalculated the forces in the structure, and the process converged under certain reasonable conditions.

2. The simulation models

Our computer simulation was performed in two stages. In the first stage, we have simulated the structure of small metallic crystalline condensing centres emerging on a substrate from vapours [5,7], with a limited migration on the support surface. The evaluation of energy of different possible configurations (trigonal, octahedral, hexagonal, pentagonal) leads to the conclusion that the minimum of energy corresponds to the pentagonal centre - the most stable geometric form of these structures. Thus, it was confirmed that the amorphous state can be formed by vacuum deposition provided that the energy of the incoming atom is rapidly absorbed by the cold substrate. In this way, the migration of an incident atom occurs only at small distances, which favours the pentagonal configuration. On the contrary, on a hot substrate, large germs of condensation centres can appear which favour another crystalline configuration.

After these preliminary simulations, which have clearly illustrated that the pentagonal configuration is incompatible with the translation symmetry necessary for the spacially ordered lattice growth, we have approached the second stage - of the amorphonic germanium models. All computations were done for germanium, because it is the only element for which some experimental values of transformation enthalpies are available. We have studied the amorphous models of 17, 41, 57 and 98 germanium atoms [6,8].

For the amorphous models, we have used a combined simulation procedure. First, we have realized a physico-mechanical model - a pentagonal dodecahedron - made of sylon connections (Fig. 1), the basic unit of amorphous germanium structure. For instance, in a 57-atom germanium amorphone, we can find four such interconnected dodecahedrons (Fig. 2).



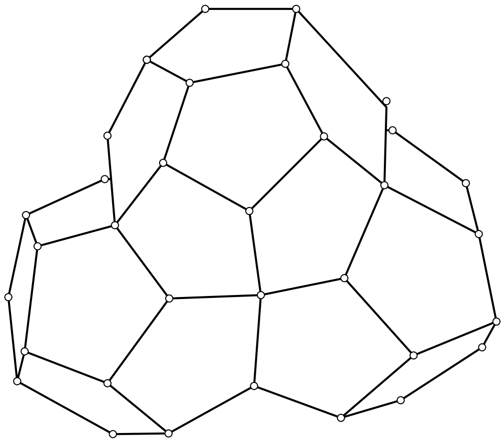


Fig. 1. The pentagonal dodecahedron - the basic fifth-order symmetry cell for amorphous germanium.

Fig. 2 (right). A 57-atom amorphone germanium model made of 4 interconnected pentagonal dodecahedrons. The fourth dodecahedron is behind the three shown in the figure.

The initial coordinates used in the computer programmes were obtained by optical methods. In the simulation, we have considered three types of deforming potential:

– the radial deforming potential:

$$V_1 = C_1(r_1^2 - r_0^2) \tag{1}$$

where $r_0 = 0.245$ nm is the equilibrium distance between the closest neighbouring atoms and $C_1 = 23.75$ fN/nm^2 (femtonewtons per square nanometer, $C_1 = 2.375 \times 10^{-5}$ μdin/Å^2) the length-stretching constant;

– the angular deforming potential:

$$V_2 = C_2(\alpha - \alpha_t)^2 \tag{2}$$

where α is the bond angle, α_t – the ideal tetrahedral angle of 109°25' and $C_2 = 2.063$ fN/deg^2 ($C_2 = 2.063 \times 10^{-}4\mu$din/deg^2) is the bond-curving constant;

– the potential of relative rotation of tetrahedrons:

$$V_3 = C_3\left(\theta - \frac{\pi}{3}\right)^2 \tag{3}$$

where θ is the dihedral angle between two adjacent tetrahedrons and $C_3 = 0.3495$ fN/deg^2 ($C_3 = 3.495 \times 10^{-5} \mu$ dyn/deg^2) is the bond-torsion constant. The potential V_3 must be included for each of the six interactions between atoms up to the third-order neighbouring.

The total potential energy is evaluated by summation over all interactions of the V1, V2 and V3 potential types and over all atom pairs in the cluster:

$$V = \sum_i \sum_j V_{ij}(k) \tag{4}$$

In order to give an idea of the complexity of the calcation, we show in Table 1 the interaction modes for the first five atoms belonging to the 17-atom amorphone with the order of first, second and third (I, II and III) neighbouring atoms.

TABLE 1. The 17-atom amorphone model. The ways of interaction for the first five atoms with first, second and third (I, II and III) neighbouring atoms.

Atom	Neighbouring order	Atoms connected
(1)	I	2, 5, 6, 7
	II	3, 4, 8, 9, 14, 15
	III	4, 10, 11; 3, 12, 13
(2)	I	1, 3, 8, 9
	II	5, 6, 7, 4, 10, 11
	III	4, 14, 15; 5, 12, 13
(3)	I	2, 4, 10, 11
	II	1, 8, 9, 5, 12, 13
	III	5, 6, 7; 1, 14, 15
(4)	I	3, 5, 12, 13
	II	3, 10, 11; 1, 14, 15
	III	1, 8, 9; 2, 6, 7
(5)	I	1, 4, 14, 15
	II	2, 6, 7; 3, 12, 13
	III	3, 8, 9; 2, 10, 11

It is obvious that for the models of 41, 57 and 98 atoms, more complicated relations are encountered.

In the computations, we use a pseudo-random number generator to choose an atom from in cluster, the length of the displacement of the atom in a certain pre-established range and the direction of displacement (independently for each X, Y and Z coordinate). Using the potentials V_1, V_2 and V_3, we first evaluate the total potential for the entire model. After that, we choose another atom with the corresponding random displacement and recalculate the new total potential. If it diminishes, we retain the new coordinates and continue the process until the total potential does not diminish any more. The final coordinates are retained and the radial distribution functions (RDF) are calculated. We compare them with the initial RDF and with the experimental RDF data obtained from X-ray diffraction experiments.

The main programmes are completed with some other programmes that are evaluating the angular and azimuthal fluctuations around RDF forms in order to evaluate which part of the model is more sensitive.

The programmes were first written in FORTRAN IV [6] and later in TURBO PASCAL and BORLAND DELPHI.

In the new versions of the programme, we have added the visualization on the computer screen of the spatial arrangement of atoms, the time evolution of the model and the rotation facilities.

3. Results and discussion

We shall comment here only the results of the simulation performed on icosahedric entity of the 57-atom amorphone with the pentagonal structure, composed of four interconnected pentagonal dodecahedrons shown in Fig. 2.

As is known, for an atomic system of the fifth-order-symmetry, the addition of a new atom to the central atom causes large strains between different parts of the amorphone, due to the angular misfit introduced by the 1.5° deviation from the tetrahedral angle, characteristic of the atomic packing compatible with the three-axis translation symmetry.

In the 57-atom amorphonic model, the total potential reaches the minimum after about 50000 iterative computation cycles, from which 40% were useful (retained) moves, while allowing the atomic displacements up to 2 pm. Although the minimum of energy was closely attained, the amorphonic configuration did not permit a perfect arrangement of atoms at the ideal equilibrium distance of 0.245 nm.

Figure 3 shows the RDF obtained from the simulation model and the experimental results obtained by Schevchik and Paul [3] by X-ray diffraction on amorphous germanium thin films as well as RDF for crystalline germanium. We can observe that the RDF from the computer simulation reproduces very well the first two coordination maxima in these models. The third maximum does not exist in the amorphonic model due to the fact that other coordination spheres are practically merged two by two. The positions of coordination spheres for non-crystalline germanium (amorphous thin film) show clear differences compared to the crystal, but noticeable resemblances with the computer amorphonic model. Indeed, the third coordination sphere of about 0.445 nm is completely absent in amorphonic model and is negligible in amorphous germanium. Further coordination spheres correspond again very well to the coordination spheres from the amorphone.

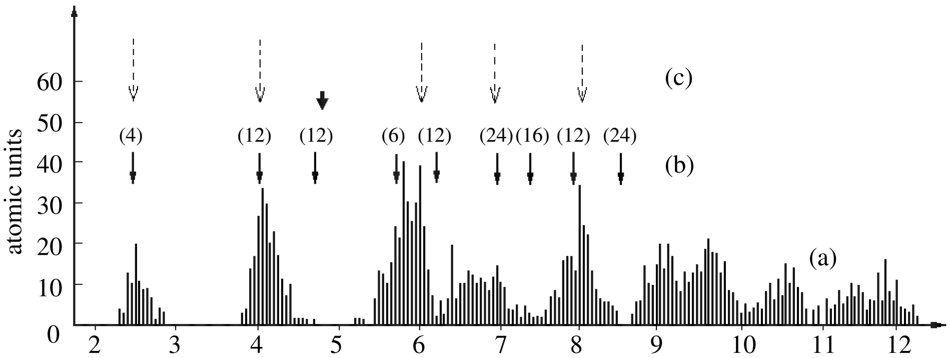


Fig. 3. The RDF a) for 57-atom amorphonic model; b) crystalline germanium; c) amorphous germanium.

The phenomenon was confirmed by running again the computer model, but only with the interaction potentials V1 and V2, neglecting the rotation potential V3 (for the dihedral angle) which seems to have a negligible influence on the final structure. Obviously, the convergence was faster, but that experiment proved once again the character of rigid closed structure of the tetrahedral germanium element.

We calculated the r.m.s. deviation of the atomic distances, and obtained $\sqrt{\overline{(\Delta r)^2}} = 20$ pm. That is much larger than the one obtained for other structural models of amorphous germanium (3.4 pm for the continuous noncrystalline network [10]). The experimental value obtained by Shevchick and Paul [3] in X-ray diffraction experiments in amorphous germanium thin film is 4.4 pm.

The size of the second coordination sphere gives important information on the angular dispersion of atomic bonds. The calculation of this dispersion in various models shows that the continuous noncrystalline network model yields a value of 7.16° for $\sqrt{\overline{(\Delta\alpha)^2}}$. The Polk and Boudreaux model [11] shows an angular dispersion of 7.1° and that of Steinhardt and others [12] a value of 6.66°. In our amorphone model, we have obtained a dispersion of 4.1° in inner rings of five atoms. This proves again that even when using the dispersion of angular length distortions, the amorphone model can explain to a certain degree the onset of amorphonic phase for germanium.

As was shown by Grigorovici [13], the amorphone represents a structure with a minimum of free-energy. The structure of covalently bonded diamond atoms or wurtzitic configurations has higher energies due to the free bonds, and consequently they would be less stable.

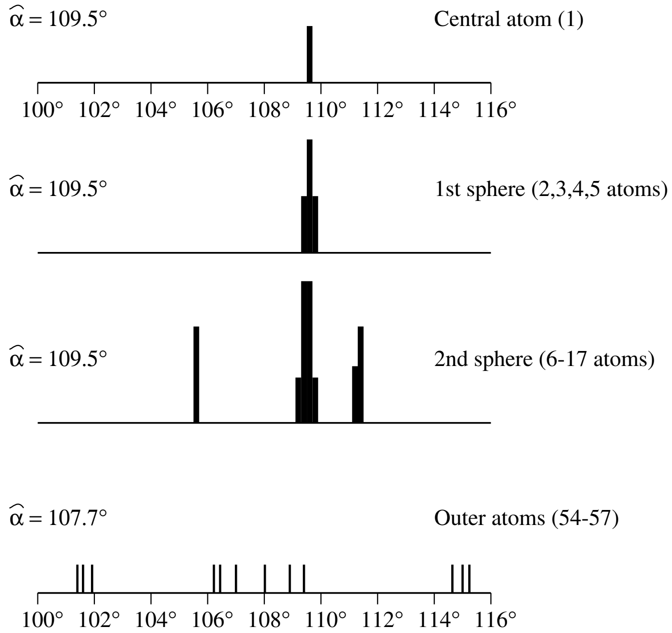


Fig. 4. The angular dihedral distribution for inner and outer rings of the amorphone structure.

In Fig. 4, we present the angular dihedral distributions for inner and outer rings of the amorphone structure. The r.m.s. deviation increases for the external rings which proves a larger deformation of amorphone in the exterior.

Compared to the case of crystalline germanium structure, where dihedral angles have only a single value of 60° (intercalated bonds), the range of values in the amorphone structure is relatively large (between 0° and 8°).

According to the present concept, the amorphone phase corresponds to a random orientation of atoms, which implies a uniform distribution of angular rotation over the interval between 0° and 60°. It is very interesting to follow the distribution of distortion energy per germanium atom. In the crystalline phase, all germanium atoms are considered to be equivalent, and the distortion energy per atom is equal to zero. In amorphous germanium, one might expect that the atoms should be equivalent, so each atom should have a bond energy of an unknown repartition. Since the amorphone model prefigurates an ideal non-crystalline structure, the repartition of distortion energy distribution on it should suggest what could really happen in a real amorphone. We have calculated the free energy per atom and represented it as a function of the distance to amorphone centres (Fig. 5).

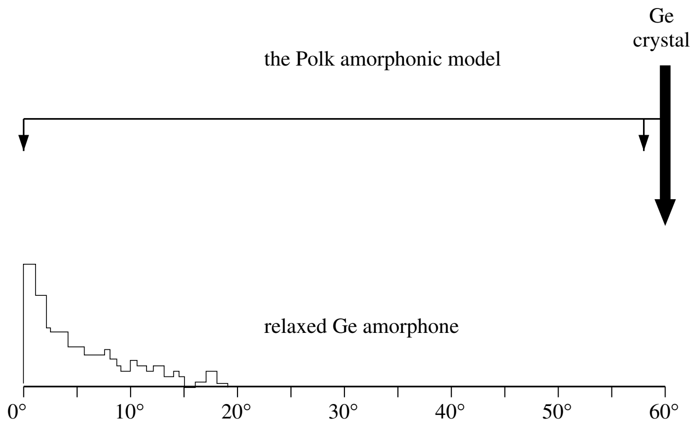


Fig. 5. The angular dihedral distribution for inner and outer rings of the amorphone structure.

4. Conclusion

When the central amorphone part corresponds to a low energy per atom, the larger coordination spheres include atoms with a higher free-energy. The low minimum-energy amorphone also presents a slow structural distortion, which may be explained by the decrease of the total distortion energy. It is obvious that the amorphone structure is an intermediate state between the real amorphone and the crystal.

From the above considerations, it follows that the model presents significant resemblance with the amorphous germanium structure, as was proved by the X-ray experiments [10]. However, at the same time some less essential differences persist, which makes this structure a limiting model that facilitates the understanding of certain aspects of the amorphonic structure.

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MONTE-CARLO SIMULACIJE NEPREKIDNOG MREŽNOG MODELA TANKIH AMORFNIH SLOJEVA GERMANIJA

Razvili smo praktičnu metodu računalne simulacije mrežnih modela amorfnih poluvodiča primjenom Monte-Carlo metode. Nasumce odabrani atom u strukturi je malo pomaknut u nasumce odabranom smjeru i za slučajno određen iznos. Nakon svakog pomaka računala se je potencijalna energija amorfne strukture, a novi se položaj zadržao u slučaju smanjenja energije. Iterativni postupak je zaustavljen kada se energija prestala smanjivati. Model se je ispitao funkcijom radijalne raspodjele prije i nakon računa, te usporedio s podacima dobivenim mjerenjem raspršenja X-zračenja.