FORMATION AND NANOHETEROMORPHOUS STRUCTURE OF VITREOUS AND NON-VITREOUS NON-CRYSTALLINE SUBSTANCES

V.S. Minaev[1], S.P. Timoshenkov[2], V.V. Kalugin[2], S.N. Novikov[2], and S.I. Kovalev[2]

[1]Joint-Stock Company "Research Institute of Material Science and Technology", passage 4806, h. 4/2, Zelenograd, 124460, Moscow, Russian Federation
[2]Moscow Institute of Electronic Technology (Technical University), passage 4806, h.5, Zelenograd, 124498, Moscow, Russian Federation
Ph.: (499) 720-8762, fax: (499) 720-8768, E-mail: viktor118@mail.ru
(Received 10 November 2008)

1. Introduction

A key to solution of the most objective problems of formation and structure of non-crystalline substance, as well as the general classification of a solid state modification, in our opinion, is the main rule of the physicochemical analysis, the rule of Kurnakov-Tananaev: properties of a substance are function of its most fundamental physicochemical characteristics – composition, structure, and dispersion [1, 2].

In this work, we will discuss a non-crystalline substance, avoiding using the term "amorphous" as the last remained ambiguously defined and understood term. As it has been shown in monograph [3], from the point of view of some researchers, the glass-forming state is a special case of amorphous; from the point of view of others, these states are identical; the others consider that these are absolutely different states.

Non-crystalline substances are formed by cooling of glass-forming melts (glass-forming non-crystalline substance), by dispersion, condensation of the vapor phase or dispergating (pulverizing) of a solid crystal body; therefore, films or micro (nano) powders of non-glass-forming non-crystalline substance are formed: nc-C, nc-Si, etc.

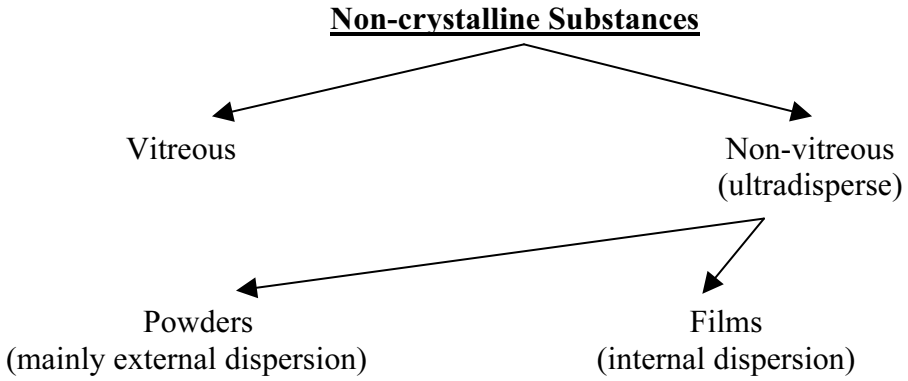
The main feature of non-glassy forms of a non-crystalline substance is high degree of dispersion (the ratio of a substance surface to its volume) – ultradispersion. Dispergating process (reduction of the ratio of a solid body surface to its volume), which facilitates nano-heteromorphous structures of non-crystalline substance formation, can be subdivided into external dispergating and internal dispergating [3].

External dispergating has three varieties: 3D – a substance size reduction on three coordinate axes (pulverizing, micro- and nanopowder formation), 2D - size reduction on two coordinate axes (fibers drawing out, "moustaches" growing), and 1D – size reduction on one coordinate axis (formation of micro- and nanofilms of substances).

Internal dispergating is characterized by formation of micro- and nanocavities in a substance (pin holes), by formation of micro- and nanochannels, by reduction of copolymerization level of structural fragments, by increasing in number of the torn bonds, for example, for ultradisperse nc-Si to $\sim 2 \cdot 10^{20}$ sm^{-3}. Glass-forming substances have considerably smaller level of internal dispergating. In v-SiO_2, concentration of uncoupled spins localized on the torn bonds reaches only 10^{13}-10^{14} g^{-1}.

For micro- and nanopowders, the main role is played by external dispergating – presence of huge number of micro- and nanoparticles, whereas for non-crystalline non-glass-forming films, "internal dispergating" is typical, being generated by a considerable quantity of micro- and nanochannels and micro- and nanocavities.

Thus, non-crystalline substances can be subdivided into glass-forming and non-glass-forming (ultradisperse) substances; the latter, into powder and film substances:



We will consider a structure of non-crystalline substance according to concept of its polimeric-nanoheteromorphous structure and its special case: concept of polimeric-nanoheteromorphous structure of non-crystalline individual chemical substance (ICS).

The fundamental ideas that are the base of this concept are following [3-5].

- The individual chemical substance in non-crystalline form is one-dimensional, two-dimensional, three-dimensional (spatially-structured), or mixed copolymer of fragments of various crystal polymorphic modifications (polymorphoids) structure, that have no translation symmetry (long-range order) and that are characterized by certain intermediate-range order and the short-range orders that are characteristic of one of the polymorphic modifications (PMs); for the structure of a non-crystalline ICS, there are always at least two intermediate-range orders that belong to various crystal PMs;
- The fundamental reasons of change in the structure and properties of a non-crystalline substance are interconversion of various PM polymorphoids and change of their concentration ratio (CRP) in non-crystalline ICS influenced by external actuation and time; CRP is the major internal parameter of non-equilibrium thermodynamic system of a non-crystalline substance;
- Polymeric-polymorphoid model of the structure of a non-crystalline substance represents, as well as the model of Zachariasen (1932) [6], net model, but polymorphoids (carriers of intermediate-range (average) orders of various crystal PMs) are copolymerized, as distinct from the Zachariasen net uniting random located polyhedrons – carriers of a near order.

The nature of a non-crystalline substance cannot be deeply cognized without the analysis of crystal (in various PMs) and liquid states. Interconversions of various states and transformation within each of them (phase: $PM_1 \leftrightarrow PM_2$ – in crystal, structural - in liquid and non-crystalline solid), under the influence of temperature, pressure, electromagnetic fields, and radiation, represent a substance relaxation, i.e., the process of settling of thermodynamic equilibrium in macroscopic physical systems [7]. Under changing influence on substance, for example, at rise in temperature T, and the potentially equilibrium state, to which tends, relaxing, the physical system, continuously varies (up to the termination of T growth). Any change in the state of a substance leads to a change in its structure and properties.

2. A Glass-forming liquid. Glass transition

Though a considerable progress has been made in understanding of the glass transition in general, some crucial questions still remain unanswered [8]. In this section, an attempt is made to obtain answers to some of these questions.

Results of diffractometer, spectroscopic (Raman-spectrum), calorimetric, and other studies of various PMs, glass-forming liquids, and glasses of SiO_2, B_2O_3, GeO_2, H_2O, Se, $GeSe_2$, $SiSe_2$, $BeCl_2$, (Bernal and Fowler (1933), Mackenzie (1960), Pauling (1970), Bruckner (1970), Yohari (1987), Gerber et al. (1988), Poraj-Koshits (1990), Golubkov (1992), Wang et al. (1996), Pavlotou and Papatheodorou (2000)), analyzed in [3, 5], allow us to formulate the following position.

The process of formation of glass-forming liquid at fusion of a high-temperature PM (HTPM) of an ICS is the process of formation of fragments of this PM structure, that have no long-range order (polymorphoids) and their partial transformation in polymorphoids of other low-temperature PMs (LTPMs) with the subsequent establishment of a concentration ratio of various PMs characteristic of each melt temperature.

Relaxation processes in the condensed state of glass-forming substance are schematically presented in Fig. 1. Ttr is the temperature of polymorphic transformation LTPM↔ HTPM. The basic feature of this transformation is the transition from low-temperature PM to high-temperature; it is accompanied by an endothermic effect; the reverse transition is accompanied by an exothermic effect [9]. Relaxations processes are completely determined by genetic interrelation of structure and properties of all three kinds of the condensed state: crystal, liquid, and glass. The Ttr and Tg temperatures are interconnected also: Ttr is a kind of Tg prototype [5]. Quantitatively, Tg value is always close to that of Ttr, but it is less in size (Tg < Ttr). So, for GeS_2, Ttr and Tg equal, accordingly, to 497ºC and 495ºC; for Se, to 70ºC and 37ºC; for P_4Se_4, to 192ºC and 180ºC; for As_2S_3, to 180ºC and 175ºC, etc. [3, 10, 11]. Both Ttr and Tg are thermodynamic characteristics of the substance that undergoes phase (at Ttr) or structural (at Tg) transformation in crystal and, accordingly, in non-crystalline glass-forming state, the transformations require the achievement of certain enthalpy level. At the same temperature T≤Ttr, a non-crystal substance always exhibits greater enthalpy than a crystal, owing to its disordering at long-range order level and to the presence in it, in addition to structure fragments of LTPM polymorphoids, of HTPM polymorphoids that exhibit rather greater enthalpy. As a result, at a substance heating, the threshold enthalpy (Htr) conformable to the beginning of "LTPM→HTPM" polymorphoid transformation in non-crystalline substance is achieved at lower temperature at Tg (in glass) than in a crystalline substance (at Ttr).

Copolymerization of nanoheteromorphous (with different structure at nanometer level) fragments that have no crystal translation symmetry (polymorphoids) taking place at melt cooling is a fundamental original cause of glass-formation that excludes the possibility of a long-range order organization (crystallization).

Glass transition of the individual chemical substance is a dual process of copolymerization-depolymerization: copolymerization of various PM polymorphoids and depolymerization of formed copolymer due to disintegration of LTPM polymorphoids unstable above Tg and HTPM polymorphoids unstable below Tg.

The analysis of such glass-formers as Se, GeS_2, $GeSe_2$, AsSe, SiO_2, and H_2O shows bi-staging process of glass transition – transformations of the super-cooled liquid at its cooling in a solid (viscosity of $\sim 10^{19}$ Pa·s) body [12, p. 240]. The first stage of glass transition is carried out in a temperature interval "melting temperature Tm – glass transition temperature Tg" (Fig. 1) and comes to an end at the substance viscosity of $\sim 10^{12,3}$ Pa·s. In this area there is a copolymerization of low- and high-temperature PM (LTPM and HTPM) polymorphoids and transformation unstable in the area LTPM polymorphoids in HTPM polymorphoids, accompanied by growth of concentration of the latter. The second stage of glass transition takes place below Tg. Its basic part extends on a viscosity interval of glass-forming substance $\sim 10^{12,3}$... 10^{16} Pa·s. 10^{16} Pa·s is the bottom edge of the viscosity interval 10^{14}.. 10^{16} Pa·s, where

the temperature curve of viscosity undergoes a bend, which agrees with transition to the fragile state (Vinter – Klein, 1953) [13]. This position correlates with the data on the activation energy of a viscous flow which is coming nearer to rupture energy of a chemical bond at viscosity of 10^{15} Pa·s (Nemilov, 1969) [14]. At glass cooling below Tg, according to the given data the dual process of glass transition – its second stage - continues. The glass-forming substance is depolymerized here due to disintegration of a part of unstable high-temperature PM polymorphoids. Their fragments are reconstructed and united in low-temperature PM polymorphoids stable below Tg, which copolymerize with non-decayed HTPM polymorphoids and are built in a glass net.

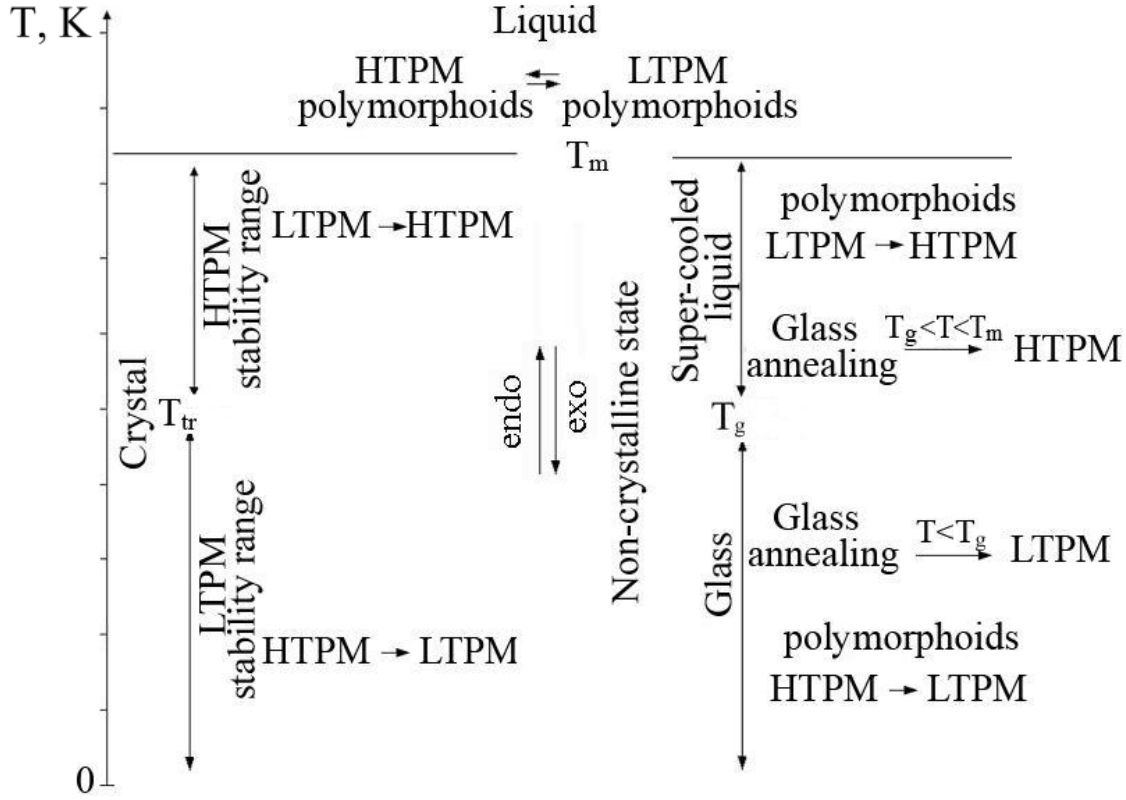
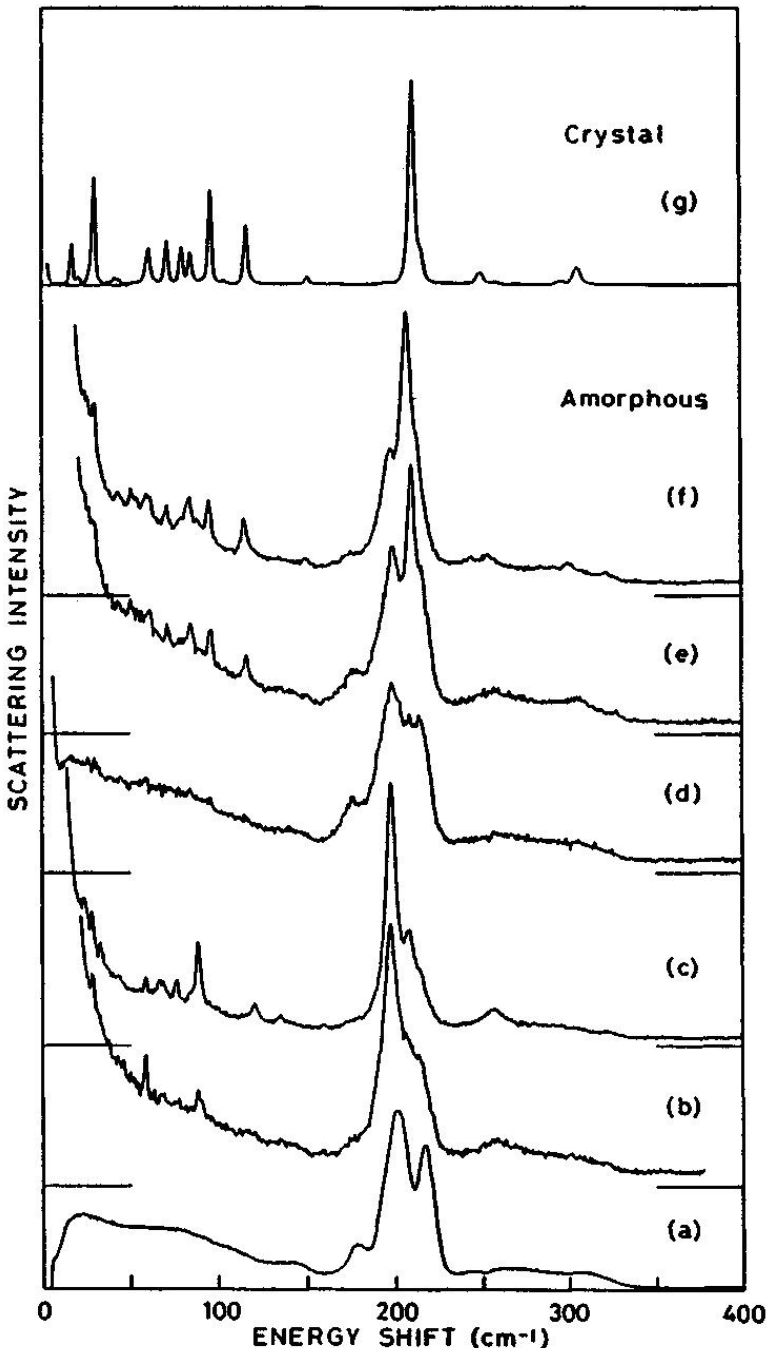


Fig. 1. The schematic view of condensed glass-forming substance relaxation processes: Tm is the melting temperature, Ttr is the polymorphic transformation temperature in crystal substance, Tg is the glass transition temperature, LTPM is the low-temperature polymorphic modification, HTPM is the high-temperature polymorphic modification.

As a result of disintegration of LTPM polymorphoids above Tg, the super-cooled liquid cooled with rate $V<V_{cr}$ (critical rate of cooling), at a certain time ceases to be nanoheteromorphous (with different structure on nanolevel) - only polymorphoids with one structure (HTPM) remain in it, and the liquid crystallizes. Similar process proceeds in glass at it annealing above Tg.

Annealing below Tg leads to disintegration of HTPM polymorphoids and its exothermic transformation into LTPM polymorphoids. This process results in LTPM crystallization. It is well illustrated by Inoue et al. [15] experiment, in which annealing of glass-forming film $GeSe_2$ at 425ºC that is above Tg (according to various data, Tg is below the range of 335... 392ºC [16]), leads to HTPM crystallization; annealing below Tg (at 325ºC), to LTPM crystallization.

Original analogue of Tg and its prototype - temperature of reverse polymorphic transformation (LTPM↔HTPM) Ttr in crystal substance - is the threshold power of light flow (LF) of laser radiation under its influence on a glass-forming film $GeSe_2$ [17] (Fig. 2). At LF of He-Ne-laser, being smaller than 0.7 kW/cm^2, the Raman-spectrum shows increasing concentration of LTPM fragments in the film. At LF greater than 0.7 kW/cm^2, the Raman-spectrum is an evidence of rising concentration of HTPM fragments [16]. In this experiment it was possible to crystallize a film in HTPM and in LTPM. Thus, in the course of photoradiation, it is evident the physicochemical essence of relaxing processes – mutual transformation of various PM polymorphoids is shown. (In brackets, we note that "comparison" of Tg (Ttr) with power of a light flow is certainly not correct. It is necessary to compare quantity of energy in glass-forming substance corresponding to temperature Tg (Ttr) with quantity of energy in the same substance at photoradiation with threshold power. Such comparison can lead to interesting practical and theoretical results).



In work [18], irradiation of a glassy film $GeSe_2$ with He-Ne laser of the same intensity at a temperature of 77 K resulted in film photodarkening - its reddening, i.e., approaching in color to red LTPM $GeSe_2$; at a temperature of 300 K, to photolightening, approaching in color to yellow-orange HTPM $GeSe_2$. In our opinion, the given experiment shows the synergetic effect of both light and heat (300 K) influence on the substance, that leads to its enthalpy increase to the level above the threshold Htr and visually in color (red - yellow) demonstrates the physicochemical essence of relaxation processes - mutual transformation of low- and high-temperature PM fragments in glass [16].

Fig. 2. The sequence of photoinduced crystallization of a-$GeSe_2$ (a) into two different structures according to the He-Ne lazer (6328Å) intensity below (b),(c) and above (d),(f) the threshold (~ 0,7 kW/sm^2) [17].

The ordinary glass transition temperature at melt cooling (Tg^-) is the temperature of the glass transition first stage termination (the α-relaxation according to the terminology of [19, 20]) and, conformably, temperature of the termination of the first stage of depolymerization process of a copolymer due to LTPM polymorphoid disintegration and their transformation into HTPM polymorphoids. Tg is also temperature of the beginning of the second (with an exothermic effect) stages of glass transition (the β-relaxation [19, 20]). HTPM polymorphoids of glass-forming copolymer break up below Tg and turn in LTPM polymorphoids, which is copolymerized with a glass. Transformation process of polymorphoids HTPM→LTPM is accompanied by the exothermic effect, which is registered, for example for Se, on a cooling curve by differential scanning calorimetry (DSC (Fig. 3)) [21].

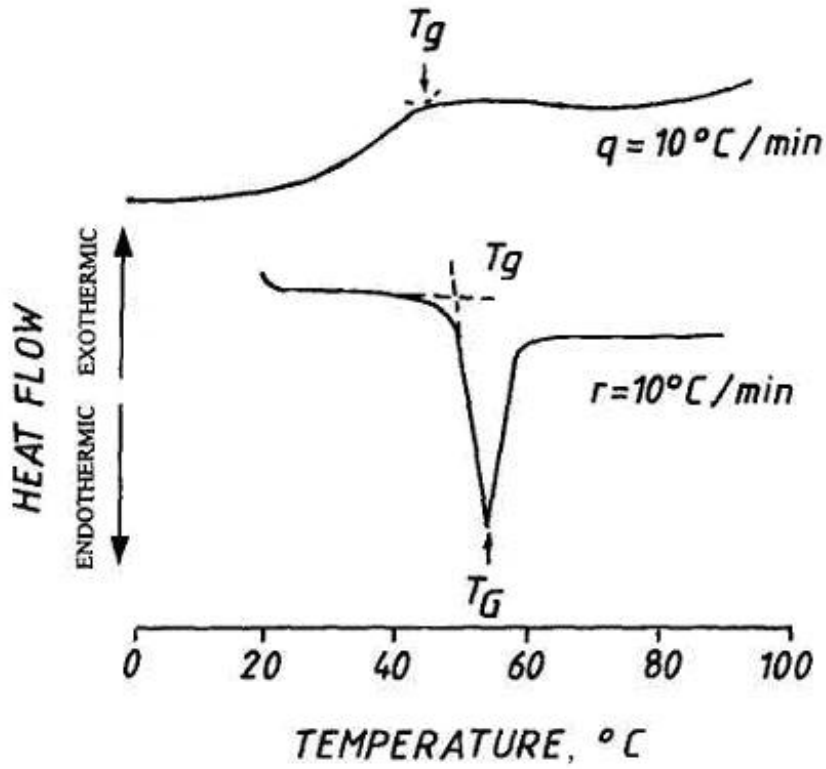


Fig. 3. Typical DSC heating and cooling scans of a-Se films: r = heating and q = cooling rate [21].

Occurrence of the same effect on differential thermal analysis curves of heated glasses is analyzed in [22] for Se, GeS_2, $GeSe_2$, and H_2O. The most informational experiment for the interpretation of relaxing processes in glass at Tg, and also above and below Tg, and, in particular, for the interpretation of the exoeffect below Tg, is the Ludwig's experiment [23] carried out more 30 years ago (Fig. 4), where three heating curves of glass As_2Se_3 with the same rate 3 °/minute are shown. Presented samples differ in melt cooling rate: 0.5 °/s, 10 °/s, and 20 °/s. The author specifies three features on DTA curves:

1) the exothermic effect before glass transformation range is the greater the higher the cooling rate is; the effect arises from the amount of heat liberated by the glass relaxation; 2) the shift of transformation area to a higher temperature at a reduction in the cooling rate; 3) at the end of the glass transformation interval, the enthalpy effect enhances due to increasing stability of glasses, as a result of more effective relaxation phenomena.

Our interpretation of the Ludwig's experiment in terms of polymeric-polymorphoid glass structures consists in the following.

At cooling of a glass-forming melt that contains a prevailing quantity of HTPM polymorphoids and also LTPM polymorphoids, in the range of temperatures below Tg, the transformation process of HTPM polymorphoids into LTPM polymorphoids proceeds. The slower the cooling is, the longer the stay of a cooled substance is in the interval of temperatures directly adjoining Tg, where most active process HTPM→LTPM proceeds, and the greater ratio of polymorphoids LTPM:HTPM is obtained. At the increase in the cooling rate by a factor of 20 (from 0.5 to 10 °/s) a significant amount of polymorphoids HTPM remains in glass; at the rate 20 °/s, much greater. Accordingly, enthalpy of the glass increases. At glass heating, the transformation process of HTPM→LTPM becomes more active. Exoeffect of this transformation is the greater the higher the ratio HTPM:LTPM in the alloy is, i.e., the higher the rate of alloy cooling is (rate of "overshoot" of the transformation area HTPM→LTPM).

The shift of the effect of glass transformation into the super-cooled liquid to higher temperatures with the reduction of cooling rate from 20 to 0.5 °/s can be explained by means of corresponding decrease in HTPM concentration, so both reduction of enthalpy in substance and late achievement of the level that necessary to start transformation LTPM→HTPM.

A last, the endothermic effect and its growth with reduction of cooling rate are connected with increasing LTPM polymorphoid quantity in the alloy, the polymorphoids formed in the course of the glass cooling below Tg, and, accordingly, with great endothermic effect of the LTPM→HTPM transformation.

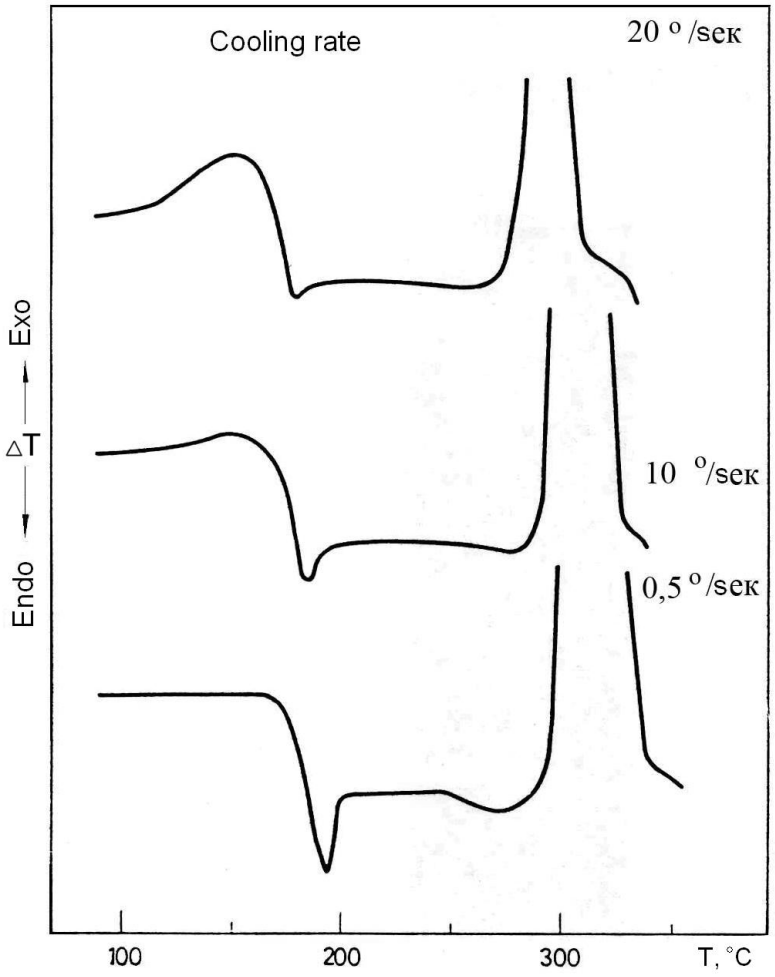


Fig. 4. Glass As_2Se_3 DTA curves depending on melt cooling rate [23].

The Ludwig's experiment shows once again that glass transition process at melt cooling tends to take place also below Tg where its viscosity is only $10^{12.3}$ Pa·s, that is less than the viscosity characteristic of a solid glass (10^{19} Pa·s) [12, p. 240].

Thus, glass heating goes up to Tg with disintegration of HTPM polymorphoids, which are unstable below Tg, and especially amplifies near to Tg. Broken up polymorphoids turn into LTPM polymorphoids and copolymerize with a glass great bulk. I.e. below Tg, as well as above Tg there is a uniform process of copolymerization-depolymerization of glass-forming substances.

The glass transition temperature at heating (Tg^{+}), to be exact, temperature of the beginning of glass transformation into the super-cooled liquid, is the temperature of termination of depolymerization with decomposition of HTPM polymorphoids, temperature of the beginning of an active endothermic stage of LTPM polymorphoid transformation into HTPM polymorphoids, accompanied by disintegration of LTPM polymorphoids, rupture of chemical bonds of glass, its depolymerization, reduction of viscosity, and transformation into the super-cooled liquid.

Depending on heating rate, the super-cooled liquid crystallizes as in the Ludwig's experiment [23] or (at a rate higher than the critical heating rate Vcr.h) above Tm turns in equilibrium glass-forming liquid.

3. Non-crystalline carbon (nc-C) and silicon (nc-Si)

Crystal carbon can exist in several polymorphic modifications: diamond; lonsdaleite; the phase characterized by cubic body-centered cell; graphite (hexagonal, rhombohedral, cubic), spherical versions of fullerene, varied in form of nanoparticles (the size from tens to hundreds nanometers): nanotubes, "bulbs", "necklaces", spirals, "tripods", fullerene-nanotubules, etc., carbine that exists in the form of cumulene $(= C = C = C = C =)_n$ and polyene $(- C \equiv C - C \equiv C -)_n$ chains (see the references in [4]). For diamond modifications, sp^3-hybridization of chemical bonds of carbon atoms is typical; for graphite and fullerene modifications, sp^2-hybridization; for carbine, sp-hybridization.

The model of a continuous random network of non-crystalline carbon that consists of atoms with sp^3-, sp^2-, sp- hybridization was proposed in work of Vang et al. (1993) [24]. In works of Popov et al. [25-28] levels of structural modifications of non-crystalline substances are investigated; in particular, electronographic research was carried out for non-crystalline carbon films obtained by ionic-plasma dispersion of a graphite target at various temperatures.

The technique of the radial distribution function analysis of non-crystalline carbon atoms proposed by the authors, based on Bellman-Zade algorithm [29], made it possible to estimate, for the first time, a percentage quantity ratio of atoms with sp^3, sp^2-, and sp-hybridization of chemical bonds in experimentally obtained carbon films (Table 1).

Table 1. Content of sp^n-components in the films of non-crystalline carbon obtained by ionic-plasma dispersion of a graphite target.

Wafer temperature, $°C$	sp^3, %	sp^2, %	sp^1, %
100	65	10	25
150	50	25	25
250	45	50	5
500	5	90	5

As we can see from Table 1, the content of the sp^n-components in the films changes in following limits: sp^3-component changes from 5 to 65%; sp^2-component, from 10 to 90%; sp^1-component, from 5 to 25%.

Films of non-crystalline carbon obtained in the given and other series of experiments differed depending on a concentration ratio of atoms with various hybridization of a chemical bond by huge distinction of properties. So, the width of an optical band differed by 2 orders of magnitude (from 0,02 eV for graphite-like films with the primary content of sp^2-bonds to 1.85 eV for films with prevalence of diamond-like structural units – sp^3-bonds, and dark conduction changes by more than 10 exponent parts (from 7 till $20 \cdot 10^{-10}$ $Om^{-1}cm^{-1}$) [25, 28].

The narrow line of 1332 cm^{-1} is typical for a diamond Raman-spectrum; for graphite, a narrow line of a stretch mode of 1581 cm^{-1}. Microcrystalline graphite exhibits the widened D-band of 1355 cm^{-1} (a diamond band - Diamond) and the widened G-band of 1580 cm^{-1} (a graphite band - Graphite). The band widening is explained by the authors as a deviation from well-ordered diamond and graphite structures [30, 31].

Up to 90% of fraction of diamond structural units (sp^3 -hybridization) were registered in a film of so-called diamond-like carbon - "an amorphous material without long-range crystallographic order" [32] obtained by a thermoionic vacuum-arc (TVA) method of carbon rod (anode) spattering. The sp^3 / sp^2 hybridized chemical bond ratio was defined here according to X-ray photoelectronic spectroscopy (Fig. 5).

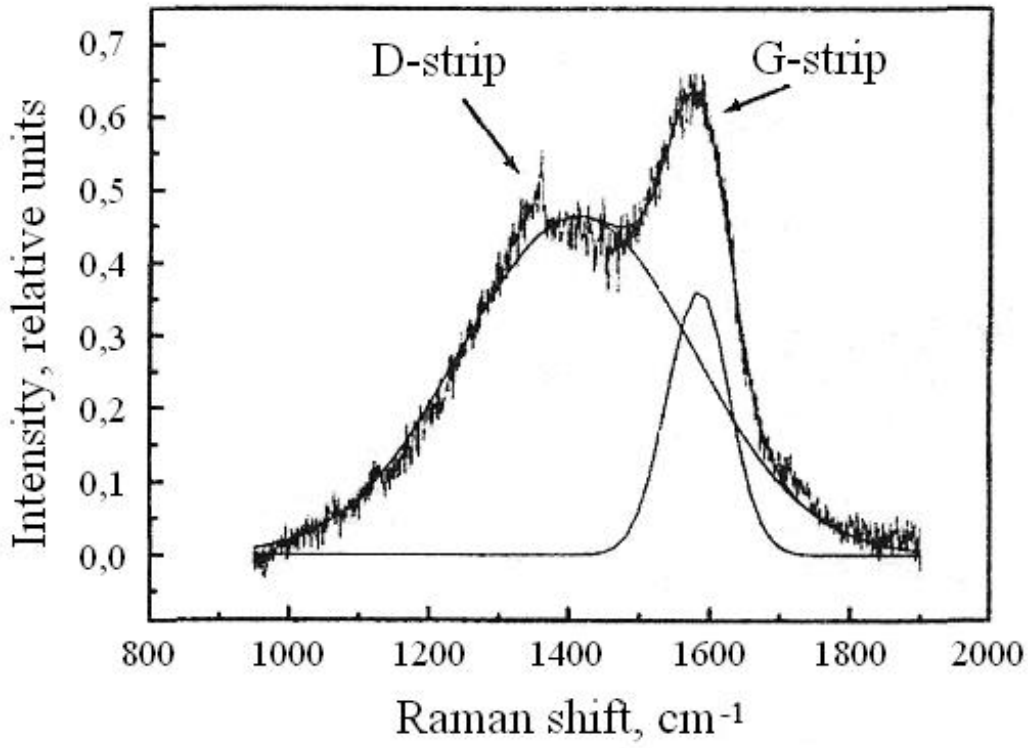


Fig. 5. The Raman spectrum of films of the non-crystalline diamond-like carbon obtained by the thermo-ionic vacuum-arc method. The Gaussian distribution is shown for the D- and G-bands [32].

Works [30, 31] present the dependence of the intensity ratio I_D/I_G D- and G-bands of the Raman-spectrum from the sizes of graphite nanocrystals, lying within the range 3-300 nanometers, which was defined according to dispersion of X-rays. As the degree of dispergation increases, the I_D/I_G ratio grows from ~0.02 to ~1.0. The dependence reflects the increase in content of diamond polymorphoids at the increase in dispersion of a substance, i.e., actually

registers the transformation process at dispergation of the crystal substance (graphite) in the non-crystalline substance (nc-C) that consists of both PM polymorphoids of carbon.

Thus, different ways (different conditions) of preparation of non-crystalline films cardinally (from 90% sp^2 to 90% sp^3) change the concentration ratio of polymorphoids of various carbon modifications.

Deep dispergating of carbon is a major factor and the main reason of formation of diamond nanofragments (polymorphoids) from atomic carbon or from it graphite-like nano-parts at low temperatures and normal pressure.

Crystal silicon can exist at various temperatures and pressures in 8 (eight) various crystal polymorphic modifications [33-35]. Apparently, for the first time, the possibility of phase polymorphic transformation in silicon in the temperature area of plasticity appearance was hypothetically considered by Stepanov (1947) [36]. In 1972 Eremenko and Nikitenko [37] found out, around temperatures 350-650ºC, overlapping with plasticity area (≥ 600ºC), at indentor pressing, layers of a new phase of silicon with hexagonal structure and parameters a = 3.86 and c = 6.31 Å.

On the basis of the analysis of experimental dependences of lengthening, linear expansion factor, and electric properties from temperature, as well as the differential thermal analysis, in work of Glazov et al. (1991) [35], the possibility of existence of phase transformation sequence with participation various PMs in a temperature interval 523-1673 K is emphasized: face-centered cubic $\xrightarrow{523-593K}$ rhombic $\xrightarrow{593-803K}$ hexagonal II $\xrightarrow{803-943K}$ double hexagonal II $\xrightarrow{943-1473K}$ body-centered tetragonal $\xrightarrow{1473-1673K}$ body-centered cubic lattices. A new rhombic PM was found in this work.

The films of non-crystal silicon received by sublimation method in vacuum in works of Mashin and Khokhlov (1999) [38, 39] had coordination number (CN) of silicon atoms 3.8. As a result of annealing at 450ºC, CN decreased to 3.6; at 500ºC-annealing, to 2.8, with respective reduction of distances between atoms from 2.33 Å to 2.31 Å and 2.15 Å. Authors come to a conclusion that at annealing the structural reorganization, leading to formation of a disorder network of sp^2 -atoms, is observed. The plasticity of amorphous silicon at annealing temperatures contributes to this process. At hydrogenated silicon annealing, the authors obtained amorphous silicine (analogue of chained carbine) with CN ~2.2 ± 0.2 with a great mass of atoms in sp^1-hybridized state.

The mentioned facts show that non-crystalline silicon is formed when incomplete polymorphic transformations of various PMs occur in it. As a result of these transformations, there takes place copolymerization of formed polymorphoids with different structure whose concentration ratio changes strongly depending on conditions of experiment.

In our opinion, in a certain temperature interval, the most intensive the polymorphic transformations, which are accompanied by rupture of chemical bonds in polymorphoids of some PMs and formation of new bonds in polymorphoids of other PMs, are the reason of plasticity of crystal and non-crystalline silicon. The temperature of the beginning of the plasticity interval is an original analogue of glass transition temperature (softening) of a substance, which is in the glassy state.

Alternation in the formed non-crystalline substance of copolymerized various PM polymorphoids with CN of silicon atoms 4 (chemical bond sp^3-hybridization), and also polymorphoids with graphite-like structure with CN=3 (sp^2-hybridization) and chained structure (=Si=Si=Si=Si= or -Si≡Si-Si≡Si-) with CN=2 (sp^1-hybridization), is a physicochemical basis of existence of non-crystalline silicon.

4. Summary

Glass-forming (SiO_2, GeO_2, H_2O, Se, $GeSe_2$, $SiSe_2$, and $BeCl_2$) and non-glass-forming (C, Si) non-crystalline substances are formed by the copolymerization of fragments of the various polymorphic modifications that arise at fusion, deposition of a gas phase, sputtering or dispersion of the crystal substance, etc., and do not have a long-range order (polymorphoids). Nanoheteromorphism and nanoheteromorphous (with different structure on nano-level) copolymerization are the necessary and sufficient condition of non-crystalline substance formation. The physicochemical essence of relaxation processes in non-crystalline substances, resulting from external influences and time (t), is interconversion of various PM polymorphoids, changing their concentration ratio in the substance and, consequently, structure and properties of the non-crystalline substances.

References

[1] N.S. Kurnakov, Introduction in the physicochemical analysis, Moscow-Leningrad, Akad. Nauk SSSR, 560, 1940.
[2] I.V. Tananaev, Bull. Akad. Nauk SSSR, 2, 21-29, (1972).
[3] V.S. Minaev, Glass-forming semiconductor alloys, [in Russian], Moscow, Metallurgiya, 406, 1991.
[4] V.S. Minaev, I.M. Terashkevich, S.P. Timoshenkov, V.V. Kalugin, and S.N. Novikov, J. Optoelectron. Adv. Mater., 9, 10, 3253, (2007).
[5] V.S. Minaev, in Semiconducting Chalcogenide Glass. Glass Formation, Structure and Stimulated Transformation in Chalcogenide Glasses – Semiconductors and Semimetals, 78, Eds. R. Fairman and B. Ushkov, Elsevier – Academic Press, Amsterdam – Boston – London, 139-179, 2004.
[6] W.H. Zachariasen, J. Amer. Chem. Soc., 54, 10, 3841, (1932).
[7] M.I. Kaganov, in Physical Encyclopedic Dictionary, [in Russian], ed. A.M. Prokhorov, Moscow, Sov. Entsikl., 633-634, 1984.
[8] Y. Yue, XXI Int. Congr. on Glass (Abstracts), Strasbourg, 199, (2007).
[9] V.I. Lithman, Brief Chemical Encyclopedia, Moscow, Sov. Entsikl., 4, 194-196, 1967.
[10] A. Feltz, Amorphe and glasartige anorganische Festkorper, Academic – Verlag, Berlin, 460, 1983.
[11] G.Z. Vinogradova, Glass-formation and phase equilibriums in chalcogenide systems. Binary and ternary systems, Nauka Publishers, Moscow, 176, 1984.
[12] S.V. Nemilov, in Physicochemical basis of the optical glass production, [in Russian], Ed. L. Demkina, Leningrad, Khimiya, 235-250, 1976.
[13] A. Winter-Klein, Verries et refract, 7, 217, (1953).
[14] S.V. Nemilov, Zh. Fiz. Khim., [in Russian], 43, 6, 1433, (1969).
[15] K. Inoue, O. Matsuda, and K. Murase, Solid State Comm., 79, 905, (1991).
[16] V.S. Minaev, J. Optoelectron. Adv. Mater., 3, 233, (2001).
[17] S. Sugai, Phys. Rev. Lett., 57, 4, 456, (1986).
[18] A.V. Kolobov, B.T. Kolomiets, V.M. Lubin, N. Sebastian, and M.A. Tagirjanov, Fiz. Tverd. Tela, [in Russian], 24, 1062, (1982).
[19] G.M. Bartenev, V.A. Lomovsky, and G.M. Sinitsina, Neorg. Mater., [in Russian], 32, 6, 754, (1996).
[20] G.M. Bartenev and D.C. Sanditov, Relaxation properties in the glass forming systems, [in Russian], Novosibirsk, Nauka, 238, 1986.

[21] S.O. Kasap, B. Polischuk, V. Aigah, and S. Yannacopoulos, J. Non-Cryst. Solids, 114, 49, (1989).
[22] V.V. Kalugin, V.S. Minaev, S.P. Timoshenkov, and E.N. Markova, J. Optoelectron. Adv. Mater., 8, 6, 2086, (2006).
[23] W. Ludwig, J. Thermal Analysis, 8, 75, (1975).
[24] C.G. Wang, K.M. Ho, and C.T. Chan, Phys. Rev. Lett., 70, 5, 611, (1993).
[25] A.I. Popov, V.A. Vorontsov, and I.A. Popov, Physics and technique of semiconductors, [in Russian], 35, 6, 665, (2001).
[26] V.A. Vorontsov, Structural modification of amorphous hydrogenous carbon properties, Cand. Sci. Dissertation, Moscow Energetics Institute, [in Russian], 2001.
[27] A.I. Popov, J. Optoelectron. Adv. Mater., 4, 3, 347, (2002).
[28] S.N. Stukach, Interrelation of atom structure, morphology and properties of hydrogenous films of carbon, Cand. Sci. Dissertation, Moscow Energetics Institute [in Russian], 1996.
[29] L. Zadeh, Fuzzy Sets and Systems, 11, 3, 199, (1983).
[30] P. Milani and C.E. Bottary, Vibrational Spectroscopy of Mesoscopic Structure, in Handbook of Nanostructural Materials and Nanotechnology, 2, Spectroscopy and Theory, ed. H.S. Nalwa, Academic Press, San Diego, Chapter 4, 2113, 2000.
[31] Ch. Pul and F. Ouens, Nanotechnologies, [in Russian], Moscow, Tekhnosfera, 336, 2005.
[32] G. Musa, I. Mustata, V. Ciupina, R. Vladoiu, G. Prodan, C.P. Lungu, and H. Ehrlich, J. Optoelectron. Adv. Mater., 7, 5, 2485, (2005).
[33] E.Yu. Tonkov, Phase diagram of elements under high phase, [in Russian], Moscow, Nauka, 190, 1979.
[34] P. Pirouz, U. Dahmen, K.H. Westmaccot, and R. Chaim, Acta Metall. Mater., 38, 2, 329, (1990).
[35] V.M. Glazov, V.B. Kol'tsov, A.R. Regel, Yu.N. Taran, G.G. Timoshina, K.Y. Uslov, and E.S. Falkevich, Fiz. Tekh. Poluprovodn., [in Russian], 25, 4, 588, (1991).
[36] A.V. Stepanov, Zh. Exper. Teor. Fiz., 17, 713, (1947).
[37] V.G. Eremenko and V.I. Nikitenko, Phys. Stat. Sol. (a), 14, 317, (1972).
[38] A.F. Khokhlov, A.I. Mashin, and D.A. Khokhlov, Pis'ma Zh. Eksp. Teor. Fiz., 67, 9, 646, (1988).
[39] A.F. Khokhlov and A.I. Mashin, J. Optoelectron. Adv. Mater., 4, 3, 523, (2002).