

277. Diagnostics of nano-particles on a surface and in volume of a solid body

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Abstract. In this research work the results of change of In, Sn, Bi, Pb nano-layers melting temperature on a surface and in Al and Ge matrixes depending on thickness and interaction character of components by methods of electron microscopy and x-ray diffractometry are presented. Layered film systems Al-Me-Al, Ge-Me-Ge (Me = Pb, Sn, Bi, In) were the object of researches. The purpose of work was the research of the general law of noted systems melting depending on the specific size and conditions of their formation. Layered film systems prepared by consecutive condensation of components in vacuum and their evaporation from independent sources. The film microstructure before and after melting was investigated by method of electron microscopy. The structure and phase composition of film systems defined using x-ray diffractometry. Melting temperatures and specified eutectic temperatures for In, Sn, Bi and Pb binary systems with aluminium and germanium registered by differential method. It is shown, that for layered film systems Al-Me-Al, Ge-Me-Ge (Me = Sn, Bi, Pb, In) eutectic temperature decreases with reduction of thickness of Me film. The urgency of the work is caused due to necessity of understanding the physics of processes in nano-systems, and wide use nano-objects in modern technologies.

Keywords: nano-layer, film, size effect, eutectic temperature

1. Introduction

Features of films phase composition and structure, and also unique physical and chemical properties of nano-particles, which are not found out for macroscopical objects, cause the interest of researchers to nano-objects. Therefore the decrease in melting temperatures, evaporation and polymorphic transformations in small particles, the change of parameter of a lattice, the mechanical, electric and magnetic properties, and their raised catalytic activity is established. It is necessary to remember also quantum dimensional effects (for example, resonant effect, electron tunnelling, Josepson quantum effect, magnetic quantum effects, etc.) in the particles, when their value become equal with such parameters of conduction electrons, as De Broglie wavelength of electrons on Fermi surface, a mean free path, coherence length, etc.

All these features give a possibility to create new materials and devices on the nano-objects basis. Using also methods of "zonal engineering" and "wave function engineering" it will be available to design quantum-sized structures (quantum holes, quantum conductors and points,

structures with tunnel-transparent barriers, photon crystals, etc.) with the particular electronic spectrum and necessary optical, electric, antifricition and other properties.

Therefore such structures are very attractive to instrument making. For example, it is possible to develop modern transistors with the sizes about 1 nanometer (the one-electronic transistor on nano-cluster), quantum dot lasers, magnetoresistance effect devises with thickness of layers in some nanometers. Due to extreme sensitivity of such sizes nano-objects to preparation conditions during their production it is necessary to supervise huge quantity of physical and technological parameters, such as structure and a material of substrate, its temperature, working pressure and composition of residual gases, sedimentation speed, etc. For manufacturing of film with particular structure and state these parameters mostly selected empirically. It is natural, that the subsequent development, the creation or use of nano-based materials is impossible without precise understanding of processes and the phenomena that occur in such structures. One of the important factors which are directly related with processes of condensation is the dependence of crystal-liquid phase transition temperature on the particles size. Experimental

data corroborate that melting temperature of particles on amorphous substrate and partially continuous film decrease with reduction of their typical size. The special attention of researchers and technologists is focused on the behaviour of nano-objects embedded in a solid-state matrix. It is caused by perspectives of practical application of such materials (the aluminium designs strengthened by nano-sized inclusions of other component; amorphous materials; thin-film and heterostructural components of microelectronics and optoelectronics of following generation, soft magnetic and hard magnetic materials, the integrated microelectromechanical devices, electric accumulators, energy converters, etc.).

There are different data about sign and value changes of melting temperature of small particles in a matrix from reduction of their sizes: from decrease to increase for the same materials in the same matrix. At such ambiguity of experimental data it is heavy to define, when fusion is caused by the small typical size, and when by other reasons, for example, processes that occur on a particle - matrix interface, which define a degree of components interaction. It is important to note, that offered thermodynamic approach [1] for a case when nano-particles are embedded in a solid-state matrix, collides with contradictions. This specifies the necessity of the subsequent research of new approaches for evaluation of law, which defines properties of nano-objects embedded in a solid-state matrix.

2. Problem description

2.1. Phase size effect

Due to the rapid development of microelectronics and nano-technologies the interest to research of structure and properties of different substances nano-objects in the form of small particles and thin film, both free and that are on different substrates or in any matrix, usually with highest melting temperature has essentially grown. Changes of such objects structure and physical properties are revealed during their investigation. Among results of a phase condition researches the significant data is cumulated about nano-objects melting temperature changes in comparison with melting temperature for massive samples. Presently it is unequivocally shown, that the melting temperature of free particles in vacuum or on a neutral amorphous substrate decreases with reduction of their size [2, 3]. Similar results are received and for thin films [4, 5]. For an explanation of the received results the [1] thermodynamic approach offered almost hundred years ago, which based on the valuation of the surface energy role, is widely used. By means of such approach in work [6] it is shown, that generally for small samples with the typical size d (diameter of a particle or a thin filament, film thickness) relative change of melting temperature is defined by equation:

$$(\Delta T/T_0) = (\Delta\Omega/\lambda)(k/d), \quad (1)$$

where $\Delta\Omega$ – changes of surface energy on the border with vacuum or environment at phase transition, λ – heat of phase transition, $\Delta T = T_0 - T$, where T – phase transition temperature for small size samples, T_0 – phase transition temperature for macroscopic objects, k – form coefficient equal to 6, 4 и 2 for particle, thin filament and film respectively.

From this equation it is obvious, that the value and a sign of the change of relative melting temperature is defined by dimension $\Delta\Omega$, which depends on environment in which there is a small sizes sample (for example: vacuum, vapour, solid or liquid environment). In work [6] it is shown, that if the sample is in vacuum or in "not wetted solid-state matrix", then at melting $\Delta\Omega = \sigma_s - \sigma_l$ (σ_s and σ_l – specific surface energy of solid and liquid phases accordingly) and $(\Delta T/T_0) > 0$, i.e. decrease of melting temperature with reduction of the typical size in comparison with melting temperature T_s of massive samples is observed. The second limiting case corresponds to full "wetting" by substance of the solid matrix sample, for which $\Delta\Omega = -(\sigma_s - \sigma_l)$ and $(\Delta T/T_0) < 0$, i.e. the melting temperature raises with reduction of the size. Experimental researches of small particles, island structures and continuous films of some metals (Ag, Cu, Al, Pb, Bi, In, Au), received by different methods, shows that the melting temperature of such objects decreases with reduction of their size [4, 7-10]. Also for dispersed particles of Al and Pb, surrounded by its own oxides, the melting temperature rise is observed [11]. So for particles with size 250 Å according to X-rays diffraction data, this increase equal for Al – 180 °C, and for Pb approximately 53 °C. Thus, the thermodynamic approach and available experimental data testify about presence of phase size effect, i.e. about change of nano-objects melting temperature with reduction of their sizes, both aside decrease and aside increases.

2.2. Changes of melting temperature in systems with nano-objects

2.2.1. The decrease of melting temperature in condensed films on different substrates

The first quantitative data about decrease of melting temperature have been received in work [12]. Dependences of relative change of bismuth and tin particles melting temperature T/T_s depending on their diameter D are presented in Fig. 1. In the same figure the research results of indium and lead particles melting are presented [8, 10]. In works [8, 10, 13] melting of particles was registered by diffractometry, and the particles size and their form were defined by electron microscopy. In [8, 10] it noted, that melting temperatures of identical size particles, which are on carbon and silicon monooxide, practically coincide. It is related, obviously, that the crystal spherical particles prepared by the melting of condensate, have the small contact area to a surface, and practically are same on noted substrates (due to affinity of values of wetting angles). Recently for research of nano-objects more perfect methods of supervision of particles behaviour at phase transitions, such as: a method of blackfield electron

microscopy, high-resolution electron microscopy, differential calorimetry and method of the backward Rutherford's dispersion, etc. are developed.

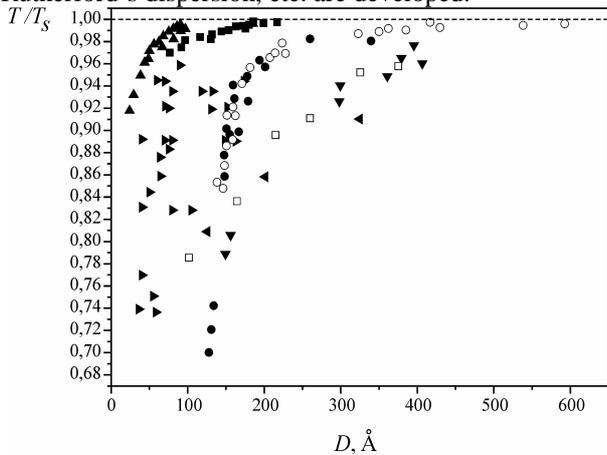


Fig. 1. The dependence of particles size on their melting temperature. For ■ – Sn [12], ▲ – Bi [12], ● – Pb [10], ▼ – In [10], □ – In [10], ◀ – In [13], ▶ – Pb [14] on C substrate; ○ – Pb [10] on SiO substrate

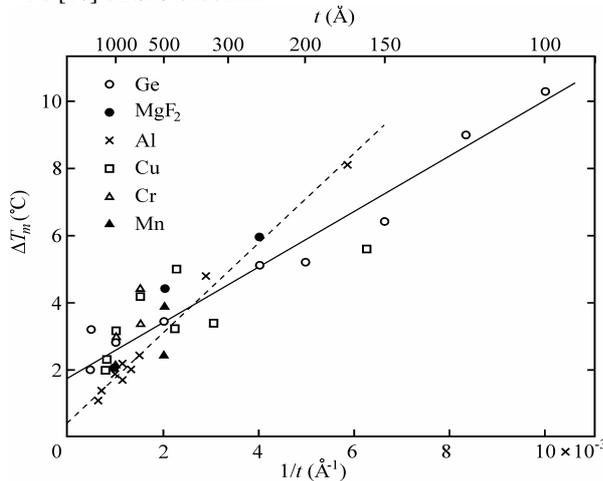


Fig. 2. The decrease of melting temperature for Pb films depending on their thickness. Different points correspond to different materials of substrate. Continuous and dotted lines corresponds to Pb/Al and Pb/Ge systems

So, in later work [14] fusion behaviour of Pb small particles (diameter less than 10 nanometers) were investigated in situ by methods of high-resolution electron microscopy. Particles of lead prepared directly in an electron microscope (JEM-2000 FXV) in vacuum $1 \cdot 10^{-7}$ Pa on an amorphous carbon substrate. Experimental results have shown, that particles of lead of noted sizes begin to melt already at 180 °C (Fig. 1) while the melting temperature of massive lead makes 327.3 °C. Using method of calorimetric measurements in work [15] researches of neutral isolated tin clusters with the size about 500 atoms have been carried out. The method is based on application of piroelectric foil as temperature sensor [16, 17]. Neutral tin clusters of such size were generated by methods of a molecular bunch. These experiments testify to decrease of melting temperature of

Sn particles on 125 °C. Melting of nano-sized indium islands on WSe₂ substrate was investigated in work [18] with use of the indignant angle correlations in connection with scanning tunnel microscopy. Indium was deposited on WSe₂ monocrystal with a speed from 0.14 up to 0.28 nanometers/sek at substrate temperature 300 and 193 K in vacuum 10^{-8} Pa. Deposited islands represented nano-sized structures about 5 and 100 nanometers diameter, depending on sedimentation conditions. The decrease of In nanoislands melting temperature with reduction of their size is revealed. The decrease of melting temperature in uncontinuous indium films with thickness 0.1 – 100 nanometers on an amorphous silicon nitride substrate are informed also in work [19]. Films were investigated by methods of ultra sensitive thin-film scanning calorimetry. Decrease of melting temperature for particles of 2 nanometers radius made more than 110 K. The effect of melting temperature decrease with thickness reduction is observed and for continuous films. So, in work [20] are obtained the quantitative data about dependences of melting temperature on thickness of bismuth films on different substrate: glass, mica and (001) NaCl side. It was found, that the melting temperature of films appears various on different surfaces. This is caused by influence of surface energy changes, and also is consequence of differences in film structure, deposited on different substrates or under different conditions of condensation. The last influences on a surface relief of the film, and also on the average size of liquid drops that are formed after melting.

2.2.2. Reduction of melting temperature in layered film systems

The first observation of liquid-crystal phase transition in three-layer films were obtained in work [21]. Investigated multilayer film system homogeneous Pb film with 2 nanometers thickness, positioned between two amorphous Ge films, has been taken. Three-layer Ge/Pb/Ge film were prepared by vacuum thermal evaporation, on a substrate from fresh KCl monocrystal surface at temperature 77 K. Film were studied by method of an transmission electron microscope (TEM Philips EM 300). The lead particles size in such layered system was in the range from 2.5 up to 25 nanometres. The range of phase transition, which was registered on change of particles image intensity in a black field of an electron microscope, was a constant and made nearby 40 K. The full melting of a lead film occurred at 40 K less temperature than melting temperature of massive Pb. The experimental observation results in work [22] adequate with the results described in work [21]. The decrease of melting temperature of thin Pb films with thickness from 10 up to 100 nanometers, condensed on different materials (Ge, Mg₂, Al, Cu, Cr, Mn), was observed and in work [23]. Researches by methods of differential scanning calorimetry and by in situ annealing in an electron microscope were performed. Layered film systems prepared in vacuum 7×10^{-7} mm mercury column, and the general thickness of investigated system made about 200

nanometers. It is shown, that for all materials used in a role of a matrix, melting temperature of thin Pb films decreases with reduction of their thickness (Fig. 2).

2.2.3. Melting temperature of nano-particles in matrixes

Recently due to arisen qualitatively new theoretical and practical problems in the nano-physics and nano-technology fields huge interest is caused by systems where fusible component is embedded in more refractory matrix. In practice such dispersions get by different methods (implantation, vacuum condensation, mechanical crushing with hashing and the subsequent pressing and sintering). Thus researchers the greatest attention paid on systems in which components are in the particles form and compose a matrix. For such systems the diagram is with practically full absence of solubility in a solid state and at presence of significant area of stratification in a liquid state. Such systems make the interest for fundamental researches due to different practical applications, especially for the nano-technology purposes [24]. First of all, the creation of new composite materials with the raised durability and weightlessness, elasticity or hardness, and also electric, magnetic and optical properties (for example, metal rubber, materials for superdense record of the information, active elements for superpower lasers, etc.), is necessary both in the heavy industry and for electronics, medicine, biology and energetics. Probably, first observation of melting temperature changes depending on the nano-particles size, embedded in a solid-state matrix, has been performed in work [25]. Authors investigated melting of In particles with radius less than 20 nanometers in Al matrix. The dispersion of inclusions was reached by fast quenching of Al-In at % 4.5 alloy from pure components (99.999 %). Applying the method of electron microscopy it has been revealed the epitaxy between an aluminium matrix and In particles, and it also is established, that melting temperature of inclusions in an aluminium matrix raises with reduction of their size. Similar melting result of (1 - 20 microns) In particles embedded in an aluminium matrix, obtained in work [26]. Samples of alloy Al-In wt % 16 In prepared by induction fusion of pure components (99,999 %). By the method of differential scanning calorimetry it has been established, that the In particles embedded in grain of aluminium matrix, melted with an overheat about 4 K whereas particles between grains, have melting temperature equal to melting temperature of massive. Authors [26] relate such melting behaviour of inclusions with stress-energy raise due to increase of particles volume during melting. Melting of In nano-particles embedded in Al matrix was observed also in work [27]. In particles were embedded (100-250 keV In⁺) in (110) monocrystal of aluminium in vacuum 10⁻⁵ Pa. By method of the backward Rutherford's dispersion it has been established, that fine In particles with 4 nanometers radius melted at highest temperature than particles with radius of 40 nanometers. The greatest overheat of In nano-inclusions made 23 K ($r = 4$ nanometers). In works

[28, 29] the changes of In and Pb nano-particles in Al matrix melting temperature depending on dispersion preparation method also was investigated. Nano-sized In inclusions in Al matrix created in two ways: fusion or mechanical crushing. In the first case composite alloys Al-In wt % 7 and Al - Pb wt % 10 prepared by arc fusion of pure Al (99,999 %) with In and Pb in water cooled crucible and argon atmosphere. In the second case samples prepared by mechanical crushing of pure Al, In and Pb powders with particles size less than 25 microns. Prepared samples were investigated by method of x-ray diffractometry, x-ray spectroscopy, electron microscopy and also diffraction scanning microscopy. Experimental data [28, 29] on research of the samples prepared by fusion have shown, that the average size of In and Pb particles was in a range 5 - 45 nanometers. It has also been established, that indium and lead has oriented parity with an aluminium matrix which can be described as (111)_{Al} || (111)_{In,Pb} and [110]_{Al} || [110]_{In,Pb}. Particles of inclusions represent the truncated octahedrons limited (111)_{Al} и (100)_{Al} sides of a matrix. By method of high-resolution electron microscopy it has been obtained epitaxy between the embedded particles and an aluminium matrix. Research of the samples prepared by mechanical crushing, has shown, that the particles size decreases with increase of crushing time. In this case the sample represents a nano-sized mix of pure aluminium and indium phases. Any fusion effect has not been established even at very small sizes of grains. During research of both kinds samples by differential scanning calorimetry in work [28] it has been established, that in case of components fusion the In and Pb nano-particles melted above typical melting temperature of a massive on 0 - 38 K, 11 - 40 K accordingly; while in case of mechanical crushing there is a decrease of In inclusions melting temperature on 0 - 22 K, and for Pb an average on 13 K. Rise of lead nano-particles melting temperature in different metal matrixes (Al, Cu, Ni) has been observed in work [30]. Nano-sized Pb dispersions have been prepared by quenching of corresponding alloys in the compound Al-Pb at % 1.4, Cu-Pb at % 3.2, Ni-Pb 3 at. % Pb. The electronic-microscopic researches have shown [30], that particles Pb epitaxially grown with Al and Cu matrixes, and are monocrystals with the form of the truncated octahedrons with (111) and (100) faces. While in Ni matrix the particles had the form of the truncated octahedrons with the smoothed corners. The particles sizes were in the range of 10 - 70, 25 - 210 and 30 - 120 nanometers for Al, Cu and Ni matrixes accordingly. Melting of such particles was studied by scanning differential calorimetry. For Al and Cu matrixes have been established overheat of particles on 103 and 125 K accordingly, whereas for Ni - no rise of nano-particles melting temperature has been fixed. Authors [30] found an overheat of nano-particles relate with the form of particles, i.e. with epitaxial system in case of Al and Cu matrixes. Bi nano-particles embedded in quasicrystalline matrix on the basis of aluminium alloy were investigated in work [31]. Alloy Al₆₅Cu₂₀Fe₁₅ performed by method of pure metals melting in an argon

atmosphere in the electroarc furnace. Bi particles have been embedded by fusion of Bi 10 wt % with matrix, and the average size of particles made about 50 nanometers. Features of fusion were studied by methods of differential scanning calorimetry and transmission electron microscopy. The Al-Cu-Fe matrix depending on annealing temperature gives different properties: at heating above 1073 K the matrix was quasicrystalline, and at temperature 873 K obtained the properties of a microcrystalline matrix. In work [31] has been shown, that melting of Bi nano-particles embedded in Al-Cu-Fe matrix strongly depends on structure of matrix. So, for isocahedral matrix the significant changes of bismuth melting temperature it was not observed, but the small part of inclusions (about 15 %) melted at 553.5 K and was observed coherence of a particle-matrix interface. Thus rise of melting temperature on 9 K above melting temperature for a solid is established. In microcrystalline matrix decrease of melting temperature approximately on 30 K has been fixed. Change of Bi inclusions melting temperature embedded in glassy and crystalline matrix it was investigated also in work [32]. The matrix represented an alloy on the basis of aluminium $Al_{65}Fe_{20}Si_{15}$. In case of a crystalline matrix the rise of Bi nano-particles melting temperature, unlike data received in work [31], it was not observed, and also it was not observed any coherence on a particle-matrix interface. For glassy amorphous matrix decrease of melting temperature has been fixed and for Bi particles with the size it has made about 5 nanometers nearby 100 K. In work [33] decrease of melting temperature of In nano-particles embedded in Al matrix was marked. Samples prepared by mechanical mixing of In and Al powders [34] in the range Al -In wt % 10 and further were investigated by electron microscopy, x-ray diffractometry and scanning calorimetry. It has been established, that the In nano-particles melting temperature decreases with increase of powders crushing time, i.e. with reduction of In particles size. So for In nano-particles with average size 15 nanometers authors obtain decrease of melting temperature in comparison with melting temperature of solid on 13.4 K. According to decrease of melting temperature in work [33] the wetting angle between In and Al surfaces makes $\theta \approx 124^\circ$. Authors relate such behaviour of In nano-particles with plump into powders mix during mechanical crushing impurities of iron and oxygen, and also influence of stresses after crushing. Using the method of differential scanning calorimetry a lot of fusible metals (In, Sn, Bi, Pb) embedded in Al matrix are investigated in work [24]. Nano-sized In, Sn, Bi, and Pb particles have been homogeneously embedded in an aluminium matrix by mechanical crushing of pure powders mix. It has been established, that the melting temperature of the embedded particles is much less concerning values for massive samples [24], and decrease of melting temperature is inversely proportional to the embedded particles size. In other work [35] melting of lead nano-particles embedded in amorphous and crystalline matrix from alloy $Al_{75}Cu_{15}V_{10}$ was investigated. Composite alloy $Al_{75}Cu_{15}V_{10}$ prepared by melting of pure components in

the induction furnace in an argon atmosphere. Depending on annealing temperature the alloy was amorphous or it had a crystalline structure. Then the alloy was alloyed with 10 wt % pure Pb for embedding of a fusible component in Au-Cu-V matrix. As a result of the researches [35] have found, that lead particles with the average size about 30 nanometers melted at temperature below melting temperature of a solid on 17 K in an amorphous matrix and on 6 K in crystalline. In work [36] also it was explained about particular decrease of Pb nano-particles in Al matrix melting temperature. Research objects are prepared by crushing of pure Pb and Al granules. Variation of Pb melting temperature was investigated by x-ray diffractometry and differential scanning calorimetry. The change of melting temperature of Sn nano-particles embedded in Al matrix was investigated in work [37]. Embedding of tin was reached by ionic implantation of Sn^+ in Al in situ matrix in an electron microscope. Prepared samples were investigated by the method of electron microscopy and the method of the backward Rutherford's dispersion. Researches have shown that the average size of Sn nano-particles embedded in Al matrix made approximately 6 nanometers. In work [37] after annealing in it has been obtained, that melting temperature of tin nano-particles embedded in an aluminium matrix decreases with reduction of their size. Decrease of melting temperature for In nano-particles embedded in Fe matrix by method of in situ heating in an electron microscope has been established and in work [38]. Samples of iron (99,999 %) with In inclusions with the size about 50 nanometers prepared by quenching of melt Fe - In wt % 7. After annealing of such samples decrease of In fusion temperature on 15 K below melting temperature of a solid ($T_s \approx 429$ K) has been established. Apparently from the above-mentioned for nano-particles embedded in a solid-state matrix it is observed both increase and decrease of melting temperature in comparison with values for massive samples. And the increase observed for In, Pb, Bi particles takes place, as a rule, in case of epitaxial connection with a matrix. In an opposite case the decrease of melting temperature is observed.

3. Technique of research

3.1. Research objects

Thin film of In, Pb, Sn, Bi metals that are between two thick Al or Ge films, which play a role of matrix research objects have been selected as object for researches. Such choice is caused by following circumstances. For free particles, for islands and partially continuous condensed films from these metals there are quantitative data about particular reduction of melting temperature [39]. Also the general for In, Pb, Sn, Bi with Al and Ge binary phase diagrams is practically full absence of solubility in a solid state with formation of eutectic, which has similar structure and melting temperature to corresponding fusible component [40]. As the melting temperature of eutectic only slightly differs from melting temperature of a fusible

component, in the literature there is no common opinion concerning their absolute values. It is necessary to specify following circumstance. The general for all selected Al and Ge binary systems is eutectic formation on the basis of more fusible component. It is possible to expect, what exactly eutectic formation in system film-forming substance – matrix can appear the main role on such film melting temperature changes and sign. On it, as it was already marked, specify available experimental data [2] about decrease eutectic temperatures in earlier investigated condensed films some binary systems.

3.2. Definition of eutectic melting temperature

It was expedient, that for the solution of a problem the best is the usage of contact fusion [41, 44], which is applied to definition of eutectic temperatures. Usually contact of samples from corresponding components is created mechanically. However it is not always effective, because for contact fusion necessary to have physical contacts at an atomic level. In work [41, 44] it was offered to apply for investigation of contact fusion the two-layer film from the corresponding components, prepared by consecutive condensation of components in vacuum and their evaporation from independent sources. In the further such approach has been used for investigation of contact fusion in a few of binary systems. As in the given work the problem of unequivocal definition of melting temperature minor alterations, the method offered in work [41, 44] was modified in differential, that allows to observe reliably insignificant (<0.2 K) changes of melting temperature of thin films fusible component due to change of their thickness and influence of a matrix. Some series of experiments, then solved specific problems are different, but which scheme was essentially similar, have been executed in the following way (Fig. 3). On a polished substrate plate (width of 30 mm, thickness 3 mm and length 150 mm) from stainless steel it was condensed in vacuum $\sim 1 \cdot 10^{-6}$ mm mercury column by evaporation a carbon film. Thickness of carbon film approximately 200 Å for prevention to substrate material interaction with investigated layered film systems Al-Me-Al or Ge-Me-Ge. Then without vacuum disturbance on half of substrate (on its width) with a carbon film thick (1000 Å) Al film was condensed. At once after it a thick film of corresponding fusible metal was created. Metals by cleanliness not below 99,999 % were applied for this film. Thus Al evaporated from a tungsten wire, and In, Sn, Bi and Pb – from molybdenum shuttles. Films thickness was supervised watching for change of frequency of the quartz sensor. For warranty of noted sequence of layers the system of mobile dividing screens was placed. After the finishing of condensation along a substrate difference of temperatures (by heating its one end above approximately on 30° of corresponding fusible component melting temperature and cooling of the second end) was created. After some period for establishment of stationary temperatures distribution along a plate that was supervised by four thermocouples located in special apertures, heating was switched off also

a substrate together with investigated films was cooled. On all samples in a direction of temperature rise there is a viewable border adequate to melting temperature of a fusible component. It is possible owing to that In, Sn, Bi and Pb in a liquid phase do not wet a carbon film (wetting angle $\theta \approx 130 \div 150^\circ$) and after melting the metal film gathers in separate spherical drops (Fig. 4).

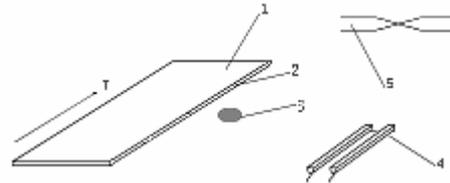


Fig. 3. The scheme of preparation of layered film systems by vacuum condensation; 1 – substrate plate; 2 – thermocouples; 3 – quartz sensor; 4 – metals evaporators; 5 – carbon evaporator

Beside on the same plate, on other half on its width, it is viewable border that adequate to contact fusion temperature in layered film system (aluminium/fusible component). Knowing distribution of temperature along a substrate and observing on the same substrate the relative positioning of borders, that pass the melting temperature of of fusible component (this temperature used for the control of absolute values of temperature) and contact fusion temperature in corresponding film system, it is possible with a sufficient reliability (± 0.2 K) to judge on sign and size of aluminium influence on melting temperature of the second component. The optical electron microscopy and x-ray diffractometry was applied to research of layered film systems structure before and after melting.

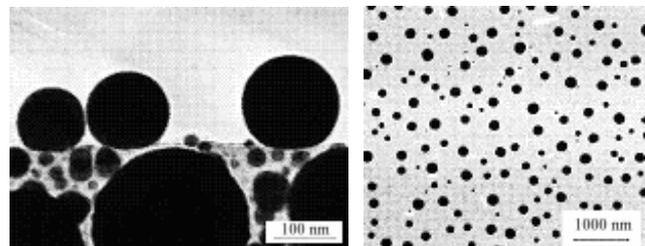


Fig. 4. Electron-microscopic pictures of drops that were formed after melting of continuous tin films on a carbon substrate

3. Results and their generalization

In the given chapter results of experimental researches of melting temperature changes in layered film systems Al-Me and Ge-Me (Me = In, Sn, Pb and Bi) prepared by thermal evaporation and consecutive condensation of components from independent sources. The choice of objects (nano-sized In, Sn, Bi, Pb layers on a surface and in Al and Ge matrixes) is caused by an character ambiguity in the literature and value of melting temperature changes in nano-dispersion systems, in case of when the fusible component is embedded in a solid-state more refractory matrix. The received results are analyzed by use of the thermodynamic approach.

3.1. Definition of eutectic temperatures in Al-Me, Ge-Me systems

In the literature there is no unique opinion concerning absolute values of eutectic temperatures, when eutectic is formed by fusible components with Al and Ge. Series of experiments at which on a substrate with a carbon film prepared on one half of plate a thick two-layer Al-Me or Ge-Me film, and beside on another part of plate a thick film of corresponding fusible metal. Photos of substrate with corresponding layered systems are showed on Fig. 5. These experiments allow defining with accuracy not below 0.2 K difference between corresponding eutectic temperatures and melting temperature of fusible element. The corresponding values of eutectic temperatures for the investigated systems, which average by 5-6 experiences, are presented in Table 1. It is visible, that application of a differential technique allow to specify value of eutectic temperatures and in particular to find, that temperature of eutectic on the basis of fusible component in Al-In and Ge-Bi systems do not coincide (as was considered till now), with melting temperatures of pure fusible metals, and exist a little below them. Given experiments were spent in vacuum $\sim 1 \cdot 10^{-6}$ mm mercury column, when in an interval after Al condensation and the beginnings of fusible metal condensation on a Al film surface possible formation of the thin film of oxides, which can influence contact fusion temperature in Al-Me film system. For the valuation and exceptions of this experiments have been prepared (for example of Al-In system). The essence consists in the following; on all substrate with the thin layer of a carbon film the thick In film was condensed, and then on half of substrate the thick Al film from above was condensed, i.e. the sequence of Al and In films changed. These experiences have shown, that contact fusion temperature in layered Al-In and In-Al film system does not vary. Accordingly to work results [6] the amorphous neutral matrix should not influence on samples of the small sizes melting temperature, i.e. they should behave as free or in vacuum. It was verified in experiments supervising the melting temperature of thin tin films (20 – 25 nanometers) that are on a carbon film and between two thick carbon films. According to research results [42] the wetting angle between tin and amorphous carbon substrate makes 152° . The precise linear border on all width of a substrate (perpendicular to substrate length) is observed as for a tin film on a carbon film and between two carbon films. It demonstrate, that the neutral not wetted amorphous substrate (Fig. 4) does not influence melting temperature of thin films and corresponding decrease of melting temperature for such layered film systems is described by the same expression, as for free films [6]. X-ray structural analysis of layered system after melting and cooling till room temperature with x-ray diffractometer Dron-3M and use K_α copper radiation have been executed. Values of lattice parameter: 1) for In $a = 0.4612$ nm, $c = 0.4935$ nm and for Al $a = 0.4049$ nm before melting; 2) for In $a = 0.4609$ nm, $c = 0.4936$ nm and for Al $a = 0.4049$ nm after melting. The received values of investigated

components lattice parameters correspond to tabular data for pure metals, which certify about absence of appreciable solubility of components in layered film systems. Insignificant reduction of parameter c for In after melting is caused by insignificant solubility Al in In. For an example, x-ray spectrum for Al-In system before and after melting showed on Fig. 6 [44]. Therefore the application of a differential method of melting temperature registration with application of thick-film layered systems allow to specify eutectic temperatures for eutectics on the basis of a fusible component and In, Bi, Pb and Sn binary systems with aluminium and germanium.

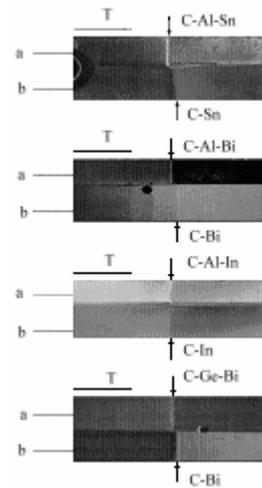


Fig. 5. Photos of thick films on a substrate with temperature gradient: a – fusible metals on Al or Ge thick film; b – fusible metals on a carbon sublayer

Table 1. Contact fusion temperature in Al-Me and Ge-Me film systems

System	Phase diagram	Eutectic temperature, T_e ($^\circ\text{C}$)	
		Experiment	Literature [43]
Al-In	Eutectic with immiscibility area in liquid state	155.6	156.4
Al-Bi		269.1	270
Al-Pb		325.3	327
Al-Sn		229.8	228.3
Ge-Bi		268.5	271
Ge-Pb	Simple eutectic	324.9	327

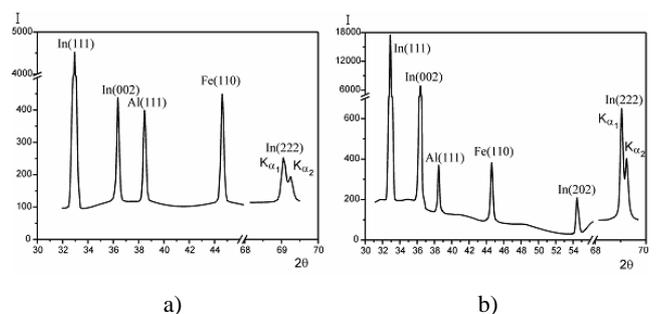


Fig. 6. X-radioscopic spectrum of Al-In system: a – before melting, b – after melting

3.2. Dependence of melting temperature in layered Al-Me-Al, Ge-Me-Ge film systems from thickness of Me (Sn, Pb, Bi, In) metal film

Group of experiments with prepared layered film systems from thick Al or Ge film and fusible metal (Me-Al or Me-Ge) and thin metal film of different thickness between thick Al or Ge (Al-Me-Al or Ge-Me-Ge) films, have unequivocally shown, that melting temperature of thin In, Sn, Bi and Pb films in such layered systems decreases with reduction of their thickness. It is well viewable in a photo (Fig. 7) of layered thick Al-In film system. For finding of melting temperature dependence in layered Al-Me-Al and Ge-Me-Ge film systems on one substrate prepared some layered film systems that differed only in Me layer thickness. For the fixed values of In, Sn, Bi and Pb films thickness corresponding values of melting temperature decrease are presented in Table 2.

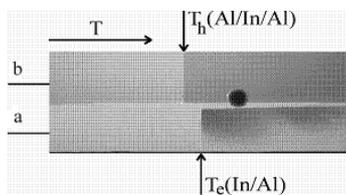


Fig. 7. Photo of layered Al-In film system on a substrate with temperature gradient: a – thick Al-In film system, b – In film with thickness 25 nanometers between thick Al films (Al-In-Al)

Table 2. Melting temperature of layered film systems

System	Experiment		For particles in matrix [43]		$\Delta T_h \cdot 3 \frac{h}{d}$ (°C)
	h (nm)	ΔT_h (°C)	d (nm)	ΔT_h (°C)	
Al-In-Al	25	3,5	15	16,9	17,5
Al-Bi-Al	25	3,8	22	14,6	13,6
Al-Pb-Al	30	3,0	13	20,5	20,7
Al-Sn-Al	20	3,0	17	12,1	10,6
Ge-Bi-Ge	40	7,0	-	-	-
Ge-Pb-Ge	20	5,0	-	-	-

Such experiments have allowed the observing change of melting temperature depending on Me film thickness. On Fig. 8 [44] and Fig. 9 presented photos of substrate plates with layered Al-Sn-Al and Ge-Bi-Ge film systems and experimental dependences of melting temperature from thickness of Me film. Thus research of layered Al-Me-Al and Ge-Me-Ge (Me-In, Pb, Bi, and Sn) film systems created in vacuum by consecutive condensation of components, which evaporate from independent sources, have shown, that the melting temperature of thin film components between two thick Al or Ge films decreases with reduction of their thickness.

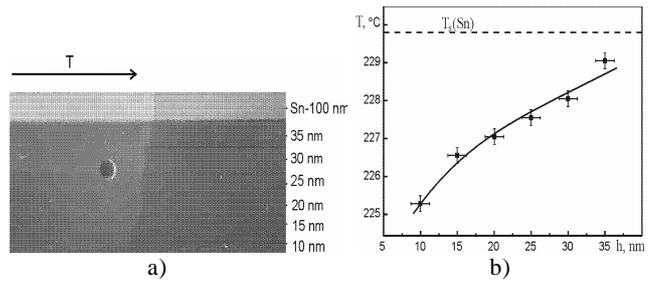


Fig. 8. Photo of substrate with Al-Sn-Al layered film systems: a – different Sn film thickness; b – dependence of eutectic temperatures T_s from tin film thickness

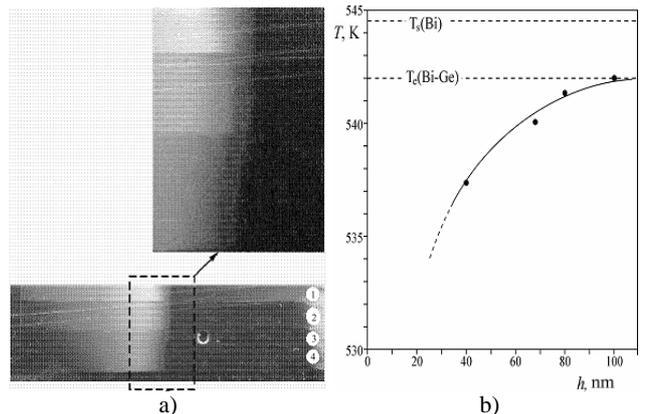


Fig. 9. Photo of substrate with layered Ge-Bi-Ge film systems: a – different thickness of bismuth films: 1 – 100 nanometers, 2 – 80 nanometers, 3 – 68 nanometers, 4 – 40 nanometers; b – dependence of melting temperature

6. Conclusions

1. The research of layered Al-Me-Al and Ge-Me-Ge (Me-In, Pb, Bi and Sn) film systems created in vacuum by consecutive condensation of components and evaporation from independent sources have shown that the melting temperature of thin films between two thick Al or Ge films decreases with reduction of their thickness.
2. The application of differential method of melting temperature registration and application of layered film systems allow to specify the eutectic temperatures for eutectics on the basis of a fusible component in In, Bi, Pb and Sn binary systems with aluminium and germanium.

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