

Crystallization of the fusible component in Ag/Bi/Ag and Ag/Pb/Ag layered film systems

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The results of studies of the supercooling during the crystallization of a fusible component in Ag/Bi/Ag and Ag/Pb/Ag layered film systems are presented. The crystallization temperatures of metastable melts are determined by using two independent *in situ* techniques. The value of supercooling and the character of crystallization in Ag/Bi/Ag samples is determined by the condensation mechanism during the bismuth deposition (vapor-crystal or vapor-liquid). This phenomenon is explained by differences in the morphological structure of the films.

Keywords: supercooling during crystallization, multilayer films, condensation mechanism.

Приведены результаты исследований переохлаждения при кристаллизации легкоплавкого компонента в слоистых пленочных системах Ag/Bi/Ag и Ag/Pb/Ag. При помощи двух независимых *in situ* методик определены температуры кристаллизации метастабильных расплавов. Показано, что в образцах Ag/Bi/Ag величина переохлаждения и характер кристаллизации определяются механизмом конденсации при осаждении висмута (пар-кристалл или пар-жидкость). Данное явление объясняется отличиями в морфологической структуре пленок.

Кристалізація легкоплавкого компонента у шаруватих плівкових системах Ag/Bi/Ag та Ag/Pb/Ag. С.В.Дукаров, С.І.Петрушенко, В.М.Сухов, Р.В.Сухов

Наведено результати дослідження переохолодження під час кристалізації легкоплавкого компонента у шаруватих плівкових системах Ag/Bi/Ag та Ag/Pb/Ag. За допомогою двох незалежних *in situ* методик визначено температури кристалізації метастабільних розплавів. Показано, що у зразках Ag/Bi/Ag величина переохолодження і характер кристалізації визначаються механізмом конденсації під час осадження вісмуту (пара-кристал або пара-рідина). Дане явище пояснено відмінностями у морфологічній структурі плівок.

1. Introduction

Studies of metastable states of melts are of interest both for fundamental science and for application. It is known (e.g., [1–3]) that the achieved supercooling value and the kinetics of crystallization significantly influence the structure of the crystallized material. From the point of view of fundamental scientific research, the determination of limiting supercoolings and the study of the kinetics of crystallization make it

possible to obtain information on the interaction at the crystal-melt boundary [4–6].

To date, there is a large number of papers devoted to the study of the crystallization of supercooled liquids. It has been established [7–10] that the limiting value of supercooling during the crystallization of a melt in contact with a solid is determined by the degree of interaction at the interphase boundary. The quantitative measure of this interaction is usually the corresponding contact angle of wetting. The

maximum relative supercoolings obtained for various metals reach 0.3–0.4 melting points (T_s) in systems with almost complete non-wetting (e.g., metal melts on a carbon or oxide substrate) and decrease linearly as the contact angle of wetting decreases [8–10].

The supercooling value is extremely sensitive to insoluble impurities present in the melt. Therefore, obtaining of the ultimate supercoolings requires maximum purification of the samples from possible impurities, which may be potential centers of heterogeneous crystallization. The most effective way to obtain maximum purity is the method of microvolumes proposed by Turnbull [11], which consists in breaking up a pre-cleaned sample into a large number of individual particles. Since the number of impurity centers in the initial sample is finite, then for a sufficient degree of partition it is possible to create conditions under which some of the particles will be completely free of insoluble impurities. In such particles the maximum supercoolings corresponding to homogeneous crystallization can be achieved. The combination of the microvolume method with experiments in high vacuum conditions also protects the melt from contamination during the experiment.

We note that large supercoolings are usually obtained either for small particles placed on an inert substrate [9, 10], or for completely free objects under conditions of electrostatic or acoustic levitation [2, 12–14]. The data on the supercooling of melts embedded in the more refractory matrix is much smaller. At the same time, the results of a theoretical analysis of systems such as "nanoparticles in a matrix" lead to the appearance of specific features in the crystallization of supercooled melts [15]. However, the results of an experimental study of melting and crystallization of a fusible component in such systems are ambiguous, and sometimes contradictory [16–18].

Difficulties in studying nanocomposite materials are due to both the theoretical and experimental complexity of their research, primarily related to the need to take into account a number of additional factors. According to [15, 19–22, 25], multilayer films obtained by the vacuum condensation method can serve as a good model of the "particle in the matrix" systems.

Studies of supercooling during the melts crystallization, carried out using multilayer vacuum condensates, were performed in [19–22, 25]. The authors showed that for the inclusion of a fusible component in a

multilayer structure, as well as for particles on the substrate surface, the magnitude of supercooling depends on the interaction at the melt-substrate boundary. In addition, it was found in [21, 22] that crystallization of bismuth embedded in a copper or molybdenum matrix occurs in an avalanche-like manner with relatively small supercoolings. This effect occurs in layered film systems in which bismuth condensation was carried out on a substrate at room temperature. At the same time, crystallization in samples in which bismuth is deposited into the liquid phase occurs diffusely at substantially higher supercoolings. Regardless to the condensation mechanism, diffuse crystallization occurs in films in which the fusible component is lead, tin or indium [21, 22], as well as in samples containing bismuth between layers of amorphous carbon [25].

The present work is devoted to the study of the crystallization of a fusible component in Ag/Bi/Ag and Ag/Pb/Ag three-layer films. The choice of the Ag/Bi contact pair is due not only to the need to expand the available results on the supercooling of bismuth in the metal matrix to other contact pairs, but also to the application that continuous and island films of noble metals have today [26, 27]. The relevance of determining the boundaries of the stability of the liquid phase in selected contact pairs is also indicated in the results of work [28] in which it is shown that thermal dispersion of continuous metallic films can be facilitated by the small amount of liquid phase of the second component present in the sample. In turn, the results of studying the dispersion of initially continuous films can be used to improve the technologies for creating nanoscale arrays, which are of great practical importance. In addition, the Ag/Bi films are interesting from the perspective of applications, due to the inverse Rashba-Edelstein effect [29], which can be used in spintronics and in the creation of full-scale quantum computers.

2. Objects and methods

As the objects of study, Ag/Bi/Ag and Ag/Pb/Ag layered film systems were used, obtained by the method of layer-by-layer vacuum condensation at a residual gas pressure of 10^{-6} Torr. Silver, bismuth and lead were evaporated from molybdenum boats, heated by electric current. The surfactant layer of molybdenum was deposited from a wire tungsten evaporator. The thickness of the films was measured during their prepa-

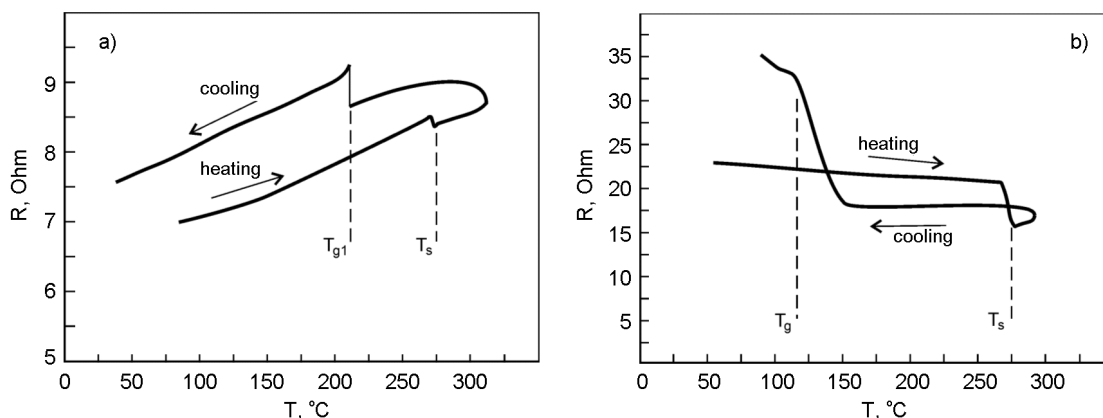


Fig. 1. Dependence of the electrical resistance on temperature in Ag/Bi/Ag films in which bismuth was condensed by the vapor-crystal (a) and vapor-liquid (b) mechanism.

ration from the frequency shift of the quartz resonator. To study of the contact pair Ag/Bi, two series of samples were obtained. The metal layers were condensed on the substrate at room temperature, i.e. by the vapor-crystal mechanism in the former one. In the latter, condensation of the bismuth layer was carried out on a substrate at a temperature of 220°C, which ensured the realization of the vapor-liquid condensation mechanism. The condensation of the components of the Ag/Pb contact pair has always been carried out at room temperature.

The melting and crystallization temperatures of bismuth in multilayer films were determined using two independent *in situ* techniques: resistance measurements in heating-cooling cycles and direct electron diffraction observations. The morphological structure of the films was studied in the JEOL JSM-840 scanning electron microscope.

To measure the temperature dependence of resistance, the films were condensed into original measuring cells, which are glass plates with applied electrical contacts. The cell temperature was measured by a chromel-alumel thermocouple, and its heating by radiation from a tungsten wire located about 1 cm from the back of the substrate. The condensation of the samples and the study of the temperature dependence of their electrical resistance were carried out in a single vacuum cycle. The thicknesses of silver films in this case were chosen for reasons of ensuring sufficient thermal stability of the sample during the heating-cooling cycles and amounted to 250–300 nm. The thicknesses of bismuth and lead films in various experiments were 30–50 nm. Samples for electron diffraction studies were deposited on fresh cleavages of KCl

single crystals with a pre-deposited film of amorphous carbon. After completion of the condensation, the samples were taken from the vacuum chamber, trapped in water on standard electron microscope grids and examined in a transmission electron microscope SELMI EMV 100BR in a diffraction mode. The microscope was equipped with an original device for heating the samples directly in its column.

3. Results and discussion

As a result of the studies, the temperature dependence of the resistance for Ag/Bi/Ag films was obtained. Fig. 1 shows the thermoresistive curves corresponding to the samples in which the bismuth condensation was carried out according to the mechanisms of vapor-crystal (Fig. 1a) and vapor-liquid (Fig. 1b). On the obtained dependences, both during heating and cooling of the films, resistance jumps occur in opposite directions. According to previous studies, such jumps in multilayer films are observed at the melting (T_s) and crystallization (T_g) of the fusible component. It can be seen that the temperature and character of bismuth crystallization, as in the previously studied Cu/Bi/Cu and Mo/Bi/Mo films [21, 22], depend on the mechanism of its condensation. For samples in which bismuth was deposited by the vapor-crystal mechanism, crystallization occurs in an avalanche manner near 200°C (T_{g1}). A relatively low supercooling ($0.12T_s$) is characteristic for these films. For those films in which the condensation of the fusible metal is carried out into the liquid phase, the crystallization temperature decreases to 115–120°C, and the supercooling value increases to approximately $0.28 T_s$. The crys-

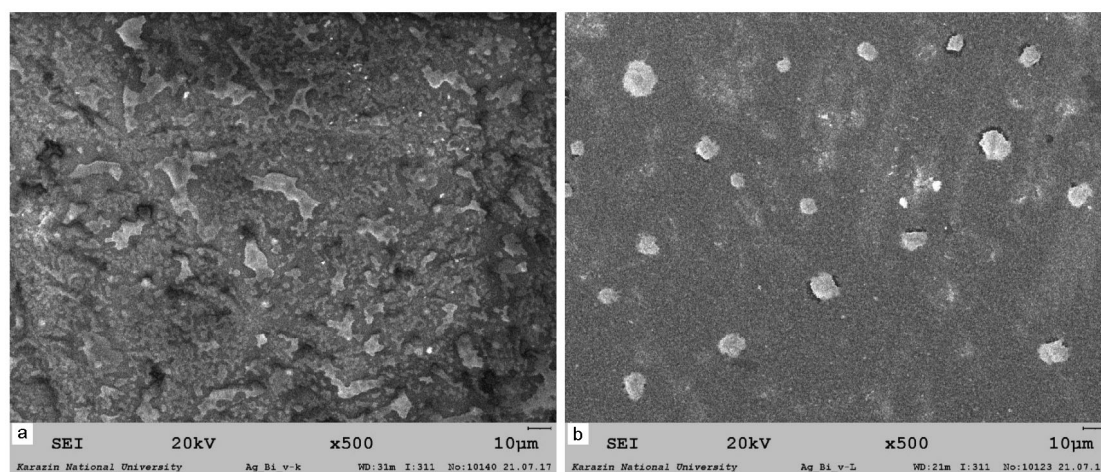


Fig. 2. SEM images of Ag/Bi films in which bismuth was deposited by the mechanism of vapor-crystal (a) and vapor-liquid (b).

tallization of bismuth in films in which it condensed into the liquid phase occurs diffusely in the temperature range of about 40 K (Fig. 1b). Unlike Cu/Bi/Cu and Mo/Bi/Mo films, whose resistance from cycle to cycle practically does not increase [21, 22], the resistance of Ag/Bi/Ag films gradually increases, which indicates their decay. This leads to the necessity to use sufficiently thick layers of silver films, between which bismuth is located.

Analogously with the previously studied contact pairs [21, 22], the effect of substrate temperature during condensation on the temperature and the character of crystallization can be related to the different morphology of the films. In films obtained by vapor-crystal condensation, even after several heating-cooling cycles, bismuth is present in the form of inclusions of irregular shape, which, on the whole, form a connected structure (Fig. 2a). Crystallization of such a structure will occur immediately after at least one critical nucleus of the crystalline phase appears.

In view of the fact that the size of a single system of inclusions is comparable to the size of the entire sample, for bismuth condensed by the vapor-crystal mechanism, the conditions of the microvolume method are not met. That is, the crystallization of bismuth can be related to the presence of external crystallization centers, the nature of which is not entirely clear. Thus, the results [21], in which Bi/Mo samples were held for a long time under low vacuum conditions, show that crystallization due to impurities, which are formed as a result of interaction with the residual atmosphere of

the vacuum chamber, is observed at lower temperatures. A possible cause of early crystallization of a bismuth connected structure can be the effect of a solid matrix on the process of formation of critical size nuclei [15]. In particular, in such systems a decrease in supercooling can be observed [15], which occurs in the case when the size of the critical nucleus is larger than the cavities of the matrix. If the critical nucleus has a size substantially smaller than the pores of the matrix, it will not affect the formation of the crystalline phase.

We can write the expression for the radius of the critical nucleus from the classical nucleation theory:

$$r_c = \frac{2\sigma_{sl}T_s}{\lambda\Delta T}, \quad (1)$$

where σ_{sl} is the interphase energy of the crystal-melt interface, λ is the latent heat of fusion normalized to the volume, $\Delta T = T_s - T_g$ is the supercooling value.

From this relation, we can estimate the size of the critical bismuth nucleus, which provides the observed supercoolings. Such an estimate, using the value of $\sigma_{sl}T_s/\lambda$ given in [15], gives a critical nucleus radius of about 1 nm. The obtained value is much less than the thickness of the bismuth layer in the films under study. Apparently, the thickness of the bismuth layer in the Ag/Bi/Ag samples is already large enough that the presence of silver films on both sides of it does not directly affect the crystallization features. However, vacuum condensates are usually highly nonequilibrium structures containing a large number of

germ pores and intergranular boundaries. It can be assumed that the melt drops captured by such defects, whose size may be smaller than the value of the critical nucleus determined in accordance with (1), crystallize first. This provokes rapid crystallization of a single system of inclusions of a fusible component, formed in samples obtained by the vapor-crystal condensation mechanism.

At the same time, in the films in which bismuth condensation was carried out by the vapor-liquid mechanism, the fusible component is present as separate inclusions (Fig. 2b). It is obvious that the crystallization of individual inclusions, regardless of its causes, does not cause the crystallization of neighbors, i.e. such particles crystallize independently of each other. Their size is already small enough to satisfy the conditions of the microvolume method, and supercooling acquires a value that is probably maximal for the contact pair under study.

The results of the determination of supercoolings obtained by measuring the electrical resistance of films were confirmed by independent *in situ* electron diffraction studies of samples with the same ratio of the components thickness. It is established that when the films under study are heated, the lines corresponding to the crystallographic planes of bismuth are present up to its melting point (T_s), after which they are replaced by diffuse haloes. Upon cooling, the reflections from crystalline bismuth begin to appear at a temperature much lower than T_s , but acquire the initial brightness after reaching the temperature T_g , which coincides with the value obtained from the measurements of the electrical resistance of the films. This directly confirms the fact that in the temperature interval between T_s and T_g , bismuth is present in the sample in a supercooled liquid state.

When studying the temperature dependence of the resistance in the Ag/Pb contact pair, it was found that the lead layer reduces the thermal stability of silver films. Thus, Fig. 4 shows the thermoresistive curves corresponding to the successive heating-cooling cycles of the silver film (curves *a*, *b*) and the next cycle, which was carried out after the lead layer was condensed to the already annealed and cooled to room temperature Ag film (curve *c*). It can be seen that in the first heating cycle of Ag films (Fig. 4, curve *a*), as for Cu and Mo samples [21, 22, 28], an irreversible decrease in their resistance due to annealing

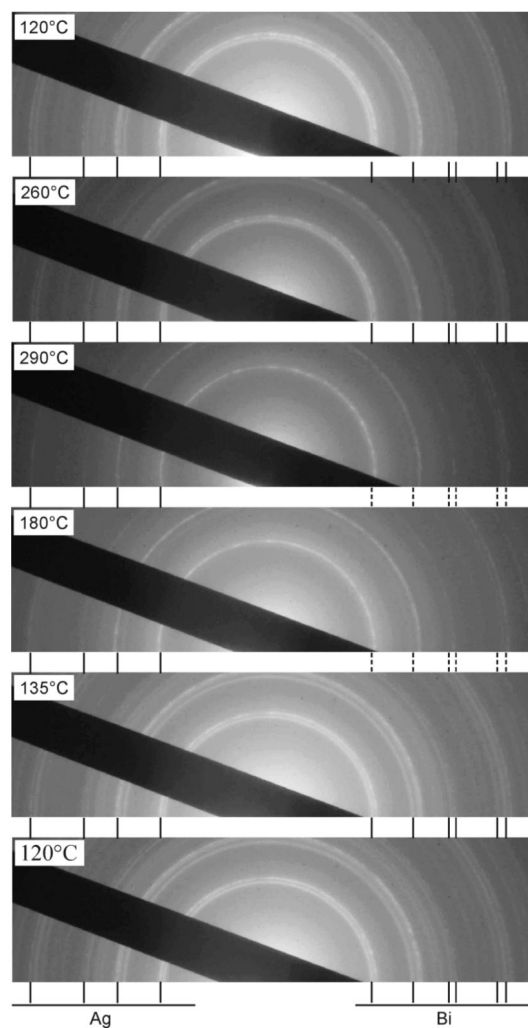


Fig. 3. Electron diffraction patterns of Ag/Bi films corresponding to the heating-cooling cycle (from top to bottom). The temperatures of the samples are indicated in the photographs. Bismuth was deposited by the vapor-liquid mechanism.

is observed. After that, the resistance of these films is practically linear on change with temperature, and does not contain any features in the temperature range under study. However, the resistance of Ag/Pb samples sharply increases when they are heated to the melting point of lead. Such an irreversible growth of resistance showed [28] the breakdown of the initially continuous silver films into separate islands. The process of decay of layered film systems in the presence of liquid lead in them can occur not only due to solid-phase diffusion, but also due to mass transfer through the liquid phase [28]. In turn, due to the size effect of solubility [30, 31], the contribution of the second process can increase with

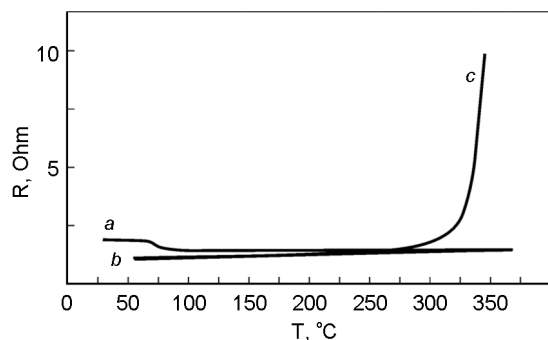


Fig. 4. Electrical resistance of the Ag and Ag/Pb films versus temperature. Curve (a) corresponds to the first, and (b) to the second heating of the silver film. Graph (c) demonstrates the behavior of the Ag/Pb film during the first heating.

the transition from bulk samples to thin films.

According to [22–24], the thermal decay process can be slowed down by using surfactant layers located between the base substrate and the layered film system under study. As a surfactant, a layer of 1–2 nm thick molybdenum was chosen, which deposited on the measuring cell immediately before the condensation of silver. This somewhat slowed the process of the samples dewetting and made it possible to observe the jumps in the resistance on the thermoresistive curves, which can be matched with the melting and crystallization of lead (Fig. 5).

A significant reduction in thermal stability due to the presence of lead in the films leads to rapid degradation of the layered film system. This limits the number of heating/cooling cycles that can be performed on a single sample. The magnitude of supercooling in this contact pair is about $0.1T_s$, and crystallization, even when lead is deposited on a silver layer at room temperature, occurs in the temperature range of about 3 K, i.e. has a diffuse character.

We note that, as in other previously studied systems [21, 22, 25], bismuth provides more noticeable jumps in resistance during phase transitions in comparison with other metals. Thus, the resistance jumps in phase transitions in Ag/Pb/Ag films, both during melting and during crystallization, are practically equal to each other and amount to about 5%. At the same time, for films containing bismuth, an asymmetry is observed between the jumps corresponding to the melting and crystallization of the fusible component. The resistance jump in the melting of bismuth in the samples ob-

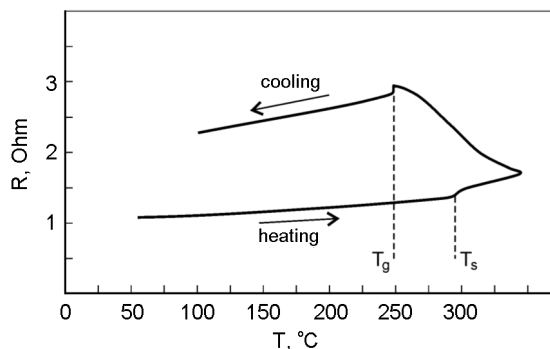


Fig. 5. Temperature dependence of the electrical resistance of Ag/Pb/Ag films deposited on the surfactant layer of molybdenum.

tained by the vapor-crystal condensation mechanism is 1–2%. At the same time, the jump in the resistance during crystallization of bismuth turns out to be much larger and amounts to 5–10%, which corresponds to a jump observed in films containing lead. For films deposited by the vapor-liquid mechanism, the magnitude of the jump in resistance is much larger, and when melting it is 10–20%, and when crystallized it reaches 80–90%. Unlike Ag/Pb/Ag films, whose thermal dispersion occurs in the presence of a liquid phase (as evidenced by the irreversible increase in their resistance observed over the entire temperature range of the existence of liquid lead), the degradation of Ag/Bi/Ag films occurs mainly during the crystallization of bismuth. This confirms the assumption made in [22] that the resistance jumps accompanying phase transitions in Cu/Bi/Cu films, unlike lead-containing samples, are mainly due to mechanical stresses arising during the crystallization of bismuth.

4. Conclusions

The temperature boundaries of the stability of the liquid phase of the fusible component in Ag/Bi/Ag and Ag/Pb/Ag films are determined. It is shown that, like for layered film systems based on copper and molybdenum, the temperature and character of bismuth crystallization depend on the substrate temperature when it is condensed. For samples in which bismuth was condensed by the vapor-crystal mechanism, the crystallization occurs in an avalanche-like manner with a relative supercooling of $0.12T_s$. For films in which bismuth condensed into the liquid phase, diffuse crystallization occurs at a much higher supercooling ($0.28T_s$). In Ag/Pb/Ag films, as in

other previously studied similar contact pairs (Cu/Pb, Mo/Pb, Mo/In), diffuse crystallization is observed irrespective of the condensation mechanism of the fusible component. Supercooling during the crystallization of lead in Ag/Pb/Ag films is $0.1T_s$. Differences in the temperature and character of the crystallization of Ag/Bi/Ag film systems obtained by bismuth condensation at different substrate temperatures are due to the different morphological structure of bismuth inclusions in the multilayer films under study.

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