
**LOW-DIMENSIONAL SYSTEMS
AND SURFACE PHYSICS**

Kinetics of the Melting–Dispersion Process in Copper Thin Films

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Abstract—The kinetics of a melting–dispersion process in copper thin films is investigated at different thicknesses of the films. It is shown that the film initially melts in local regions and then the melting front propagates over the sample. Melting of copper thin films of the same thickness can occur within different time periods depending on the temperature (from almost instantaneous melting at higher temperatures to melting proceeding over the course of a few hours at lower temperatures). The dependence of the activation energy for the melting–dispersion process on the film thickness is determined and explained in terms of hydrodynamics. The mechanism of the melting–dispersion process is considered.

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1. INTRODUCTION

It is well known that small-sized objects have lower melting temperatures [1–8]. According to the classical equilibrium thermodynamics, the phase transition temperature decreases in a system bounded by a surface whose energy is comparable to the bulk energy of the system. In particular, the melting temperature T_m of a thin film at a constant volume can be described by the relationship [8]

$$T_m = T_0 \left(\frac{\Delta H(T)}{\Delta H_0} + \frac{\sigma_L A_L}{\Delta H_0 V} - \frac{\sigma_S A_S}{\Delta H_0 V} \right), \quad (1)$$

where T_0 is the melting temperature of the system in the absence of a surface; σ_L and σ_S are the surface energies of the liquid and solid phases, respectively; A_L and A_S are the surface areas of the liquid and solid phases, respectively; $\Delta H_0 = H_L - H_S$ is the change in the enthalpy of the system upon transition from the solid state to the liquid state; $\Delta H(T)$ is the heat of melting at the melting temperature T of the thin film; and V is the volume of the system.

The analysis of relationship (1) demonstrates that one of the main factors responsible for the decrease in the melting temperature of thin films is a change in the shape, because the system tends to reduce the surface energy due to the phase transition and the decrease in the surface area of the system [the second and third terms in relationship (1)]. Another factor is the temperature dependence of the heat of melting ΔH [the first term in relationship (1)]. A decrease in the temperature results in a decrease in the heat of melting. In turn, this process leads to a further decrease in the melting tem-

perature of the thin film. In our earlier study [8], we showed that, owing to the above factors, the melting temperature of a copper film with a sufficiently large thickness (50 nm) at the Ta–W–N inert surface appears to be approximately 250 K lower than the melting temperature of bulk copper (1356 K according to the data available in the literature).

In studying the melting of copper thin films, we revealed that melting of copper thin films of the same thickness can occur within different time periods depending on the annealing temperature in the range 100–150 K (from almost instantaneous melting to melting proceeding over the course of a few hours with a decrease in the annealing temperature). To the best of our knowledge, this phenomenon in thin films and its origin have never been described in the literature.

There is a similarity between the revealed phenomenon in thin films and the crystallization of bulk melts [9, 10]. Despite the dissimilarity of the objects of investigation, a feature common to both phenomena is the tendency of the system toward relaxation of the excess surface energy. Owing to this tendency, there occur a number of evolution processes (such as fluctuational heavy local nucleation of a new phase and coalescence), which proceed at different rates, i.e., have a kinetic nature [9, 10].

In this work, we experimentally investigated the kinetics of melting of thin films and proposed a mechanism to explain the observed phenomenon.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Figure 1a shows the samples used in investigating the kinetics of melting of 10- to 100-nm-thick copper films. The samples were prepared on rectangular sapphire substrates 10×30 mm in size. Before depositing the metal films, the substrates were washed according to a standard procedure in a hydrogen peroxide–ammonium hydroxide ($\text{H}_2\text{O} : \text{NH}_4\text{OH} : \text{H}_2\text{O}_2$) solution and a Caro ($\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4$) solution in order to remove contaminants from the sapphire surface. Then, the substrates were washed in deionized water and dried in isopropanol vapors, followed by sputtering of a carbon layer 60 nm thick. Thick-film electrodes providing reliable electrical contact with the film under investigation were applied at the sample edges (Fig. 1a). The carbon and copper layers on the substrate were deposited through magnetron sputtering of the respective targets.

The block diagram of the automatic measurement system is depicted in Fig. 1b. This system was designed to determine the temperature of the onset of melting of the thin films under investigation. The system made it possible to measure the electrical conductivity of the sample immediately in the course of heating under vacuum at a residual gas pressure of 1×10^{-5} mmHg. Heating was performed using a resistance furnace. The temperature of the surface was controlled by thermocouples. A change in the sample resistance due to heating leads to an increase or a decrease in the current passing through the sample and, hence, to a corresponding decrease or increase in the voltage across a fixed resistor. The voltage across the resistor was registered with an electronic recorder.

This method allows one to determine accurately the temperature of the onset of melting of the copper thin films, because the underlying carbon layer has a considerably higher resistance. Hence, the measured electrical conductivity is predominantly determined by the copper film. The characteristic time dependences of the electrical conductivity for the copper films 20 and 100 nm thick at different temperatures are plotted in Figs. 2a and 2b, respectively. It can be seen from Fig. 2a that, once the necessary temperature is reached, the electrical conductivity of all samples with a small thickness of the copper film (20 nm) remains constant for a certain period of time. Since the melting of a thin film on an inert substrate is accompanied by dispersion into droplets, the electrical conductivity at the instant of the onset of melting decreases rapidly to a background value corresponding to the electrical conductivity of the carbon layer. For this reason, the instant of the onset of melting was determined from the instant of a sharp decrease in the electrical conductivity. It can also be seen from Fig. 2a that, as the annealing temperature decreases, the portions of the dependences with a rapid decrease in the electrical conductivity become flatter. This indicates a retardation of the melting process. The copper film with a larger thickness (100 nm) behaves in

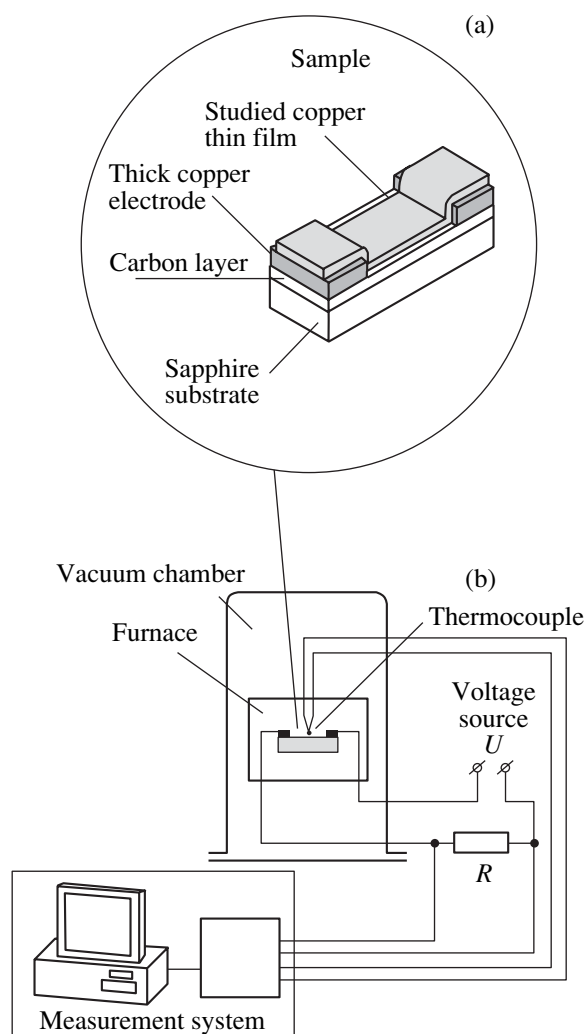


Fig. 1. Block diagram of the automatic system for measuring the electrical conductivity of thin films in the course of annealing under vacuum: (a) the sample under investigation and (b) schematic drawing of the measurement system.

a similar manner only to a temperature of 913 K. At higher annealing temperatures, the electrical conductivity begins to decrease immediately after the required temperature is reached. However, examination of the samples under a scanning electron microscope (SEM) revealed that no melting occurs at this stage. The observed decrease in the electrical conductivity of the 100-nm-thick film at the initial stage is associated with the processes leading to improvement of the defect structure (such as an increase in the grain size and a decrease in the concentration of point defects). On the one hand, these processes result in a decrease in the resistivity and, hence, should seemingly increase the electrical conductivity. However, on the other hand, these processes are attended by an increase in the temperature coefficient of resistance. It was experimentally found that the resistivity of the copper thin film upon

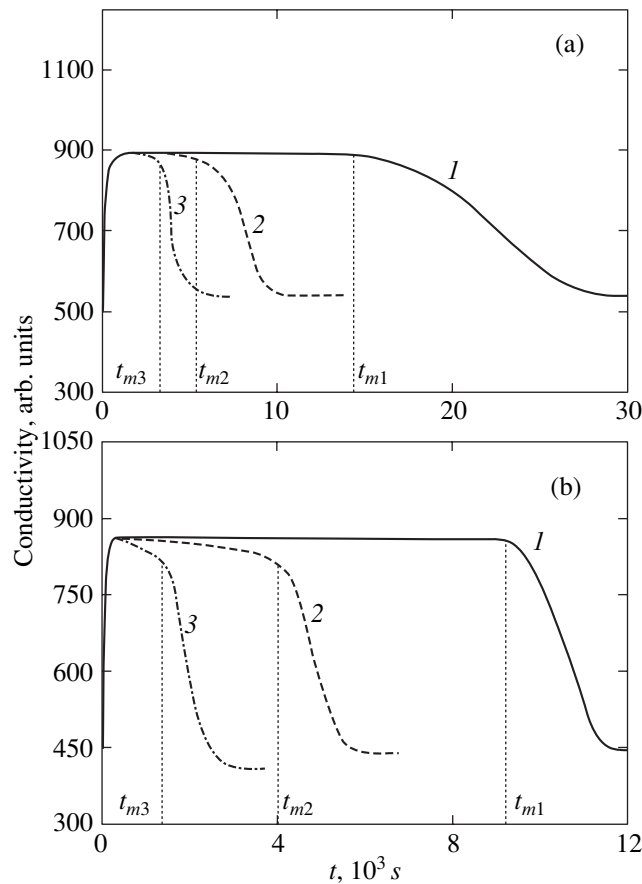


Fig. 2. Experimental time dependences of the electrical conductivity measured for copper thin films (a) 20 and (b) 100 nm thick under vacuum at annealing temperatures $T =$ (a) (1) 743, (2) 773, (3) 803 and (b) (1) 913, (2) 943, (3) 973 K. Vertical dotted straight lines indicate the times t_m (on the horizontal axis) corresponding to the onset of melting of the thin films at the specified temperatures.

heat treatment decreases by 30–50%. However, by assuming that the temperature coefficient of resistance of this film is equal to $4 \times 10^{-3} \text{ K}^{-1}$, heating of the copper thin film by 700 K should result in an increase in the resistance by a factor of approximately 3. This suggests that a decrease in the number of defects in the structure should actually be accompanied by a decrease in the electrical conductivity.

3. RESULTS AND DISCUSSION

As can be seen from Fig. 2, the melting of a 20-nm-thick copper film begins within 53 min of the onset of the process at a temperature of 803 K and within 3 h 40 min at 743 K. The melting of a 100-nm-thick copper film begins within 20 min of the onset of the process at a temperature of 973 K and within 2 h 25 min at 913 K.

The analysis of the SEM images demonstrates that the film initially melts in a particular local region and then the melting front propagates over the sample

(Fig. 3). The characteristic feature of the process is the presence of three regions in the sample: the film is continuous in region I (Fig. 3a), melts in narrow region II (Figs. 3b–3e), and is completely dispersed into droplets in region III (Fig. 3f).

Figure 4 depicts the dependences of the time of the onset of melting of the copper thin films on the annealing temperature at different film thicknesses. The experimental points are fitted fairly well (with a correlation coefficient of 0.98–0.99) by the function

$$t = \frac{A}{\exp\left(\frac{E_a}{RT}\right)},$$

which follows from the Arrhenius equation. The performed approximation of the experimental data permits us to calculate the activation energy E_a of the melting–dispersion process for films of different thicknesses. According to the calculations, the activation energy E_a varies from 120 to 260 kJ/mol depending on the thickness of the copper film. In particular, the dependence $t(T)$ for the 100-nm-thick copper film is approximated by the relationship

$$t = 1 \times 10^{-11} \exp\left(-\frac{260 \times 10^3}{8.31T}\right). \quad (2)$$

Since dependences of this type are characteristic of different processes, including diffusion, we can assume that the observed dispersion process occurs through the diffusion mechanism. Note that the diffusion coefficient D_0 calculated from relationship (2) is approximately equal to $10000 \text{ cm}^2/\text{s}$, which is two orders of magnitude larger than the copper self-diffusion coefficient ($70 \text{ cm}^2/\text{s}$) given in [11].

The activation energies E_a and the diffusion coefficients D_0 obtained in our work are close to those experimentally determined by Dolbak et al. [12], who studied copper diffusion from copper thin strips ($\approx 12 \text{ nm}$ thick) along a clean silicon surface. In [12], this large diffusion coefficient D_0 was explained in terms of the surface diffusion that occurs via the solid-state spreading or “unrolling carpet” mechanism [13].

There are many experimental works in which the researchers have obtained diffusion coefficients D_0 that are considerably larger than those observed in the case of bulk diffusion in solid and even liquid phases. As a rule, this has been attributed to surface or grain boundary diffusion and, hence, has been described using the diffusion equations. It should be noted that an extremely high mobility of atoms along the surface as compared to the atomic mobility in the bulk can only be explained by an excess energy of the surface or grain boundaries.

In [14], it was revealed that the self-diffusion coefficient of gold in the case of grain boundary diffusion in a polycrystalline thin film is equal to the diffusion coef-

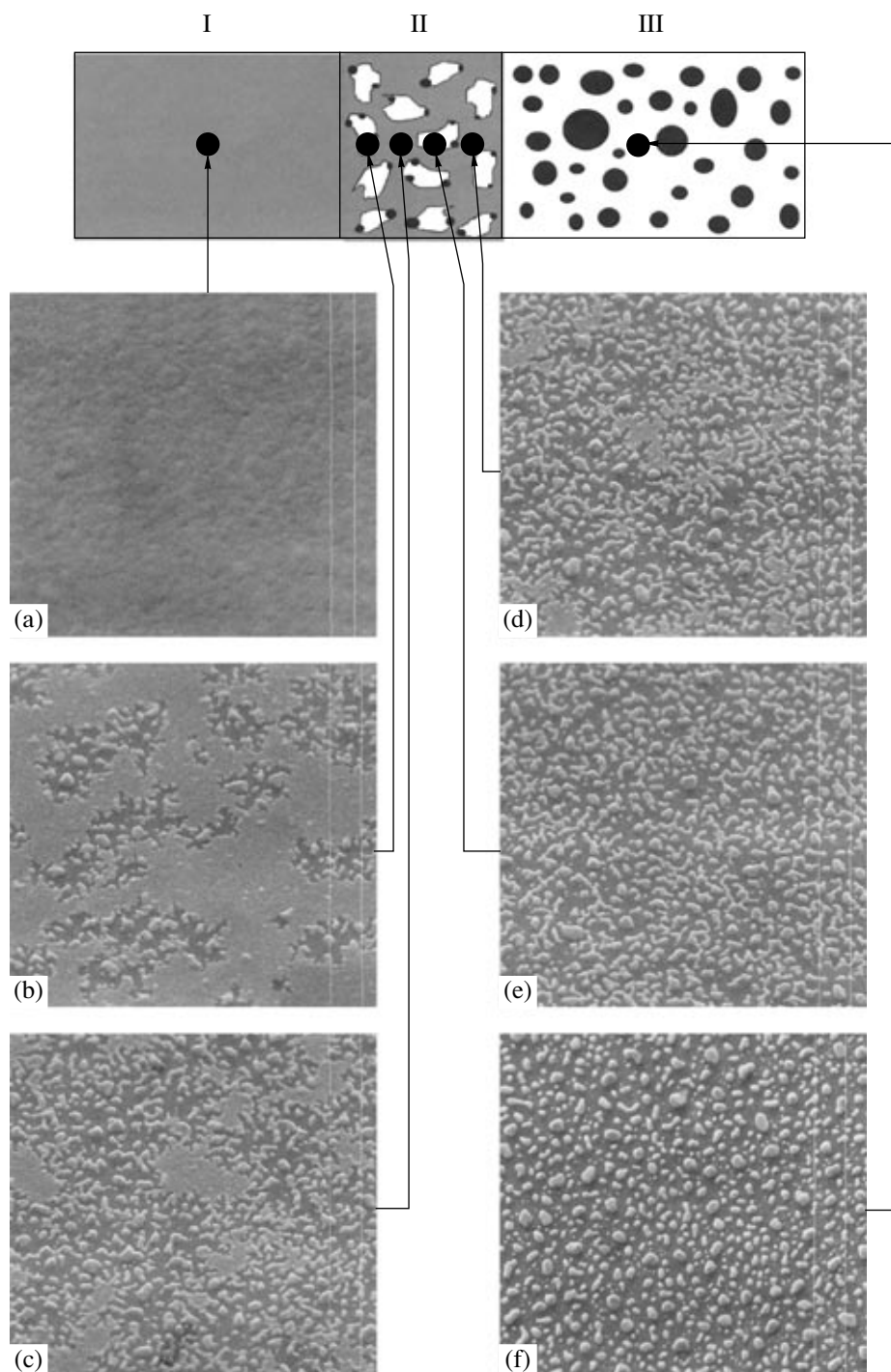


Fig. 3. SEM images of the copper thin film at different stages of melting: (a) continuous film (region I), (b–e) melting film (region II), and (f) film dispersed into droplets (region III).

ficient in the liquid phase. Furthermore, the inference was made that the grain boundary has a strongly disordered liquidlike structure and, therefore, is characterized by a high concentration of mobile defects responsible for the high-rate diffusion. Possibly, this liquidlike

structure of the grain boundary is a more important factor than the high concentration of defects.

Since the surface is the main defect of a three-dimensional crystal lattice, the vibrational spectrum of surface regions differs from that of bulk regions. The

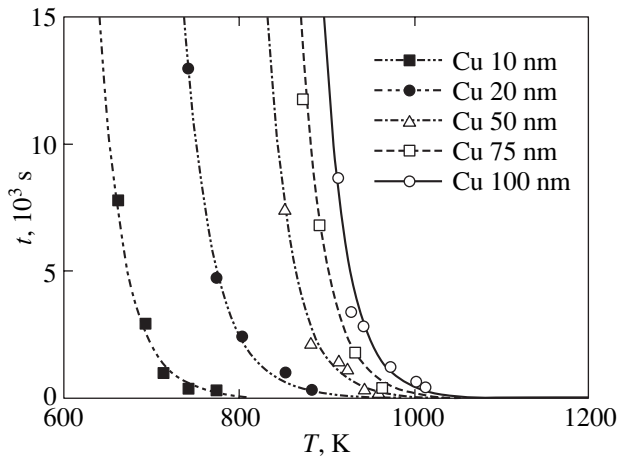


Fig. 4. Time of the onset of melting for copper thin films of different thicknesses as a function the temperature of annealing under vacuum.

amplitude of vibrations of surface atoms is always considerably larger than that of bulk atoms. As a consequence, the Debye temperatures of surface phases in a large number of metal and semiconductor single crystals are approximately equal to one-half the Debye temperatures of bulk phases [15]. This means that the crystal surface can melt at a temperature that is approximately equal to one-half the melting temperature of the bulk material. Therefore, melting always begins from the surface and then the melting front moves inside the crystal. The temperature dependence of the thickness of the molten layer d for metals is described by the expression [15]

$$d \sim \ln(T_0 - T_m)^{-1}.$$

Here, the case in point is the surface melting of a thin film and, hence, the behavior of this film on an inert surface can be explained in terms of hydrodynamics. Let us consider a steady fluid flow between two parallel stationary solid planes (i.e., the fluid is represented by layers that slide over each other) spaced apart at a distance h in the presence of a pressure gradient along the plane. The solution of the Navier–Stokes equation for this system leads to a parabolic dependence of the fluid velocity v on the coordinate y in the direction normal to the surface [16]; that is,

$$v \sim y^2. \quad (3)$$

This behavior of the dependence is determined by both the friction between the fluid layers during motion and the continuity condition (the fluid layer velocity at the stationary planes is equal to zero).

In the case under consideration, the upper surface of the thin film is free (Fig. 5). Since the lower surface of the thin film is contiguous to the inert surface, we can assume that the continuity condition is not satisfied. The surface tension forces σ_1 and σ_2 act along the sur-

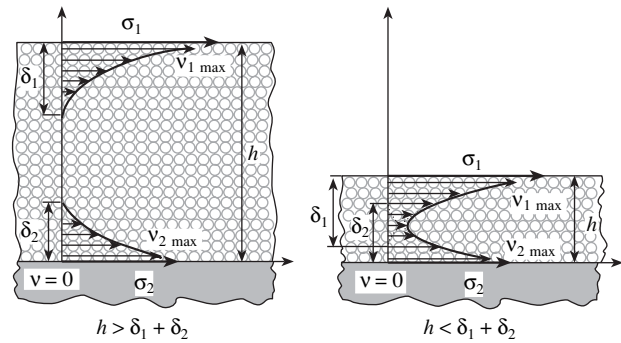


Fig. 5. Schematic diagram illustrating the origin of the dispersion of a copper thin film during melting on an inert surface. Liquid layers in the surface region move under the action of the surface tension forces σ_1 and σ_2 . The velocity of motion v of the liquid layers decreases from the surface deep into the film due to the friction between the liquid layers. At a critical depth δ , the velocity of motion of the liquid layer becomes zero.

faces and are responsible for the motion of liquid layers. As in the previous case, the velocity of layers decreases according to the parabolic law due to the friction between the liquid layers, with the only difference that the velocity decreases away from the surface deep into the film. At a critical thickness δ , the velocity becomes equal to zero. It can be seen from Fig. 5 that, at film thicknesses $h \geq \delta_1 + \delta_2$, melting of the surface layer can occur but cannot lead to dispersion of the film into droplets. However, this process can proceed at film thicknesses $h \leq \delta_1 + \delta_2$, when all layers have nonzero velocities.

If the experimentally measured times of the onset of melting are determined by the rate of dispersion of the molten film, the relationship for the approximation of the experimental activation energies as a function of the film thickness can be obtained by setting the Arrhenius equation equal to expression (3). As a result, we have

$$E_a = a \ln(h^2/b), \quad (4)$$

where a and b are constants. The experimental dependence of the activation energy for the melting–dispersion process on the thickness of the copper film is plotted in Fig. 6. The solid curve in this figure indicates the approximation of the experimental data by relationship (4). As can be seen, the approximation curve fits the experimental data fairly well (the correlation coefficient is equal to 0.99).

Making allowance for the above results, we propose the following mechanism of the melting–dispersion process in the copper thin film. According to relationship (1), equilibrium melting of a thin film with a particular thickness begins at a temperature that can be substantially lower than the melting temperature available in the literature for the bulk material. This is determined primarily by the contribution of the surface energy to the total energy of the thin-film system and by

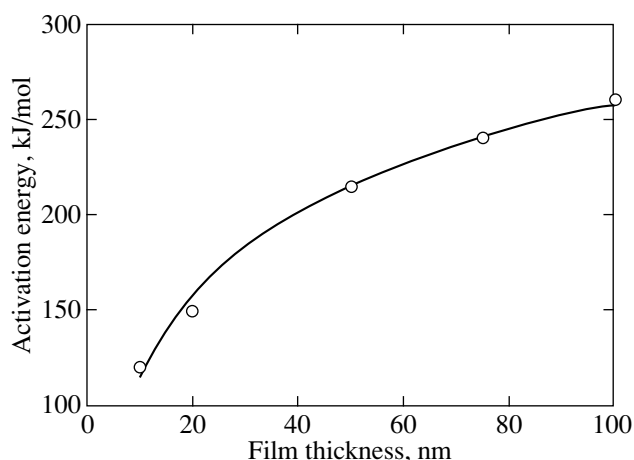


Fig. 6. Experimental dependence of the activation energy for the melting-dispersion process on the film thickness h for the copper thin film (circles) and the fit of the experimental data with function (4) (solid line).

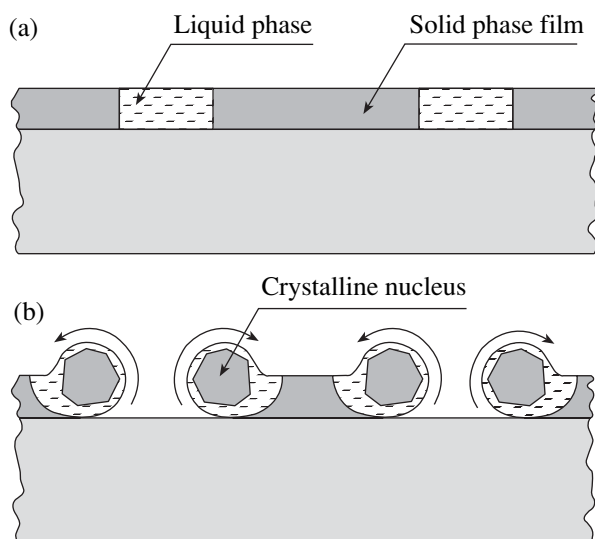


Fig. 7. Schematic diagram illustrating the melting-dispersion process in a copper thin film on an inert surface: (a) local melting of the thin film and (b) droplet formation with subsequent crystallization accompanied by a release of heat responsible for further melting of the film.

the possibility of changing the surface energy as a result of a phase transition. However, owing to the existing energy fluctuations (in particular, the surface energy fluctuations), the melting process can begin in local regions of the film (Fig. 7a) at a temperature that is a few tens of degrees lower than the equilibrium temperature determined by relationship (1). The transformation into the liquid phase is responsible for the properties that are characteristic of the liquid state, such as the fluidity and the viscosity. These properties eliminate the diffusion limitation inherent in solids at tempera-

tures that are not high and provide a way for the surface tension force to do work on the displacement of liquid layers (Fig. 5). The surface tension forces can break a film whose thickness does not exceed a critical value. This critical thickness depends on the surface tension forces along either of the two film surfaces and on the dynamic viscosity of the liquid (Fig. 5). When local breaks appear in the film, droplets are formed on the poorly wettable surface (Figs. 3b–3f). This process is energetically favorable and leads to a decrease in the total energy of the system due to the decrease in the absolute surface energy as a result of a decrease in the surface area of the system. This decrease in the total energy of the system due to the shape optimization renders the existence of the liquid impossible at such large a supercooling. Hence, the liquid at the same temperature begins to crystallize. The crystallization is accompanied by a local release of heat, which induces melting of the remaining thin film (Fig. 7b) and, as a consequence, the formation of the moving front of the melting-dispersion process (Fig. 3, region II).

Therefore, the melting-dispersion process occurring in a thin film on an inert substrate involves several competing physicochemical processes, such as local melting, shape optimization as a result of a decrease in the surface area, crystallization, and melting of the remaining film.

4. CONCLUSIONS

Thus, it has been established that, owing to the kinetic factors, the melting-dispersion process in thin films can proceed at different rates depending on the temperature. Melting of copper thin films of the same thickness can occur within different time periods depending on the temperature (from almost instantaneous melting at higher temperatures to melting proceeding over the course of a few hours at lower temperatures). This means that the process under consideration has an activation nature. The melting-dispersion process originates in local regions of a thin film, and then the front of this process propagates over the sample. The main factor responsible for the process is a tendency of the system to reduce its energy due to the decrease in the absolute surface energy. This results from the decrease in the specific surface energy upon transition from the solid state to the liquid state and a decrease in the surface area of the system. In turn, these processes become possible in the liquid state when the system possesses fluidity and the surface tension force can do work.

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