EFFECT OF TEMPERATURE ON THE PORES GROWTH IN THE POLYCRYSTALLINE FILMS OF FUSIBLE METALS

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The paper presents the results of study through porosity in polycrystalline films of lead, tin and indium deposited on amorphous carbon substrate. It is established that the heating of film exponentially increases of the average size of through pores and do not leads to an increase of their concentration, which is practically independent of the temperature until to the melting point. We have determined the activation energy of the surface self in the films of these metals.

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INTRODUCTION

The study of structural and morphological changes which occur in the thin film systems while heating and annealing is of considerable interest, both for understanding fundamental diffuse and relaxation processes proceeding in these systems, and also for tackling manifold practical problems. Due to the wide use of films as different kinds of protective coating, the analysis of continuous porosity that occurs during their formation and thermal effect, is of great applied importance.

Study of microstructure and porosity of polycrystalline metal films has a long history[1-4]. As it is stated in the research [4], the temperature of condensation has determining influence on the structure of the films. According to [4], if the temperature of the substrate (T) on which condensation is performed is higher than half of the melting temperature of the condensed substance (Ts), i.e. $T > 0.5T_s$, a structure, consisting of rather large mono-crystals, which are formed by diffusion, is formed. Under $T < 0.3T_s$, the vacuum condensates consist of small domed crystallites, which have a block structure and pores along the boundaries. A columnar structure is formed in the range of $0.3 T_s < T < 0.5T_s$, which is caused by the formation of surface self-diffusion. In accordance with the research results [5], concentration of the through pores decreases nonlinearly with the growth of the film thickness.

The present paper studies the pore formation processes while heating and annealing the fusible metals polycrystalline films of different thickness which are condensed on the amorphous carbon substrate at room temperature.

1. EXPERIMENTAL

Continuous polycrystalline films of lead, tin and indium with thickness of 200…2000 nm were used in this paper as the object of research. These films were condensed on the carbon sublayer that is poorly wetted by the melts of the studied metals. This significantly decreases interaction of the metal film with a substrate material while the studied films can be considered to a certain degree free.

The experiments were carried out in vacuum of 10^{-6} mm. Hg in the following way. Amorphous carbon film with thickness of 20 nm was condensed onto a rectangular glass substrate holder by evaporation from the voltaic arc. Then a layer of the metal under study with the desirable thickness was deposited from the molybdenum or tantalum evaporator. The film thicknesses were determined in the course of their deposition with the help of a quartz resonator. Once the condensation stopped, one end of the substrate holder was heated to a temperature above the melting point of the metal under study while the other was kept at the room temperature. As a result the gradient of the temperatures along the substrate was set which was controlled by several chromel-alumel thermocouples pressed to the back side of the substrate holder. Using this method one can observe, in one experiment, i.e. for the films formed under the same conditions on a substrate, the set of states corresponding to the systems heating to various temperatures and annealing during the same period of time [6, 7]. The obtained samples were cooled in vacuum to room temperature, removed from the vacuum unit and then studied using a scanning electron microscope Jeol JSM-840.

2. RESULTS AND DISCUSSION

Electron-microscopic study showed that the obtained films in different parts of the substrate have different morphology. In the area of the substrate, where the temperature exceeded the melting point of the metal under study, the film represented individual crystallized spherical drops. The film was solid polycrystalline below the melting temperature. In this area, through pores were formed as a result of condensation processes. Their surface area was changing during the heating and annealing processes. The melting point of indium, tin and lead is 429.3, 505 and 600.6 K correspondingly while condensation was carried out on a substrate which has room temperature (293 K). Under these conditions, these films, according to [4], are characterized by the formation of columnar and large crystallite structure.

A computer program has been developed for a quantitative study of electron microscopic images of the films. It allows to determine the pore sizes of crystallites, as well as the filling factor of the substrate with the film. In electron microscopic pictures (Fig. 1) of metal films deposited on a carbon substrate, one can see that at transition to low-temperature areas smaller pores are observed and the filling factor of the substrate with the film increases. Measurement data of average pore area and filling factor of the substrate from its temperature are presented in (Fig. 2).
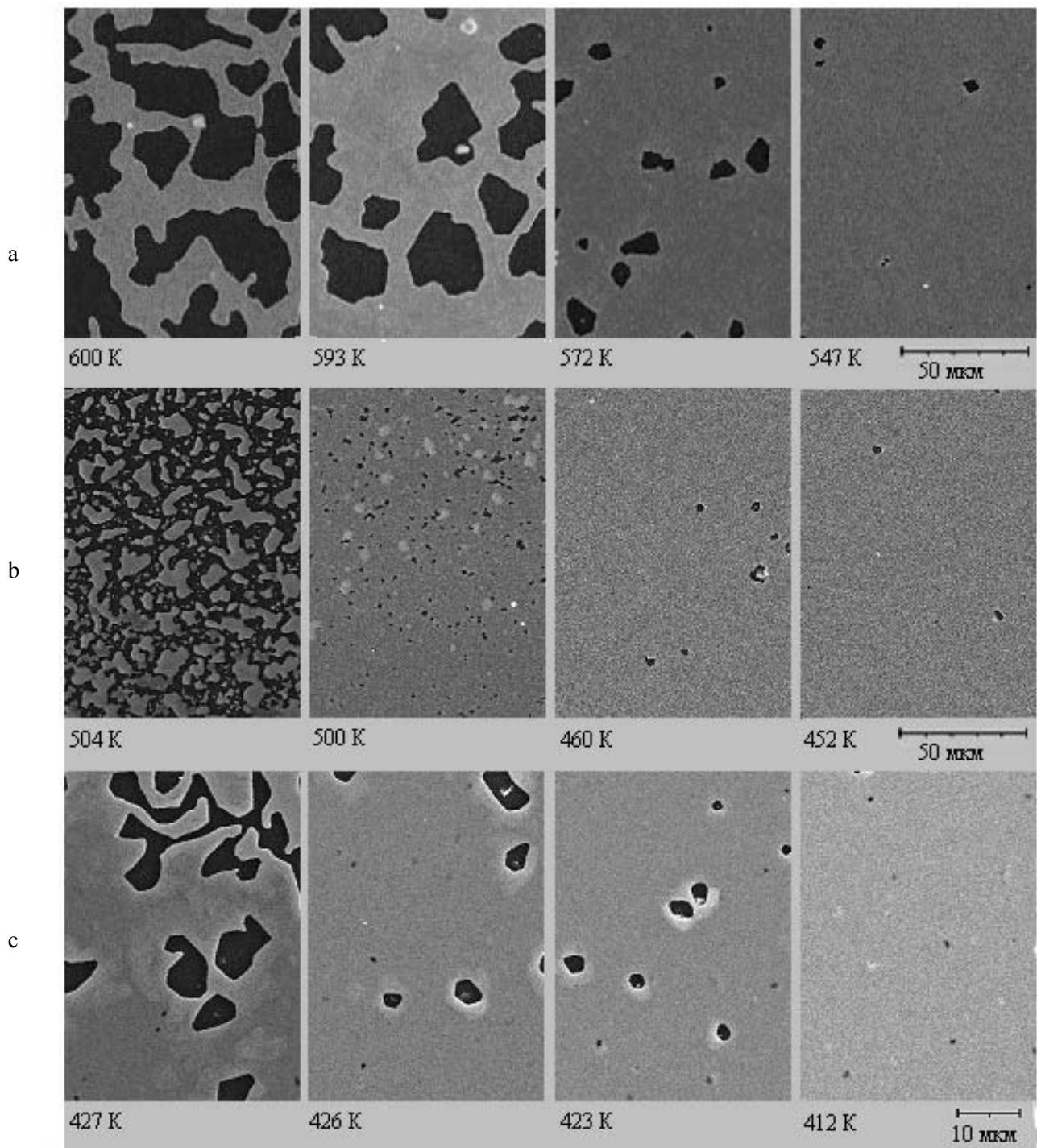
Fig. 1. SEM images of lead film (a), tin film (б), indium film (в) corresponding to different temperatures (indicated under the shot)

The diagrams show that above the melting temperature, i.e. in the area where the film is completely melted, the filling factor of the substrate with the film approaches to small constant meaning (the filling factor for completely melted lead and indium film is about 6%, tin – 12%). With transition to low-temperature areas the filling factor of the substrate with film increase, and the average size of pores decreases exponentially.
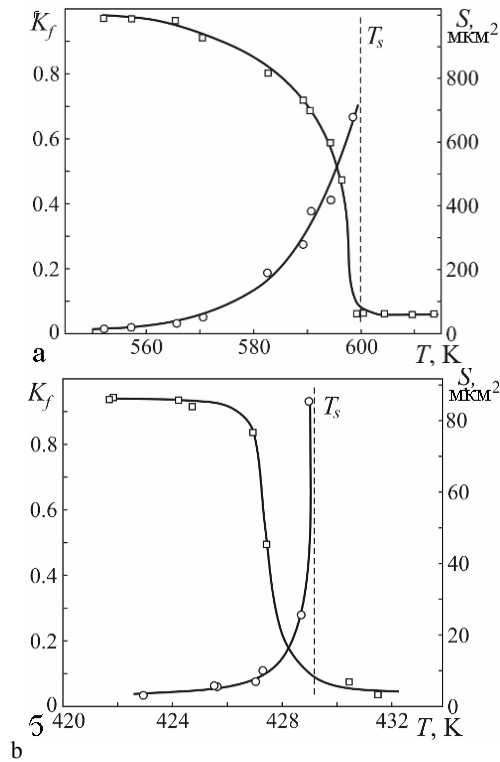
Fig. 2. Temperature dependency of the filling factor of the substrate (□) and average pore area (○) for lead film (a), indium film (b)

In the "ln(R) – 1/T" coordinates, the average size of pores depends on temperature linearly (Fig. 3).
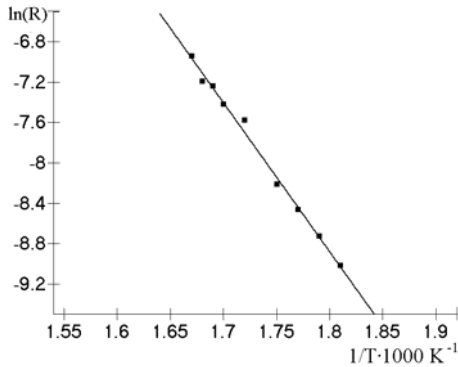

Fig. 3. Dependency of logarithm of the average pore size of the inverse temperature in the films of lead

According to [1, 8], the kinetics of pore growth is determined by surface self-diffusion and is described by the following:

$$\ln(R) = \ln\frac{2D_0\frac{\mu\sigma}{L}e^{\frac{E_a}{kT}}t\Omega}{h^2kT} = \frac{E_a}{kT} + \ln\frac{2D_0\frac{\mu\sigma}{L}t\Omega}{h^2kT}, \quad (1)$$

where R is the radius of a pore, D_0 – the surface self-diffusion coefficient, L – the characteristic average size of crystallites which surround the pore, t – the time of annealing, σ – the specific surface energy, Ω – atomic volume, μ – the width of the boundary layer, E_a – activation energy of surface self-diffusion, k – Boltzmann constant, T – temperature, h – film thickness.

In [8] is shown that in the mentioned temperature range one can neglect the temperature dependence of the second term of equation (1) and consider it a constant. Then the activation energy of the surface self-diffusion can be determined from the following:

$$E_a = \alpha k, \quad (2)$$

α – tangent line to an Arrhenius graph (Fig. 3).

The activation energy of surface self-diffusion, defined in this way, constitute 1.22, 1.62 and 1.7 eV for lead, tin and indium, correspondingly.

In literature one can find the following values of activation energy of volumetric self-diffusion: 1.11; 1.07 and 0.6 eV for lead, tin and indium, correspondingly. Obtained values seems reasonable as the activation energy of self-diffusion of surface is usually bigger than the volumetric one by 20…50%, and also the self diffusion activation energy increases when the temperature approaches to the melting point of the metal [10].

Processes of self-diffusion on the surface providing pore growth, result in an outflow of substance from a growing pore to its boundary, formation of the growths of metal around the growing pores promote rounding surfaces that limit the pores. This can be clearly seen in the pictures made by the electron microscope at a sharp angle to the plane of the substrate (Fig. 4).
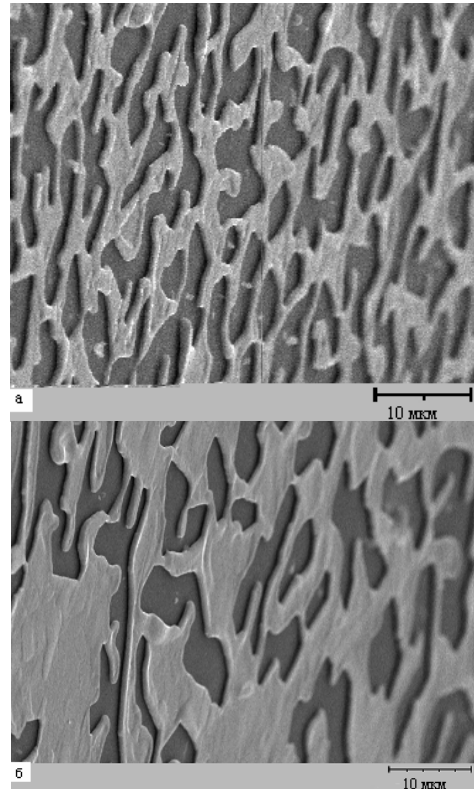

Fig. 4. SEM images of the indium (a) and lead (б) films. The angle of the substrate is 60°. The *angle of the substrate is 60°*

Study of pore density temperature dependency, i.e. their number per unit area of the film, showed that despite increasing the average size of pores as well as temperature their density actually does not change. However, there is strong dependence of pore density on the thickness of these films, namely, the density is increased when the thickness of the film is decreased

(Fig. 5). It is consistent with the model proposed in [11–13], according to which pore density of thick films decreases while the thickness grows according to the law $\approx h^2 e^{-Bh}$ (B – constant).

Such dependency of density of the pores on annealing temperature shows that the pores observed by us are not formed during heating and annealing of the film but are formed during deposition [14], besides their number increases with decreasing of thickness. It corresponds to the results of the papers [15-18], the authors of which studied the formation of porosity in the deposited films. In our experiments, the average values of density of crystallites in the studied films of lead are in the range of $(4.5…7.7) \cdot 10^4$ mm^{-2}. The average value of pores density relates to the crystallites density in lead films is about 0.015, i.e. the nuclei of pores are formed only in 1.5% of crystallites. During heating, the pores only increase in size.
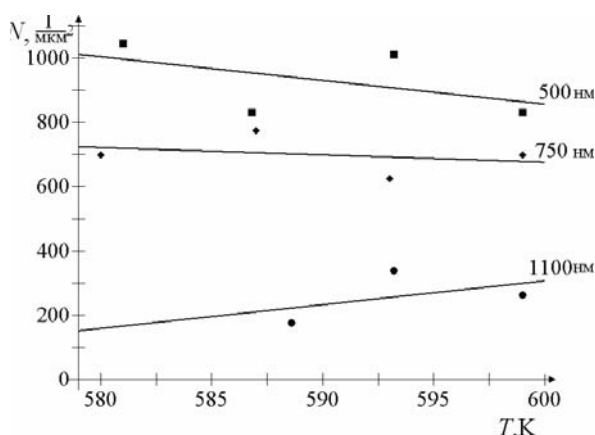

Fig. 5. Dependency of pore density on temperature for lead films with different thickness
(shown in the diagram)

The nuclei inside pores are formed in the sites with the large number of accumulations of the grain boundaries which usually are represented by triple junctions of grains. As follows from the geometric considerations the number of triple junctions, in case of completely mono-crystal films which consist of hexagonally-packed crystallites, is twice the number of the nuclei. Thus inside the pores in the studied films Pb/C, appear only in about 0.75% of triple junctions. [1] It is probably connected with the fact that according to [1] the nuclei of pores can only be triple junctions which are formed by nuclei with high degree of mutual disorientation which is related to significant excess energy.

Low degree of coalescence of the pores under temperatures of substrate close to the melting point of bulk samples, shows the fact that the internuclear space was depleted by vacancies the concentration of which determines the pore motion dynamics. The favorable vacancy sink is the growth of pores whose growth process, by-turn, is caused by holes, thus the coalescence of pores slows down, and the form of pores becomes irregular, broken (see Fig. 1). It is also clearly seen in (Fig. 4) on which the favorable region of film is captured at an angle of 60°.

CONCLUSION

In the paper the activation energy of surface self-diffusion for films of lead, tin and indium was determined. It was established that heating and annealing of the samples didn't lead to an increasing of concentration of through pores and only increased their average size. It is shown that due to depleting space between pores by vacancies, for which growing pores appear to be favorable vacancy sink, in the completely polycrystalline film of lead with thicknesses greater than 500 nm, coalescence of the pores almost can't be found up to melting point.

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ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА РОСТ ПОР В ПОЛИКРИСТАЛЛИЧЕСКИХ ПЛЁНКАХ ЛЕГКОПЛАВКИХ МЕТАЛЛОВ

С.В. Дукаров, С.И. Петрушенко, В.Н. Сухов, И.Г. Чурилов

Приведены результаты исследования сквозной пористости в поликристаллических плёнках свинца, олова и индия, напыленных на аморфные углеродные подложки. Установлено, что нагрев плёнок вызывает экспоненциальное увеличение среднего размера сквозных пор и не приводит к увеличению их концентрации, которая практически не зависит от температуры вплоть до температуры плавления. Определена энергия активации поверхностной самодиффузии в плёнках этих металлов.

ВПЛИВ ТЕМПЕРАТУРИ НА РІСТ ПОР У ПОЛІКРИСТАЛІЧНИХ ПЛІВКАХ ЛЕГКОПЛАВКИХ МЕТАЛІВ

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Наведено результати дослідження наскрізної пористості в полікристалічних плівках свинцю, олова та індію, що напилені на аморфні вуглецеві підкладки. Встановлено, що нагрівання плівок викликає експоненційне зростання середнього розміру пор та не призводить до збільшення їх концентрації, яка залишається незмінною майже до температури плавлення. Визначено енергію активації поверхневої самодифузії в плівках цих металів.