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Determination of Solid State Solubility of the Components in the Ag-Ge Film System

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The efficiency of determination of solid state solubility of the components in the system with an eutectic type of interaction (Ag-Ge) by means of measuring the sample electrical resistance during thermal cycling has been shown. Film systems were formed in a vacuum by sequential condensation of components. The solubility curve of germanium in silver, obtained from the study of the samples with silver film thickness of 100 nm, is in good agreement with available literature data. The activation energy of grain-boundary diffusion has been estimated as 0.8 eV.

Keywords: Thin films, Ag-Ge system, Mutual solubility.

PACS numbers: 64.70.kd, 64.75.Bc, 73.61.At

1. INTRODUCTION

Successful application of multicomponent films systems in modern technologies is impossible without a clear understanding of the character of the interaction between the system components. Such interaction, as a rule, is described using the phase state diagram. Methods of the X-ray structural analysis of the samples annealed at different temperatures are the most widely used for the construction of phase diagrams. However, the necessity of preparation and study of a large amount of different in composition samples makes the investigations an extremely labor intensive problem. Moreover, in the case of thin films, the X-ray scattering amplitude is often insufficient for a reliable detection of the structure of objects with the reduced dimension. The method proposed in [1] and developed in [2] allowed to simplify the construction of phase diagrams substantially in films. The given method allows to visualize the main loops of the phase diagram due to the changes in the morphology of the films which are in different phase states. However, the specified techniques, as well as any ex situ methods, have a significant disadvantage, namely, they allow to investigate only the initial and final system states and do not give information about the kinetics of the occurring processes. Moreover, such techniques are boundedly applicable for the study of the properties of nanosized systems in which, because of the increased diffusion mobility, it is not always possible to ensure that the system state will not be changed during cooling of the sample after its annealing. Therefore, development of new in situ techniques, i.e. methods in which preparation and investigation of nano-objects occurs in a single experimental cycle is actual at present [3-6]. Unfortunately, each in situ technique imposes certain constraints on the test subject. For example, in situ electron diffractometry, which is a very power tool for the investigation of the interaction of components in a solid state in film systems [4, 5], possesses an insufficient resolution and is well suited, mainly, to the systems, whose components have similar crystal structure.

In this paper we propose to use the sample electrical resistance measuring during heating – cooling cycle method for the study of mutual solubility of the components in binary film systems regardless of the type of their crystal structure. The given in situ method is extremely sensitive to the changes of the system state and established itself earlier in the study of mutual diffusion in film systems [6, 7]. One can expect that measurements of the electrical resistance of a layered film system during its heating will allow to detect the temperatures of the beginning and completion of the solid solution formation process in the investigated system. Moreover, taking into account the diffusion nature of the given process [6], one can estimate the energy of its activation. It is natural that this method is indirect one, but it can substantially supplement the existing direct investigation methods of solid state solubility of the components in binary systems.

2. INVESTIGATION OBJECTS AND TECHNIQUE

For approbation of a new technique it is convenient to use the model systems with a simple interaction type, and Ag-Ge system is one of them. Components of the given system form phase diagram of the "simple eutectic" type with mutual solubility of the components limited in a solid and unlimited in a liquid state. Eutectic composition is formed at 24.5 at. % of Ge and temperature of 651 °C. Terminal solubility of germanium in silver is equal to 9.6 at. % at the eutectic temperature, while at room temperature it does not exceed 0.1 at. %. We should note that solubility of silver in solid germanium is negligibly small [8].

The investigated film systems were formed by the sequential condensation of the components during their electron-beam evaporation from independent sources in the vacuum of $1 \cdot 10^{-7}$ mm Hg. A glass plate with predeposited sublayer of amorphous carbon was used as the substrate (Fig. 1). Carbon film prevented interaction between the substrate and studied system. Then, silver contacts were deposited on the carbon sublayer through a special mask. Further, the substrate was placed into a copper block-heater where contacts were annealed up to the temperature of 550 °C during the first heating –

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cooling cycle. Components of the studied film system were sequentially condensed on the substrate after its cooling to room temperature without breaking vacuum. Thicknesses of silver and germanium layers were controlled by the frequency drift of quartz resonator. Mass thickness of the silver film for all samples was equal to 100 nm, and of the germanium one was varied in the range of 1.5-7 nm that corresponded to the germanium concentration in the system of 2-9 at. %. Thickness of the silver film of 100 nm was chosen in order to provide sufficient electrical resistance of the layer and exclude the influence of the size effects on the studied processes.

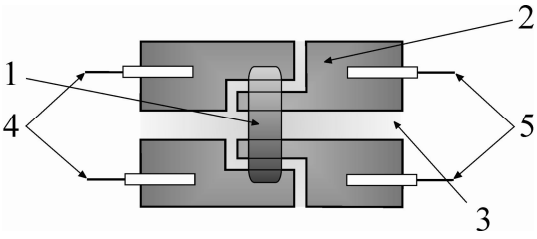

Fig. 1 – Substrate for film systems: 1 – studied sample; 2 – silver contacts; 3 – carbon sublayer; 4 – current contacts; 5 – measuring contacts

Temperature dependence of the electrical resistance of the sample was detected using four-point measurement scheme. The rate of temperature change in the heating – cooling cycles did not exceed 1 K·min^{-1}. Thermocouple of the K-type was used as a temperature sensor, measurement error was equal to ± 5 K. The error of electrical resistance determination did not exceed ± 0.1 Ohm. Measurements were performed in the automated mode by using hardware-software complex based on precision ADC, current source and PC software. In this case, maximum current through the sample did not exceed 10 μA that made it possible to ignore the effects associated with electrostimulated diffusion [9].

3. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 2 we illustrate the temperature dependence of the electrical resistance of the 100 nm thick pure silver film. It is seen that as the temperature increases, the sample resistance monotonously increases according to the temperature coefficient of resistance (TCR) up to the temperature of 450 °C. Slight bending of the curve at the temperature of 250 °C is, probably, conditioned by the relaxation of the initially non-equilibrium silver film. Upon reaching the temperature of 500 °C, the resistance begins to increase exponentially, and at 550 °C the film loses conductivity. This fact is related to the activation of the re-crystallization processes, pore formation and growth leading ultimately to the decay of a continuous polycrystalline silver film to an island one (see [10]).

Addition of Ge changes the behavior of the Ag film electrical resistance drastically. Thus, in Fig. 2 we show the temperature dependence of the electrical resistance of Ag film with the same thickness covered by a germanium layer of the thickness of 3 nm (4 at. % of Ge). As seen, up to 200 °C the resistance of Ag-Ge film system is changed similarly to the resistance of the pure silver film. Upon reaching the above mentioned temperature, the insignificant decrease in the resistance takes place due to the drift of defects and stresses in the initially non-equilibrium sample. Further, behavior of the electrical resistance is changed, and, starting from the temperature of 275 °C, its growth is observed. This is associated with the activation of the diffusion processes in the film system [6]. Ge atoms, chiefly diffusing along the Ag grain boundaries, are dissolved in silver according to the phase diagram. As the temperature increases, concentration of Ge in Ag grains increases leading to the increase in the electrical resistance, and when the temperature achieves 380 °C, the del process is completed, i.e. formation of a uniform silver-based solid solution is completed in the system in accordance with the phase diagram. With further increase in the temperature, electrical resistance of Ag-Ge solid solution monotonously increases similarly to the resistance of the pure silver film.

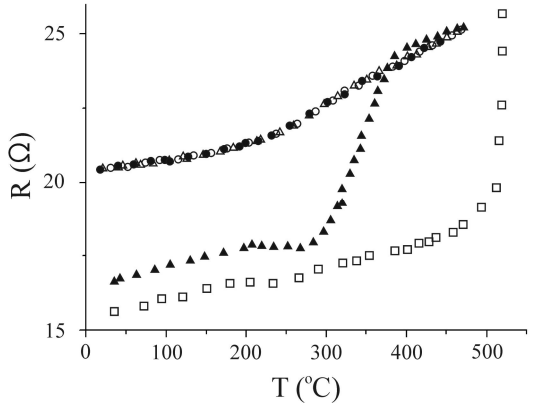

Fig. 2 – Temperature dependence of the electrical resistance of the Ag film (□) and Ge(4 at. %) / Ag film system (the first cycle: ▲ – heating, ● – cooling; the second cycle: Δ – heating, ○ – cooling). Ag film thickness is 100 nm

Upon cooling to room temperature, the film system resistance gradually decreases and undergoes a bend in the vicinity of 200 °C that is probably related with a partial decay of supersaturated Ag-Ge solid solution. It is important to note that temperature dependences of the sample electrical resistance, obtained in the repeated heating – cooling cycles, totally coincided with the cooling curve of the film system in the first cycle (Fig. 2). This indicates that all the processes typical for the investigated temperature range are completed during the first heating – cooling cycle.

Therefore, the sample electrical resistance measuring during heating – cooling cycle method allows to determine the start and finish temperatures of the solid solution formation process in layered Ag-Ge film system. Comparing the initial concentration of the components with the homogenization temperature in Ag-Ge system, one can define the terminal solubility of germanium in silver at the specified temperature. Thus, homogenization temperature in Ag-(4 at. % Ge) system was equal to 380 °C.

The similar investigations were also carried out for other film systems with different concentrations of Ge atoms. In Fig. 3 we present the results of the determination of the terminal solubility of germanium in silver at different temperatures. It is seen that the values of the solubility, obtained using the sample electrical resis-

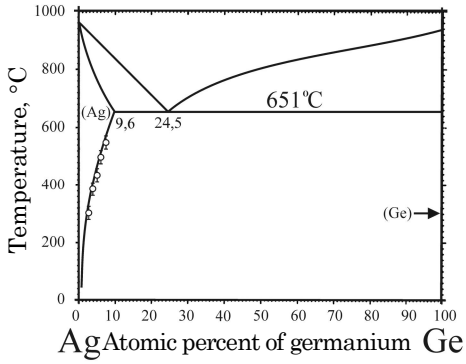

Fig. 3 – Phase state diagram of Ag-Ge system [8]. ○ correspond to the terminal solubility of germanium in silver obtained in the framework of the present study

tance measuring method, agree well with the known literature data.

By means of the technique used in the work [6] for the determination of the diffusion activation energy, the activation energy of the process occurring in the range of an abrupt increase in the Ag-Ge film system resistance was estimated. Based on the estimation, the given energy was equal to 0.8 eV. The obtained value should be, probably, considered as the grain-boundary diffusion activation energy, since electron scattering exactly on the grain boundaries makes the main contribution to the electrical resistance of polycrystalline film system [11].

Thus, as the result of the performed investigations, we have shown the effectiveness of the films electrical resistance temperature dependence measuring method for the determination of solid state solubility of the components in the systems with an eutectic type of interaction. The ability to study the nanosize film systems regardless of their crystal structure is the main advantage of the del technique. It is natural that the proposed in situ technique has some drawbacks and limitations. Thus, measurement of the electrical resistance is mainly applicable for the films of materials with good electrical conductivity and thickness sufficient for the electrical current passing.

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