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Critical thickness of contact melting in the Au/Ge layered film system

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ABSTRACT

We investigate the melting behavior of Au/Ge bilayer (Ge: 5 or 2 nm; Au: 0.1–1.1 nm) thin films using transmission electron microscopy and high energy electron diffraction. It was found that the liquid-phase formation in the system at eutectic temperature takes place only if the gold film mass thickness values are greater than the critical one (0.2 nm). This effect is revealed to be independent of the contact-heating sequence of the components.

1. Introduction

It is known [1] that the heating of contacting crystals of two substances, which form an eutectic system, gives rise to their melting at a temperature lower than the melting temperature of each of them. This effect has come to be known as contact melting.

In recent years, the problems of nanotechnology, micro- and nanoelectronics have motivated numerous investigations of phase transformations in binary alloys, including those the components of which form eutectic-type diagrams [2]. It has been found [3] that if one of the components in the form of a thin film is on the surface of the macroscopic sample, or is between two films of the second component, then with a decrease in the film thickness the contact melting temperature decreases. This was observed for binary layered film systems, where the film of a more readily fusible component (In, Sn, Bi, Pb) was embedded between two thick films of a higher-melting-point aluminum. The melting temperature behavior has been investigated [3] as the film thickness of a more easily fusible component was reduced only down to ~10 nm. At smaller thicknesses the films of the mentioned metals are islands in accordance with the Volmer–Weber mechanism and it is difficult to determine the melting point from the changes in their morphological structure. Therefore, it has remained unclarified to what minimum thickness value the contact melting temperature depression would be observed, though the contact melting effect is generally considered [1] not to be associated with a definite mass ratio of contacting crystals, but the complete transition to the liquid state at eutectic temperature occurs only at eutectic relationship of their masses.

In the studies of condensed films of variable composition and variable state of the Sn–Bi binary system (the films being produced by simultaneous condensation of the components as these are evaporated from independent sources), an increase of bismuth solubility in tin with a rise in temperature was visualized along with the attainment of the maximum value of solubility at eutectic temperature [4]. On this basis, it has been suggested that there might exist a critical thickness of contact melting, i.e., the thickness, below which the liquid phase of eutectic composition should not be formed in the contact zone, as the film is brought into contact with the macroscopic sample of the second component [5].

Gladkikh [5] has investigated the melting of Sn–Bi bilayer films obtained by way of successive vacuum condensation of the components at different ratios of layer thicknesses, including the ratio corresponding to the eutectic composition. Their electron microscope investigations have revealed the existence of the critical thickness, which was found for the mentioned system to be about 1.5 nm. However, since in the Sn–Bi system the two components are easily fusible at such small thicknesses there emerge difficulties [5] in determining the critical thickness on the basis of electron microscope investigations of morphological restructuring under melting. Therefore, it appeared reasonable to continue the critical thickness studies with the use of layered film systems of eutectic type having rather high melting temperatures of contacting components at a relatively low eutectic temperature. From methodical considerations, it seems most justifiable in this case to choose such systems, the components of which will permit the formation of continuous films at small thicknesses. The mentioned studies are also of importance for clarifying and extending the existent notions about the mechanism of eutectic melting.

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2. Materials and methods

For the subject of research we have chosen a nanosized Au/Ge bilayer film system, the components of which form the phase diagram of simple eutectic type with a rather restricted solubility in a solid state. The eutectic point lies at 12 wt.% Ge and 356 °C. The solubility of germanium in solid-state gold makes 1.17 wt.% and less than 0.1 wt.% at eutectic temperature and room temperature, respectively; the solubility of gold in solid-state germanium is negligible [6]. The choice of the Au–Ge system has been specified first of all by the fact that with rather high melting temperatures of individual components (Au – 1063 °C and Ge – 958.5 °C), together they form the eutectic with the melting temperature being approximately by a factor of ≈3 lower. Methodically, this substantially simplifies the experiments aimed to determine the critical contact melting thickness. Besides, the germanium films, produced in vacuum by means of thermal evaporation and condensation on the substrate at room temperature, are amorphous and remain in this state at the subsequent annealing up to ≈500 °C [7]. At the same time, in the process of condensation the films are formed to be continuous at comparatively small thicknesses (beginning with a few nanometers).

The layered film systems were prepared by means of successive condensation of Ge (99.99%) evaporated from a tantalum source and of Au (99.999%) – from a tungsten heater on carbon amorphous substrates. The process was performed in a high vacuum chamber at residual gas pressure less than 5×10^{-8} mm Hg. An extended copper block served as a substrate holder. The block included the built-in heater, thermocouples and a system of masks for accommodating and fixturing thin NaCl crystal cleavages, onto which a ≈10 nm thick amorphous carbon film was precondensed from the arc discharge. The geometrical arrangement of the substrate holder, evaporators and the system of shutters between them enabled us to produce in a single experiment both the germanium films of nearly the same thickness along the whole length of the substrate holder and the gold films of variable thickness in the desired interval. The mass film thickness was determined with a piezo-quartz sensor. Prepared and investigated were two types of systems: (i) the layered systems produced by successive condensation of germanium and gold at room temperature of the substrate, after heated at a temperature somewhat over the eutectic temperature; (ii) the systems, where the germanium film was condensed at room temperature of the substrate, then was heated to a certain temperature and the gold was condensed. After the samples were cooled down to room temperature and were separated from NaCl crystals, they were examined in the transmission electron microscope Selmi PEM-125K.

3. Experimental results and discussion

According to the task assigned, electron microscope investigations were made with two series of Au/Ge layered film systems.

In one of them, as mentioned above, the germanium film of approximately the same thickness (≈2 nm) was successively condensed at room temperature, and the gold film mass thickness varied in the range between 1.1 and 0.1 nm. After the condensation was stopped, the system was in situ heated up to 361 °C, and then was cooled down to room temperature.

In the other series of experiments, the germanium film, ≈5 nm thick, was condensed on the substrate at room temperature; then the substrate holder was heated up to a temperature of 250 °C. It is just at this temperature that the gold film of thickness ranging from 1.1 to 0.1 nm was condensed. After that the resulting Au/Ge system was cooled down to room temperature. In the process of gold condensation on the germanium film, the temperature of the latter was chosen to be 250 °C, because in this case the liquid-eutectic particles, initially formed at condensation owing to the dimensional dependence of the melting temperature, persist in the supercooled liquid state even at larger sizes. This is due to the fact that in accordance with the data available in the literature [8], the temperature of spontaneous crystallization of supercooled Au–Ge eutectic on solid germanium is expected to be below 250 °C.

The investigation of the mentioned two series of film systems has been motivated by the following fact. The macroscopic sample observations [1] have established that the eutectic temperature is independent of the contact-heating sequence, i.e., it has one and the same value both at creating at first a contact and then heating of the system, and conversely, at first heating of individual samples up to the eutectic temperature, and then bringing the samples into a contact.

The electron microscope studies of layered film systems with a variable gold film thickness, which were produced in the two mentioned series of experiments, have given identical results.

The layered samples prepared at room temperature of the substrate with relatively thick gold films clearly exhibit spherical particles over the whole area of the film system (see Fig. 1(a)–(c)).

Judging from the spherical form, the mentioned particles have probably resulted from the formation of liquid eutectic followed by its crystallization on cooling. With a reduction in the Au film thickness the size of isolated spherical particles decreases, and below a certain critical thickness, which makes 0.2 nm, the particles are no longer seen. The bilayer systems have a homogeneous structure with a practically unresolved relief (Fig. 1(d)), though the elemental analysis (Fig. 2) unambiguously points to the presence of gold in this sample.

For the series (ii) of layered samples prepared at a substrate temperature of 250 °C, the electron microscope examination reveals similar structural changes with thickness. With a reduction in the Au film thickness the amount of liquid phase decreases, and below a certain critical thickness the eutectic particles are no longer observed. In this case, the critical thickness is equal to ≈0.25 nm, i.e., the thickness values for the both series of samples are close (Fig. 3). At these small values of the Au film mass thickness it can be supposed that the critical thickness values of contact melting for the two series of samples are the same.

It is also necessary to take into account the difference in the nature of the liquid phase and the mechanisms of its formation in both the Au/Ge systems condensed at room temperature of the substrate with a subsequent heating up to 361 °C, and the systems with Au condensation on the germanium film at 250 °C. In the first case, the spherical particles result from the crystallization of equilibrium liquid phase formed at the eutectic temperature. In the second case, the spherical particles represent liquid eutectic, the formation of which in the process of condensation is associated with the dimensional dependence of its melting temperature and persistence in nonequilibrium state at greater thicknesses.

Considering the critical thickness value obtained, it should be pointed out the following. In the studies of gold condensation on the silicon single-crystal surfaces being at temperatures between 700 and 800 °C, the slow electron microscopy examination has revealed that with a growth of the gold layer there occurs the formation of terrace steps, and then, of completely ordered facets (1 1 9) [9]. As the thickness of condensed gold becomes greater than the thickness approximately corresponding to a monolayer, liquid-phase drops appear. This corresponds to the thickness 0.3–0.4 nm.

Attention is drawn, particularly at a rather substantial gold film thickness, to a total absence of monocrystalline particles having a spherical shape; most of the particles are two-crystal. For comparison, it may be noted that, generally, in the case of pure metal films, the spherical particles formed after melting–crystallization are mainly monocrystalline, the more so for the sizes studied in the present work.

The undertaken elemental analysis of separate particles (see the spectrum in Fig. 4) unambiguously points to their two-phase nature, which is the result of liquid-eutectic formation and subsequent crystallization in the layered film system. In the contact zone, as a result of diffusion processes at eutectic temperature, there occurs the formation of concentration dipoles on the basis of solid solutions of the one and the other components [10]. If the solution concentrations attain the maximum values at eutectic temperature, and their mass ratio corresponds, according to the lever rule, to the eutectic ratio, then at a sufficient total mass there arise critical nuclei of the eutectic. Naturally, during crystallization the eutectic immediately decays into two phases that represent solid solutions based on the contacting components.

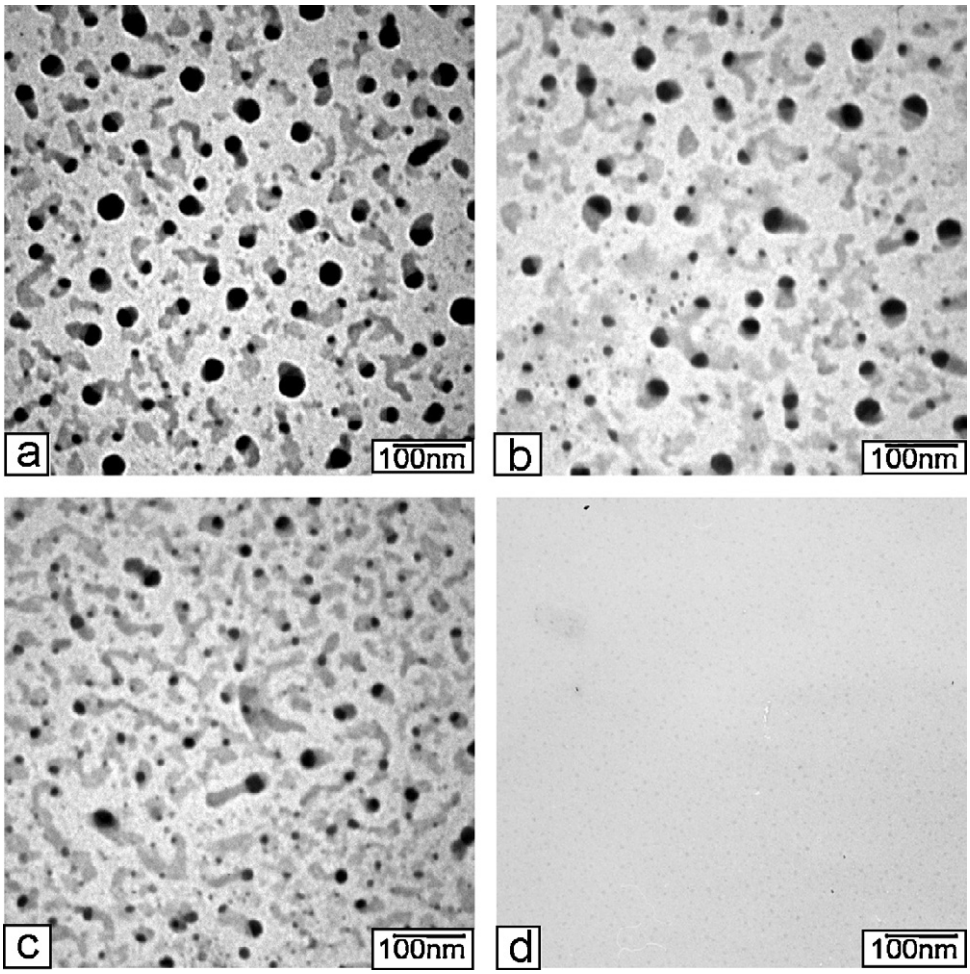

Fig. 1. Microscopic pictures of the Au/Ge films prepared on the substrate at room temperature and then heated up to 361 °C. The Ge film thickness is 1.9 nm; the Au film mass thicknesses are 1.1 nm (a), 0.8 nm (b), 0.4 nm (c), and 0.2 nm (d).

Diffraction examinations of the sets of samples under study provide a direct strong evidence for the liquid eutectic formation in the layered Au/Ge system and its subsequent crystallization with production of a phase mixture with gold and germanium as the basis.

The diffraction pattern of the layered system with the gold film thickness below the critical value shows only diffuse haloes corresponding to the amorphous germanium film (Fig. 5(b)). In view of the small amount of gold, its reflections are not seen, though, as mentioned above, the presence of gold is confirmed by the elemental analysis.

The diffraction patterns taken from the samples of the layered systems comprising spherical particles, i.e., at the gold film thickness greater than the critical value, exhibit not only the haloes from the amorphous film of germanium, but also the diffraction rings corresponding to crystalline germanium, and also the lines of gold (Fig. 5(a)). At the same time, in the layered systems, immediately after condensation at room temperature of the substrate, the lines of crystalline germanium are not observed at all.

The electron diffraction studies in combination with electron microscopy data unambiguously point to the production of liquid eutectic in the Au/Ge system at Au mass film thicknesses exceeding the critical value. In the process of crystallization the liquid eutectic decays to produce a two-phase system of crystalline solutions based on gold and germanium. Presumably, this is also testified by the fact that the lattice parameter of gold in the crystallized spherical particles is somewhat higher than the tabulated value and the value that corresponds to the initial layered film system condensed at room temperature of the substrate. This may be due not only to the fixation of the oversaturated solid solution of germanium in

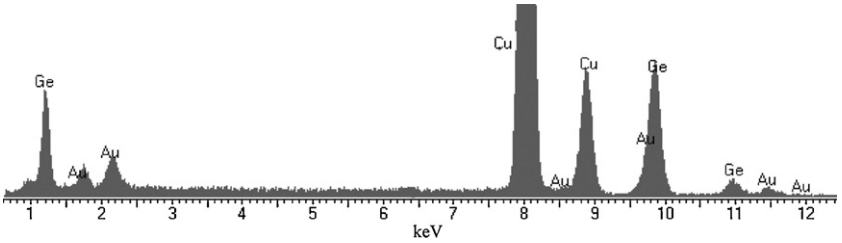

Fig. 2. Energy spectrum of characteristic X-ray radiation of the Au/Ge film system presented in Fig. 1(d) (copper peaks relate to TEM grid).

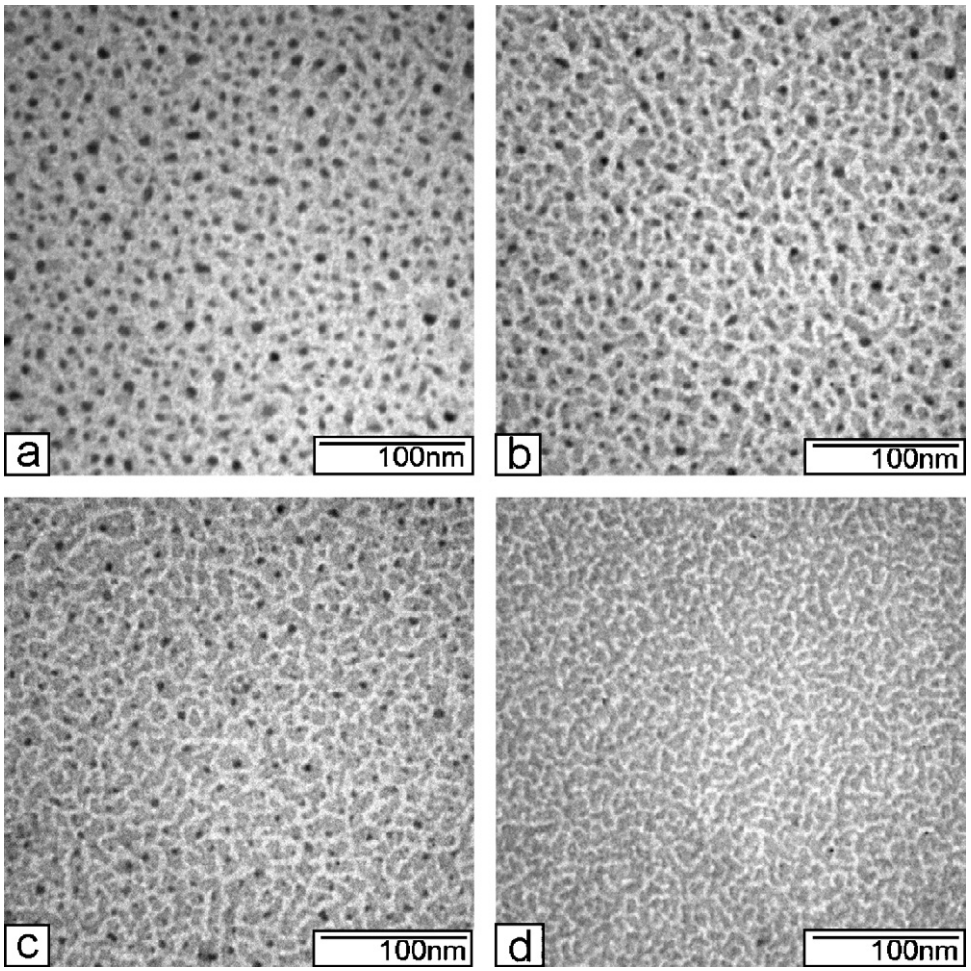

Fig. 3. Microscopic pictures of the layered Au/Ge system, prepared by condensation of germanium on the substrate at room temperature, with subsequent heating up to 250 °C and gold condensation. The Ge film thickness is 5 nm; the Au film mass thickness values are 1.1 nm (a), 0.8 nm (b), 0.5 nm (c), and 0.25 nm (d).

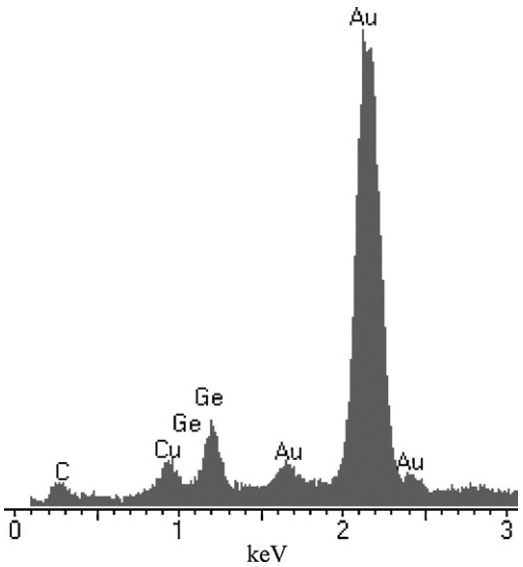

Fig. 4. Energy spectrum of characteristic X-ray radiation of a separate crystallized particle of Au/Ge eutectic on a carbon substrate (Cu peak relates to TEM grid).

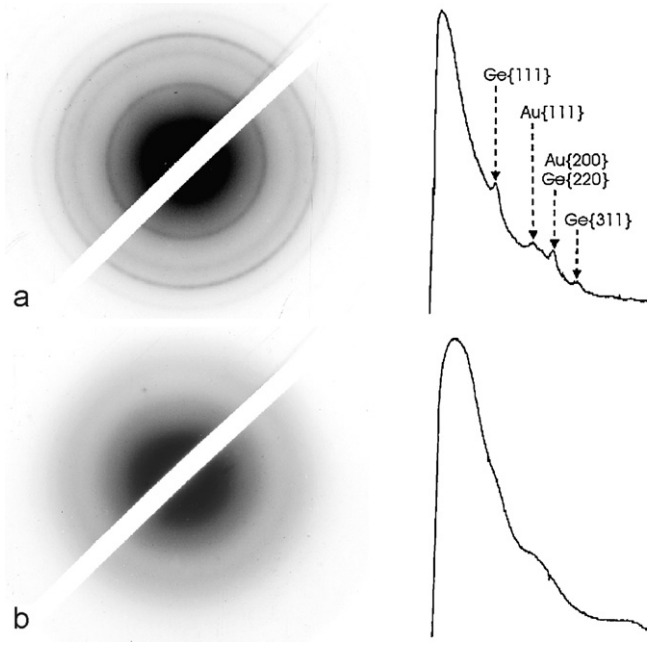

Fig. 5. Diffractograms and the corresponding photometer curves of the Au/Ge films prepared on the substrate at room temperature and then heated up to 361 °C. The Ge film thickness is 1.9 nm, the Au film mass thicknesses are 0.4 nm (a) and 0.2 nm (b).

gold, but also to the known increased solubility in small particles as compared to the macroscopic samples.

4. Conclusion

The undertaken investigations and their analysis have indicated that in the Au/Ge layered film system prepared by means of successive condensation of the components and consisting of a germanium film of constant thickness and a gold film of variable thickness, the liquid-eutectic formation at eutectic temperature takes place only if the gold film thickness is greater than the critical value.

The use of amorphous films of germanium in the layered system under study has provided direct diffraction evidence for the formation of liquid eutectic in the films. In the process of crystallization the liquid eutectic decays into two phases that represent the crystalline solutions with gold and germanium as the basis.

Acknowledgment

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