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Interactions in Ga–AgAu thin film system

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Interaction of Ga layers with thin films of AgAu alloys with variable Au content (2–62 % by mass) are shown to result in formation of AgAuGa ternary phases having lattices similar to those observed in binary systems: γ-AgGa, γ-AuGa, AuGa, $AuGa_2$. As the Au concentration in the binary AgAu alloy increases, the transitions are observed from the single-phase region to the double- and triple-phase ones and then the double-phase one again (phase types γ-AgGa → γ-AgGa + AuGa($AuGa_2$) → γ-AgGa + → γ-AuGa + $AuGa_2$ → γ-AuGa + $AuGa_2$).

Показано, что при взаимодействии слоев Ga с тонкими пленками сплавов AgAu переменной концентрации (2–62 мас.% Au) образуются фазы тройной системы AgAuGa с решетками, по типу сходными с наблюдаемыми в двойных системах: γ-AgGa, γ-AuGa, AuGa, $AuGa_2$. При увеличении концентрации Au в двойном сплаве AgAu наблюдается переход от однофазной области к двух-, трех- и снова в двухфазную (фазы типа γ-AgGa → γ- AgGa + AuGa($AuGa_2$) → γ -AgGa + → γ-AuGa + $AuGa_2$ → γ-AuGa + $AuGa_2$).

The solid surface wetting by a liquid phase is known to be determined by the ratio of interphase surface energies on the solid-liquid-environment interfaces [1]. In systems where an interaction takes place, as for example metal pairs Ga–Ag, Ga–Au, the wetting is affected considerably by dissolution, diffusion processes, chemical reactions on the solid-melt interface, etc. In [2, 3], data are presented on the interaction of thin Ga layers with Ag, Au and some AgAu alloy films. It has been shown [2] that in the thin-film Ga–Ag system where the Ga interaction with Ag results in formation of the AgGa γ-phase, an unrestricted wetting (spreading) is observed while no wetting at all takes place in the Au–Ga system. The wetting of AgAu alloy thin films by Ga is of a non-monotonous character [4]. The purpose of this work is to study the Ga interaction with thin films of AgAu alloys in a wide range of composition variations resulting in changes of the interphase surface energy on the Ga–AgAu interface.

The Ag–Au alloy films were prepared by the consecutive evaporation of Ag and Au in 10^{-4} Pa vacuum from two separate sources and their condensation onto extended glass plates where a NaCl layer was deposited preliminarily. Then, after one day of exposure at ambient temperature (for homogenization and formation of variable alloy content along the substrate), a 20 nm thick Ga layer was condensed onto the film surface. The concentrations of components in bilayer (AgAu) and three-layer (AgAuGa) films were calculated using the laws of the condensate thickness distribution on the substrate. To provide a more smooth concentration change in the bilayer Ag–Au films, three sets of samples were studied where the component masses corresponded to different $m_{Ag} : m_{Au}$ ratio values: 22:1 (1), 4.65:1 (2) and 1.39:1 (3). In that manner, the bilayer

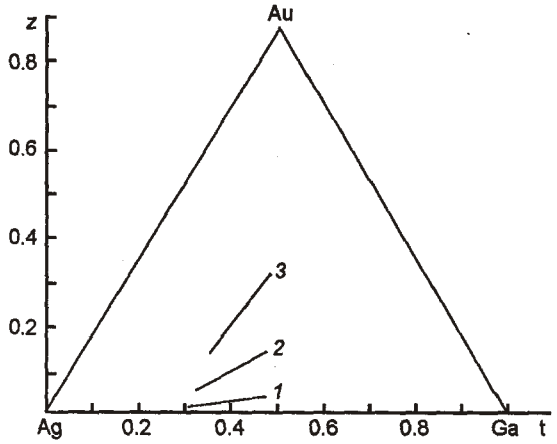

Fig.1. Mutual arrangement of oblique coordinates c_{Ag}, c_{Au}, c_{Ga} of concentration triangle Ag–Au–Ga and orthogonal coordinates z, t and concentration relationships of studied ternary Ag–Au–Ga alloys: Ga + AgAu (2–8 % Au) (1); Ga + AgAu (12–24 % Au) (2); Ga + AgAu (25–62 % Au) (3).

Ag–Au films were obtained exhibiting the concentration intervals along the substrate (2–9), (8.8–32) and (25–62) % Au by mass.

The calculated concentration relationships in three-layer AgAuGa films for three film sets (1), (2) and (3) are presented in Fig.1. To construct these plots, a z, t coordinate system was used associated with Ag, Au, Ga concentrations by expressions $z = c_{Au}\sin 60°$, $t = 1 - c_{Ag} - c_{Au}\cos 60°$. It is seen from Fig.1 that the concentration dependences for the prepared ternary alloys Ga–Ag–Au are shaped as straight lines having different slopes with respect to the t axis: $\varphi_1 = 8.4°$, $\varphi_2 = 30.3°$, $\varphi_3 = 54.9°$.

The structures of ternary Ga–Ag–Au films corresponding to compositions presented in Fig.1 were studied. The films were separated from the substrate, transferred onto copper gauze and examined using transmission electronography. The electron diffraction patterns were interpreted using the standard structure analysis methods and taking into account that in the ternary Ga–Ag–Au system, phases with lattices identical with those being formed in binary Ag–Ga and Au–Ga ones are probable to be formed. In the bulk Ag–Ga system state, two hexagonal phases exist: the AgGa γ-phase (a = 7.767 Å, c = 2.8778 Å) and the high-temperature β-phase (a = 2.8869 Å, c = 4.6753 Å) [6]. In the Au–Ga system, the following phases exist: Au_7Ga_2 (~Au_3Ga; hexagonal lattice, a = 7.724 Å, c = 8.751 Å), Au_2Ga (rhombic lattice of Pd_2As type, a = 3.199 Å, b = 18.023 Å, c = 6.998 Å; high-temperature, being formed at T = 350°C), AuGa (the MnP type lattice, a = 2.874 Å, b = 6.267 Å, c = 3.421 Å), γ-phase (an electron compound with the electron concentration 21/13, the lattice is not described), Au_7Ga (the Ti_3Ni lattice, a = 2.874 Å, c = 9.426 Å) [6–9].

For all known phases of binary systems, the interplane distance sets were calculated which were used to interpret the electron diffraction patterns obtained.

Ga interaction with Ag–Au alloys at Au contents from 2 to 8 % by mass results in formation of a phase with hexagonal lattice having parameters close to the AgGa γ-phase ones and amounting to a = 7.72 Å, c = 2.88 Å. As the Au concentration increases, along with lines of the ternary system γ-phase, a line set (reflections from planes with interplane distances d_{hkl} 3.45; 2.14; 1.81; 1.60; 1.35 Å) is observed which can be ascribed with the same probability either to a phase with the MnP lattice or to that with the $AuGa_2$ type one. In the last case, the most intense lines are those resulting from the reflection from (111), (200), (310), (311) planes with interplane distances 3.507; 2.148; 1.92; 1.831; 1.358 Å. The phase with the lattice of MnP type (AuGa) is characterized by the line set corresponding to interplane distances 3.42 Å (010), 2.14 Å (211), 1.60 Å (004), 1.35 Å (222).

At Ga interaction with AgAu alloys having Au concentration from 12 to 24 % by mass, three phases are observed: those with γ-phase type lattices AgGa, $AuGa_2$ and a cubic phase (a = 11.17 Å). The phase with the $AuGa_2$ (CaF_2) type lattice exhibits, along with intense (111), (220), (310), (311), (400) lines, a set of weaker ones with intensities proportional to $16(f_1 - 2f_2)^2$ where f_1, f_2 are atomic function of electron scattering by gold and gallium atoms, respectively. These lines are due to reflections from (200), (222), (321), (420) planes with interplane distances 3.04; 2.18; 1.82; 1.35 Å. The reflections ascribed to the cubic lattice with the parameter a = 11.17 Å were succeeded to be indexed due to that the phase

Table 1

d_{exp}	(hkl)	a, Å	(hkl)	a, Å
3.77	(300)	11.3	–	–
3.45	–	–	(111)	6.0
2.78	(400)	11.2	–	–
2.61	(330)	11.1	–	–
2.50	(420)	11.18	–	–
2.28	(422)	11.18	–	–
2.18	(510)	11.11	–	–
2.16	(511)	11.2	–	–
2.12	(520)	11.4	–	–
1.97	(440)	11.10	–	–
1.88	(600)	11.30	–	–
1.80	–	–	(311)	6.00
1.59	(550)	11.20	–	–
1.50	(642)	11.20	–	–
1.39	(800)	11.10	(331)	6.00
1.37	–	–	(420)	6.12
1.34	(653)	11.20	–	–
1.29	(622)	11.21	–	–
1.25	(840)	11.18	(422)	6.12
1.22	(842)	11.18	–	–
1.20	(664)	11.20	–	–
1.15	(763)	11.15	–	–
1.08	(1022)	11.20	(440)	6.11
	a_{aver} = 11.19		a_{aver} = 6.06	

has the single-crystal structure in some cases.

The reflexes arranged in vertices of a square network correspond to reflections from planes with d_{hkl} values 2.78; 1.97; 1.40; 0.925; 0.88 Å. When the cubic lattice is oriented so that the [001] direction is parallel to the normal to the film plane, the reflexes observed can be indexed as those corresponding to reflections from (*h*00), (*hh*0), etc., plane types. We have taken into account that in the ternary system, as well as in the binary Au–Ga one, a Hume-Roserie γ-phase can be formed having a complex cubic lattice based on the tripled cubic lattice of the solvent. Therefore, we have ascribed indices (400), (440), (800), etc., to those reflections. As a result, the parameter of the single-crystal cubic lattice turned out to be from 11.17

Table 2

d_{exp}	(hkl)	a, Å	(hkl)	a, Å
3.50	(111)	6.06	–	–
3.05	(200)	6.10	–	–
2.55	–	–	(420)	11.40
2.31	–	–	(422)	11.3
2.15	(220)	6.08	–	–
1.83	(331)	6.07	–	–
1.76	(222)	6.09	–	–
1.62	(321)	6.05	(444)	11.20
1.51	(400)	6.04	(642)	11.30
1.39	(331)	6.06	–	–
1.36	(420)	6.08	–	–
1.23	(422)	6.03	–	–
	a_{aver} = 6.07		a_{aver} = 11.3	

to 11.30 Å (at $a_{Au} \approx a_{Ag} \approx$ 4 Å). Thus, compositions of the films arranged on the curve (2) in Fig.1 correspond to the three-phase region.

Ga interaction with Ag–Au alloys at Au contents from 25 to 62 % by mass results in formation of three-component alloys Ga–Ag–Au with compositions corresponding to the curve 3 (Fig.1). These relate to the biphase region of the ternary diagram and contain a mixture of phases with $AuGa_2$ type lattices, a = 6.06 to 6.07 Å, and a complex cubic one with a = 11.2 to 11.3 Å. Table 1 contains calculated data for the Ga–AgAu system with (20–40) % Au by mass that are typical for the whole concentration range. As the Au concentration in alloys characterized by the curve (3) increases, the number of diffraction lines due to $AuGa_2$ type phase grows (weaker (200), (222), (321), (420), etc. reflections appear) while the line number due to γ-AuGa Hume-Roserie phase diminishes, that is seen from Table 2 presenting the calculation data for Ga–AgAu alloys containing 50 to 60 % of Au. Note that this trend is typical for alloys with compositions corresponding to the curve 2, too. Thus, Ga–AgAu alloys according to the curve (3) are related to the biphase region.

Thus, the electronographic examination of the phase composition for alloys formed under interaction of about 20 nm thick gallium layers with thin films of silver-gold alloys with continuously variable composition in the range from 2 to 62 % Au by

mass have shown that the phases being formed under that interaction have lattices similar to those observed in two-component systems Au–Ga, Ag–Ga, namely, γ-AgGa, γ-AuGa, $AuGa_2$, AuGa. When the composition varies according to the curve (1), Fig.1, the transition from the single-phase to biphase region is observed. The alloys with compositions corresponding to the curve (2) belong to the triphase region. At higher Au contents (curve 3), the layer interaction results in formation of a mixture of two phases.

The structure changes found do not allow to interpret the oscillation character of Ga spreading on the AgAu alloy surface observed in [4] as a phenomenon due only to changes of the interphase energy on the drop (Ga)-substrate (AgAu) interface.

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Дослідження взаємодії в тонкоплівковій системі Ga–AgAu

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Показано, що при взаємодії шарів Ga з тонкими плівками сплавів AgAu змінної концентрації (2–62 мас.% Au) утворюються фази потрійної системи AgAuGa з гратками, подібними тим, що існують в подвійних системах: γ-AgGa, γ-AuGa, AuGa, $AuGa_2$. При збільшенні концентрації Au в подвійному сплаві AgAu спостерігається перехід від однофазної області до двох-, трьох- і знову до двофазної (фази типу γ-AgGa → γ-AgGa + $AuGa(AuGa_2)$ → γ–AgGa + γ–AuGa + $AuGa_2$ → γ–AuGa + $AuGa_2$).