Металлофиз. новейшие технол. / Metallofiz. Noveishie Tekhnol.
2017, т. 39, № 10, сс. 1299–1306 / DOI: 10.15407/mfint.39.10.1299
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ЭЛЕКТРОННЫЕ СТРУКТУРА И СВОЙСТВА

PACS numbers: 61.05.cp, 61.66.Dk, 68.37.Hk, 72.15.Eb, 73.61.At, 81.15.Ef, 81.40.Rs

Electrical Resistivity of the $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ Solid Solutions with Structure of AlB_2 Type

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Electrical properties (resistivity and temperature coefficient of resistivity) of the $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ solid solutions are studied using the model coatings deposited on mica substrate. Analysis of temperature dependences of the resistivity reveals that YGa_2 compound as well as the solid solutions on its base possess a metallic conductivity. Substitution of a certain part of the gallium atoms in YGa_2 compound belonging to AlB_2-type structure with germanium, silicon or aluminium atoms leads to decrease of resistivity in the Ga → Ge → Si → Al series that may be caused by both the nature of atoms themselves and technological parameters of coatings' preparation (primarily, by their homogeneity).

Key words: intermetallics, electrical properties, crystal structure, x-ray diffraction.

Електричні властивості (електроопір і температурний коефіцієнт електроопору) твердих розчинів $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ та $Y(Ga,Ge)_2$ досліджено з використанням модельних покриттів відповідних стопів на слюді. Аналіза температурних залежностей електроопору показала, що як сполука YGa_2, так і тверді розчини на її основі мають металічну провідність. Заміщення певної частини атомів Ґалію в сполуці YGa_2, що належить до структури типу AlB_2, на атоми Ґерманію, Силіцію або Алюмінію приводить до зменшення електроопору в ряду Ga → Ge → Si → Al, що може бути зумовлено як природою самих атомів, так і технологічними особливостя-

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Please cite this article as: M. P. Semen'ko, N. M. Bilyavina, and O. I. Nakonechna, Electrical Resistivity of the $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ Solid Solutions with Structure of AlB_2 Type, *Metallofiz. Noveishie Tekhnol.*, **39**, No. 10: 1299–1306 (2017), DOI: 10.15407/mfint.39.10.1299.

ми одержання покриттів (перш за все, їх гомогенністю).

Ключові слова: інтерметаліди, електричні властивості, кристалічна структура, рентґеноструктурна аналіза.

Электрические свойства (электросопротивление и температурный коэффициент электросопротивления) твёрдых растворов $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ и $Y(Ga,Ge)_2$ исследованы с использованием модельных покрытий соответствующих сплавов на слюде. Анализ температурных зависимостей электросопротивления показал, что как соединению YGa_2, так и твёрдым растворам на его основе присущ металлический тип проводимости. Замещение определённой части атомов галлия в соединении YGa_2, которое относится к типу AlB_2, атомами германия, кремния или алюминия приводит к уменьшению электросопротивления в ряду $Ga \to Ge \to Si \to Al$, что может быть обусловлено как природой самих атомов, так и технологическими особенностями изготовления покрытий (прежде всего, их гомогенностью).

Ключевые слова: интерметаллиды, электрические свойства, кристаллическая структура, рентгеноструктурный анализ.

(Received January 12, 2017; in final version, September 26, 2017)

1. INTRODUCTION

Binary intermetallic YGa_2 is a congruently melting at 1350°C compound [1] with the enthalpy of formation defined by the high temperature reaction calorimetry method equals to –64,4 kJ/(g·atom) at 298°C and –61,8 kJ/(g·atom) at 1125°C [2]. Gallide YGa_2 is crystallized in the AlB_2-type structure ($a = 0.4217$ nm, $c = 0.4111$ nm). Structurally Ga atoms in YGa_2 are centred the trigonal prism of yttrium atoms and form itself the graphite-like nets. Calculations of the charge density distribution by using the plane wave pseudopotential method have revealed that Ga–Ga bond in these gallium nets possess strong covalent nature, which results in shorter distances between Ga atoms [3].

According to Refs. [4–7], in the Y–{Al, Si, Ge}–Ga ternary systems, intermetallic YGa_2 forms substitutional solid solutions with homogeneity regions that extended along the 33.3 at.% Y isoline up to (at.%) 18 Al, 12 Si and 4 Ge, respectively. Moreover, the crystal structure of these solid solutions is characterized by the replacement of some gallium atoms in the graphite-like nets by atoms of the third component. As far as we know, results on study the electrical and magnetic properties of these solid solutions are not published yet. Thus, it would be fascinating and beneficial to study electric properties of this system and to analyse the connection between crystal structure transformations and features of these materials.

Here, we present our study of electrical resistivity of the $Y(Ga,Al)_2$,

$Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ solid solutions with the AlB_2-type structure.

2. EXPERIMENTAL DETAILS

The alloys of the Y–{Al, Si, Ge}–Ga systems (33.3 at.% Y) were prepared by arc melting from yttrium (99.8% wt.) and gallium (99.999% wt.) with electrolytic aluminium (99.99% wt.), silicon (99.999% wt.) or germanium (99.999% wt.) under purified argon atmosphere. The metal foils of these alloys have deposited by vacuum resistivity evaporation method (W-evaporator) simultaneously on K8 optic glass (of 22 mm diameter) and the mica strips (of 2–3 mm wide) (the temperature of a single folder was about 600°) using a standard vacuum VUP-5M equipment. The compactness, homogeneity, elemental composition, and thickness of the deposited coatings have been monitored by both scanning electron microscopy (SEM) and microprobe analysis (BS-340 Camebax equipment).

X-ray powder diffraction (XRD) data of the alloys and deposited coatings were collected with DRON-3 automatic diffractometer ($Cu K_\alpha$ radiation). The diffraction patterns were obtained in a discrete mode under the scanning parameters as follow: observation range $2\theta = 20–130°$, step scan is of 0.05°, counting time per step is of 3 s. The original software package [8] elaborated for the automated DRON equipment and including full complex of standard Rietveld refinement procedure has been used. This software package is created for the following: determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out qualitative and quantitative phase analysis using PDF data for phase identification and least square method for lattice-constants' refinement; testing of the structure models and refining the crystal structure parameters, *etc*.

Resistivity of coatings deposited on mica strips was measured at 300–900 K under purified argon atmosphere by the standard four-probe method with platinum contacts.

3. RESULTS AND DISCUSSION

Because of the high fragility of alloys prepared by the arc melting, it was not possible to synthesize thin samples of regular geometric shape being suitable for the resistivity measurements. Therefore, it was decided to carry out the measurements on the coatings deposited on mica strips instead of the bulk alloys. Assurance to obtain a coating being isophase to alloy studied is based on following facts. Foremost, YGa_2 compound is formed congruently and it is characterized by high enthalpy of formation (–64.4 kJ/(g·atom)) [2]. Next, the enthalpy of mix-

ing of liquid gallium and yttrium reaches its extreme value near YGa_2 stoichiometric composition (at 40 at.% Y) [9].

As a result of deposition mode tuning, the crystalline coatings with chemical and phase compositions relevant to the initial alloys have been synthesized (Table 1, Fig. 1, *a*). Besides, it was shown that amorphous thin film or textured coatings ([001] direction) could be prepared by varying the temperature of substrate (Fig. 1, *b*, *c*). Further improvement of synthesis technology allowed us to prevent the oxidation of coating (caused by Y_2O_3 appearance) as well as the overheating of alloy (caused by the YGa_6 formation).

SEM study has revealed the compact dendritic structure (Fig. 2) of the most coating obtained, which is quite important to provide the electrical contacts between individual grains.

Results of microprobe analysis have shown that the prepared coatings are homogeneous enough and contain an additive metal (aluminium, silicon or germanium) except yttrium and gallium. However, the content of these additive metals in coatings (right part of Table 1) differ from those in initial alloys (left part of Table 1) that causes a change of lattice constant values.

Resistivity measurements have been carried out for the coatings

TABLE 1. Results of study of the coatings obtained from initial alloys (solid solution on the base of YGa_2).

No.	Initial alloy prepared by arc melting				Coating deposited on mica substrate					
	Me[1], at.%	Phase composition	Lattice constant, nm		Me[2], at.%	Phase composition	Lattice constant, nm		$\alpha \cdot 10^{-3}$, K^{-1}	ρ, $\mu Om \cdot cm$
			a	*c*			*a*	*c*		
1	–	YGa_2	0.4197(1)	0.4094(1)	–	YGa_2	0.4237(8)	0.4142(8)	1.63(7)	48(2)
2					–	Amorphous	–	–		
					Y–Al–Ga system					
3	5	$Y(Ga,Al)_2$	0.4211(8)	0.4094(2)	2(1)	$Y(Ga,Al)_2$	0.4198(2)	0.4085(2)	2.46(5)	20(1)
4	10	$Y(Ga,Al)_2$	0.4218(2)	0.4085(2)	3(1)	$Y(Ga,Al)_2$	0.4230(1)	0.4119(1)		
5	16	$Y(Ga,Al)_2$	0.4234(3)	0.4075(3)	6(2)	$Y(Ga,Al)_2$	0.4238(1)	0.4137(1)		
6					–	Amorphous	–	–		
					Y–Si–Ga system					
7	7	$Y(Ga,Si)_2$	0.4178(1)	0.4086(2)	10(2)	$Y(Ga,Si)_2$	0.4240(1)	0.4142(1)	1.72(6)	29(1)
8					–	Amorphous	–	–		
9	12	$Y(Ga,Si)_2$	0.4157(2)	0.4079(3)	5(2)	$Y(Ga,Si)_2$	0.4222(4)	0.4116(7)		
10					8(2)	$Y(Ga,Si)_2$	0.4199(9)	0.4103		
					Y–Ge–Ga system					
11	5	$Y(Ga,Ge)_2$	0.4214(2)	0.4130(2)	8(2)	$Y(Ga,Ge)_2$	0.4190(4)	0.4106(3)	1.64(5)	33(2)

[1] Metal content according to charge composition.

[2] Metal content according to microprobe analysis data.

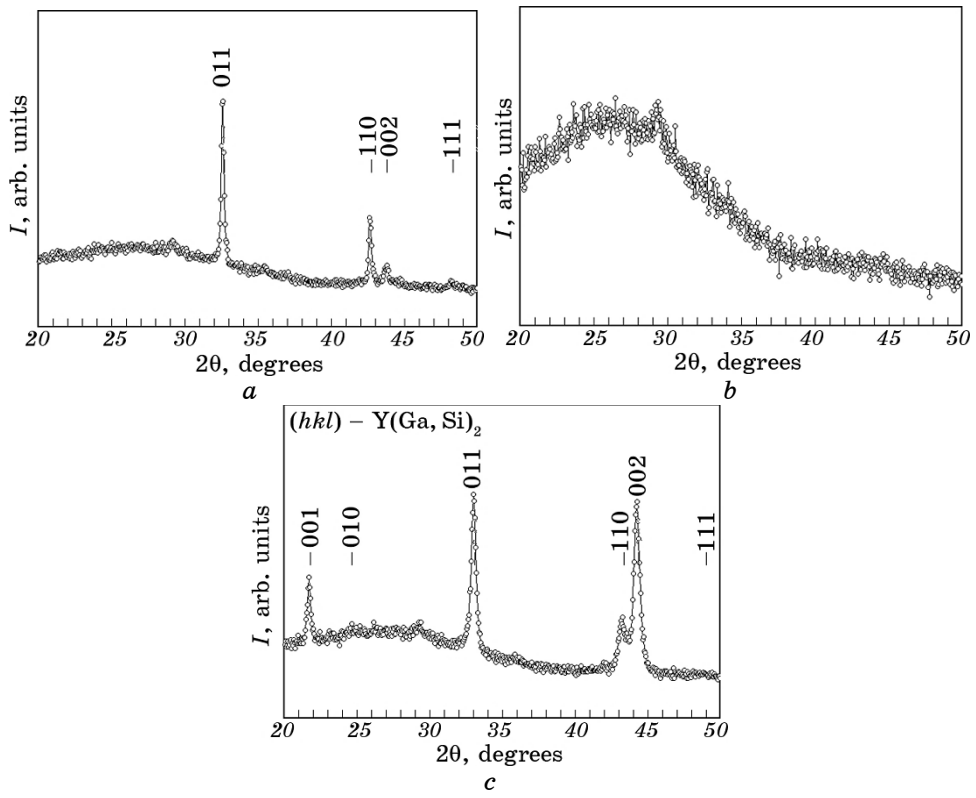

Fig. 1. XRD patterns of $Y(Ga,Me)_2$ coatings deposited by different modes: crystalline non-textured coating (*a*), amorphous coating (*b*), crystalline coating with [001] texture (*c*).

with the closest to the initial alloy phase and chemical compositions. The typical temperature dependences of electrical resistance (R_T/R_{300}) for YGa_2 as well as for the $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ solid solutions are shown at Fig. 3.

The obtained results have revealed that all coatings studied here possess the conductivity of metallic type. By means of analytical treatment of the temperature dependences of resistivity, the temperature coefficient of resistivity (α) and the electrical resistivity at room temperature (ρ) have been determined (Table 1). It should be mentioned that the thicknesses of the coatings has been determined (during the study) by microprobe analysis method and its value has been used for the ρ calculations.

So, the study of temperature dependences of electrical resistivity has revealed that YGa_2 compound and the $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ solid solutions on its base have the metallic conductivity.

Moreover, substitution of the gallium atoms onto germanium, silicon or aluminium ones results in a decrease of the resistivity value as well in increase of temperature coefficient of resistivity as in the Ga → Ge → Si → Al series (Table 1, Fig. 4). It should be noted that ac-

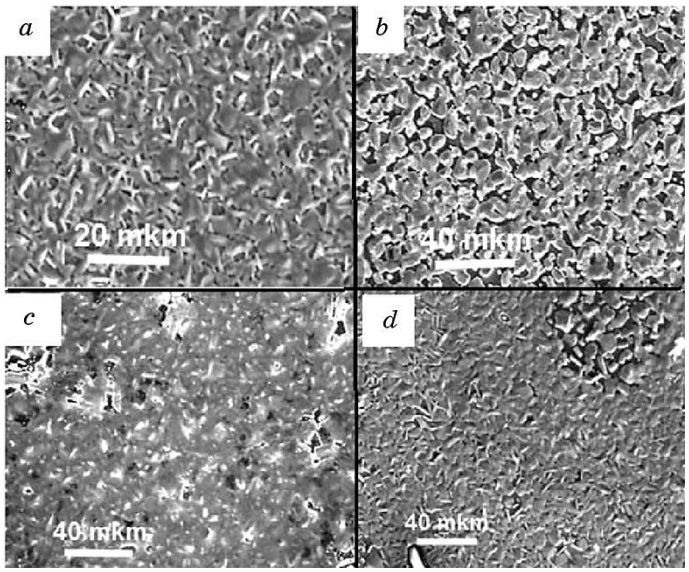

Fig. 2. SEM images of the coating contained aluminium (*a*, *b*), silicon (*c*) and germanium (*d*).

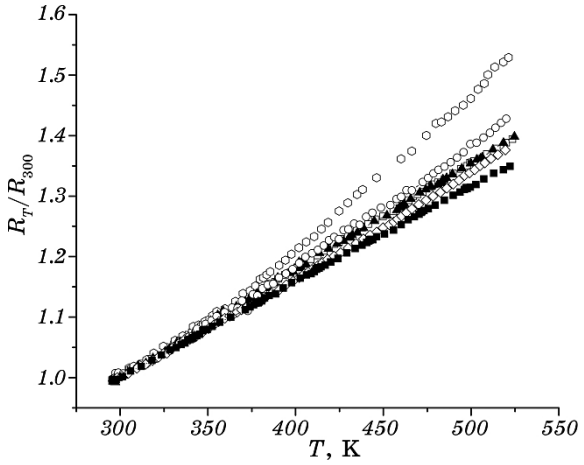

Fig. 3. Temperature dependences of the relative electrical resistance R_T/R_{300} for YGa_2 compound (marked by ■), $Y(Ga,Al)_2$ (○), $Y(Ga,Si)_2$ (▲) and $Y(Ga,Ge)_2$ (◊) solid solutions.

cording to the microprobe analysis data the compositions of formed solid solution (8–15 at.% of Me, Table 1) are similar and close to the compositions corresponding to replacement of gallium atom occupied the graphite-like nets in the crystal structure of YGa_2 onto an atom of additive metal (Ge, Si or Al). This phenomenon along with Pauli paramagnetism of the gallium rich alloys of these systems [10, 11] indicates that the changes in properties of studied solid solutions are caused by the change in the electron concentration.

In our opinion, the formation of solid solutions of substitution is accompanied by a change in the configuration of *spd*-hybridized atomic orbitals that leads to delocalization of some of the interatomic bonds of the YGa_2 compound. This peculiarity causes an increase in the conduction electrons' concentration and, hence, leads to a change in ρ values and R_T/R_{300} temperature dependences. The degree of delocalization (the number of delocalized bonds) depends on a size of the component dissolved and determines the changes of resistivity. The tendency of an increase in α values (Fig. 4) is caused by a decrease in ρ value since $\alpha = (1/\rho)(d\rho/dT)$. In general, the specific resistivity is determined not only by concentration of the conduction electrons, but also by defects of the crystal structure and by the microstructure of material as $\rho = \rho_D + \rho(T)$, where ρ_D is the temperature-independent contribution from the defects, and $\rho(T)$ is the temperature-dependent contribution to electrical resistivity. According to data of crystal structure refinements, the structural defects (vacancies and included atoms) are absent in the structures of the studied $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ solid solutions and do not contribute to the ρ_D value. However, parameters indicating the non-homogeneity of the coating (the presence of a dendritic microstructure) can contribute to ρ_D. Thus, both these factors, namely the electron concentrations and inhomoge-

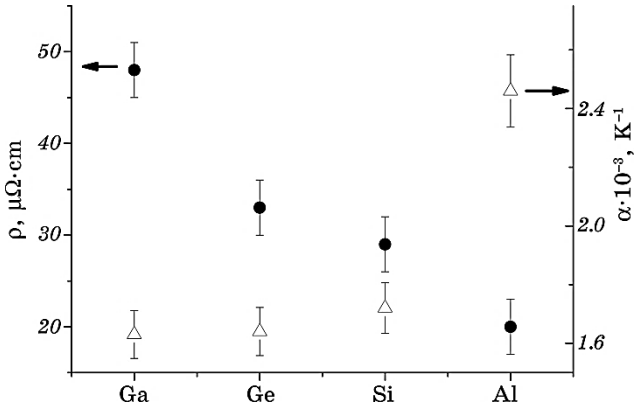

Fig. 4. Resistivity values (ρ) (circles) and the temperature coefficient of the resistivity values (α) (triangles) for the components solved in YGa_2 compound.

neity of the obtained coatings, determine the decrease in electrical resistivity of the studied solid solutions according to the Ga → Ge → Si → → Al series.

4. CONCLUSION

Electrical properties (resistivity and temperature coefficient of resistivity) of the $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ solid solutions have been studied. Based on XRD and electron microprobe analysis results, the deposition modes have been tuned and allowed to synthesize a model coating, which is isophase to the initial alloy. Study of the temperature dependences of electrical resistivity has revealed that YGa_2 compound as well as the $Y(Ga,Al)_2$, $Y(Ga,Si)_2$ and $Y(Ga,Ge)_2$ solid solutions on its base have metallic conductivity. Substitution of a certain part of the gallium atoms onto germanium, silicon or aluminium ones leads to a decrease of resistivity in the Ga → Ge → Si → Al series may be caused both by the nature of atoms themselves and by technological parameters of coatings' processing (primarily, by homogeneity).

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