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METALLIC SURFACES AND FILMS

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1. INTRODUCTION

Problems of microelectronics make it necessary to forecast the effects of thermal influence at a semiconductor metal contact, in particular for the thin film system Ni—Ga—As. The data on the interaction of a chemically deposited Ni layer 0.1—0.5 μm thick with the single crystal GaAs substrate in course of the hydrogen annealing at 300—500°C are given [1]. The interaction has been shown to begin at 250°C. Annealing at 450°C leads to the formation of phases $NiGa_4$, NiGa, NiAs. The results of the investigation of the interphase interaction of thin (30 nm) GaAs films with the Ni layers of a variable thickness (3—50 nm) are presented in reference of GaAs was 20 and 400°C, at condensation of Ni, temperature was 400°C. As a result of the interaction the formation of the phases of ternary Ni—Ga—As system was observed, similar to phases of the Ni—Ga and Ni—As binary systems. A transition is observed from the phases with higher Ni concentration (α-phase, Ni_5As_2, γ-Ni_3Ga_4, Ni_3Ga_4) to the phases with lower Ni concentration (α-$NiAs_2$, NiAs) as the Ni film thickness is decreasing. The $NiGa_4$ phase with the maximum Ga content is an exception, and its formation was observed with practically any relationships of thickness of the contacting Ni and GaAs layers.

Thus the interaction of Ni and GaAs thin layers leads to the formation of various phases of the Ni—Ga—As ternary system both variation of the contacting films thickness and the temperature conditions at their condensation. However, while the film thickness ratio [2] was changed in a sufficiently broad range (0.1—2), the influence of the substrate temperature on phase formation was investigated only for 20 and 400°C. Since the processes of interaction are by diffusion and in thin films they may be accelerated even at sufficiently low temperatures, it is advisable to study an interaction of the Ni and GaAs layers over a broad range of substrate temperature in the process of condensation. For revealing a temperature effect it is necessary to complete measurements of the films of a constant composition.

2. RESULTS AND DISCUSSION

This study describes the results of an investigation of the temperature effect on the interphase interaction of Ni and GaAs in process of Ni condensation.

The objective of the investigation were thin Ni and GaAs films (of the order of several tens of nanometers) obtained by successive evaporation and condensation in a vacuum 10^{-4} Pa. A long polished stainless steel plate was used as the substrate, which was sputter coated with a NaCl layer immediately before the condensation of the samples. The gallium arsenide film was deposited by an explosive evaporation method at room temperature of the substrate. Then a temperature gradient (90—500°C) along the plate was created and the Ni layer was condensated. At a sufficient distance between the substrate and evaporators the thickness of the layer remains approximately constant. The films obtained in this way were cooled naturally under vacuum to room temperature and then were subjected to transmission electronography. An additional stabilising annealing for 1 h was used with the same temperature gradient along the substrate.

Three series of samples were studied with a ratio of the film mass $M = m_{Ni}/m_{GaAs} = (0.5; 1; 2)$, that corresponds to the following composition (in at.%): 38.1; 30.95; 30.95 (1.2:1:1), 55.22; 22.4; 22.4 (2.5:1:1), 71.2; 14.4; 14.4 (5:5:1). The electronograms obtained from the films indicated their mainly polycrystalline and partly amorphous structure. The investigation of the electronograms from the phases formed at the interaction was performed by standard methods and also by comparison of sets of the interplanar distances for the known phases of the binary systems with values of d_{hkl} observed experimentally. A definite support for the interpretation of the electronograms was found in the comparison of Ni, Ga, As components content in the films shown as dots 1, 2, 3 at the concentrational triangle with respect to the position of the phases at the binary diagrams (Fig. 1). For comparison

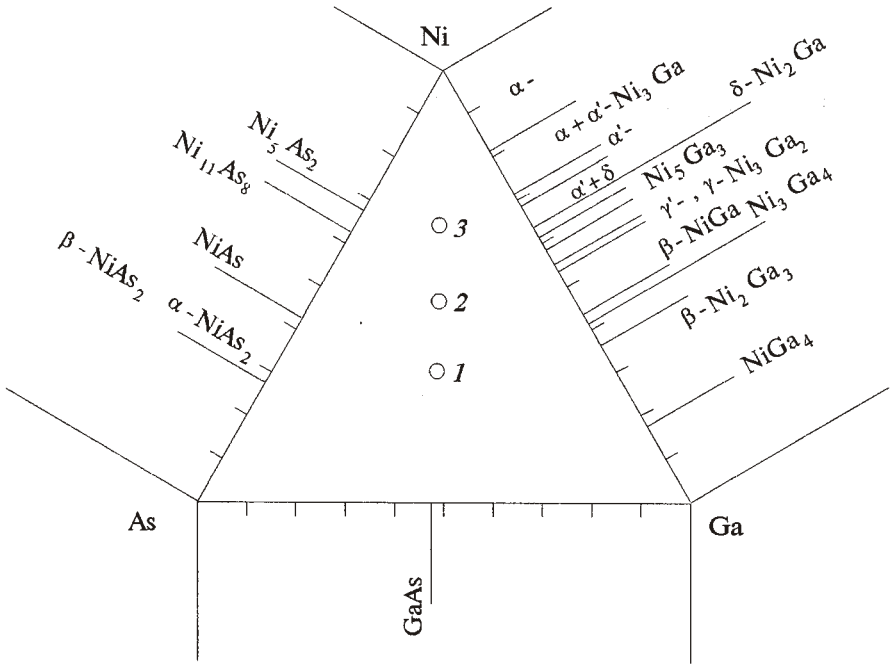

Figure 1. Concentrational triangle of the Ni—Ga—As system; numbers 1, 2, 3 indicate composition of the double-layer Ni/GaAs films under investigation. Phases formed in corresponding binary systems are schematically shown at sides of the triangle.

of the d_{hkl}, tables were compiled containing calculated interplanar distances for all known phases of the binary systems [5—8] with taking into account the possibility of the appearance of the reflexes of identical phases of ternary systems forbidden by the structural factor. In the Ni—As system these are 5 phases: Ni_5As_2, $Ni_{11}As_8$, NiAs, α-$NiAs_2$, β-$NiAs_2$, in the Ni—Ga these are 10 phases: α'-Ni_3Ga, δ-Ni_2Ga, Ni_5Ga_3, γ-Ni_3Ga_2, γ'-Ni_3Ga_2, β-NiGa, Ni_3Ga_4, β'-Ni_2Ga_3, Ni_3Ga_7, ε-$NiGa_4$.

The comparison of experimental values of d_{hkl} with those calculated for some phases of the binary systems are shown in Tables 1—3. Data on existence of amorphous phases are not indicated in the tables, and their presence in the films is discussed below.

For the samples of all the series investigated at condensation of Ni at the GaAs substrate at temperatures up to 100—150°C the electronograms contain strong halos from an amorphous phase and at this background for the films with the ratio $M = m_{Ni}/m_{GaAs} = 0.5$ a system of weak lines corresponding to reflections from the planes with $d \approx 4.0$; 3.31; 2.34; 2.04 Å is observed, and $T = 160$—180°C a reflection from a plane with $d = 5.05$ Å is observed. For the films with a layer mass ratio $M = 1$ in the substrate temperature range 90—215°C, at a background

of bright halos, highly eroded lines with $d \approx 2.05$; 1.80 Å can be seen (the f.c.c. Ni $d_{111} = 2.03$; $d_{200} = 1.76$ Å). In the case of $M = 2$ at the substrate temperature up to 170°C as a result of the layer interaction the reflections from the planes with $d \approx 2.80$; 2.70; 2.02; 1.97; 1.92; 1.38; 1.24 Å are observed.

As follows from Tables 1—3, a common feature for all three series of the films is the formation of a hexagonal phase of the nickel-arsenide type. A characteristic of this phase is that it has a practically constant lattice parameter c and changing of the lattice parameter a with the substrate temperature. This phase coexists at low temperatures with the amorphous phase NiGaAs.

For films with a composition with $M = 0.5$, the parameter a with rising temperature from 140 to 210°C decreases from 3.78 to 3.60 Å, ration c/a increases from 1.325 to 1.39 and preservs the value of $c \approx$ ≈ 5.0 Å.

In the case of $M = 1$ the temperature range in which the interaction leads to formation of hexagonal phase is 220—310°C (in the presence of the amorphous phase) and parameter a is changed from 3.80 to 3.67 Å ($c = 5.0$ Å).

For the films with $M = 2$ the nickel-arsenide type phase is formed starting with the substrate temperature of 170°C, and the magnitude of parameter a changes from 3.84 to 3.52 Å, and c from 4.96 to 5.03 Å ($c/a = 1.29$—1.42). For comparison: for the NiAs phase $a = 3.619$ Å, $c = 5.034$ Å, $c/a = 1.39$; for the γ-Ni_3Ga_2 nickel-arsenide type phase $a = 4.00$ Å; $c = 4.98$ Å; $c/a = 1.25$. Close to the observed parameters is also the hexagonal β'-Ni_2Ga_3 phase of the Ni_2Al_3 type: $a = 4.06$ Å, $c =$ $= 4.90$ Å, $c/a = 1.21$.

At higher substrate temperatures the interaction of the layers for various compositions leads to differing results. So, for a composition with the layer mass ratio $M = 0.5$ the electronograms obtained from the films, deposited at the substrate temperature 350°C, contain a maximum number of the lines. The interaction of the layers at this temperature leads, most probably, to the formation, in parallel with the hexagonal phase of the nickel-arsenide type, of a phase with a lattice having parameters close to those observed in the α-$NiAs_2$ phase of the binary system (Table 1). The presence of the most intensive lines of this phase is observed in electronograms from the films also deposited at the lower substrate temperatures.

For the composition $M = 1$ changes occur starting with the substrate temperature 320°C when the electronograms disappear with lines corresponding to reflexes from the planes with $d = 2.48$; 1.51; 1.35; 1.18 Å. At the same time reflexes appear from the planes with $d = 3.42$; 2.80; 1.68; 1.63; 1.41; 1.34; 1.14 Å. The largest number of lines at this ratio of the layers mass is observed at condensation at the substrate with temperature 355°C, when in parallel with the lines enumerated in

TABLE 1. Interplanar distances of phases formed in contacting Ni and GaAs films ($m_{Ni} = 0.5m_{GaAs}$) and calculated data on interplanar distances of some phases of binary Ni—Ga, Ni—As and Ga—As systems.

No.	Experimental values d, Å									Calculated values of d, Å				
	Temperature, °C													
	120	140	150	160	180	210	230	320	350	α-$NiAs_2$	γ-Ni_3Ga_2	GaAs	NiAs	$NiGa_4$
1				5.05	5.05		5.05	5.05	5.05	5.00				
2	4.00								3.85	3.86				
3	3.31								3.41		3.46			
4		3.26	3.24	3.23	3.21	3.15	3.14	3.26	3.27			3.26	3.14	2.97
5							2.80	2.82	2.83	2.83	2.84			
6		2.74	2.73	2.72	2.69	2.66	2.66	2.65	2.66				2.66	
7		2.50	2.52	2.52	2.52	2.56		2.50	2.51	2.52	2.49		2.52	
8	2.34							2.16	2.27	2.29				2.25
9	2.04							2.03	2.02	2.02	2.01	1.99		1.99
10		1.99	1.99	1.99	1.99	1.97	1.96	1.94	1.96		1.99		1.96	
11		1.89	1.87	1.89	1.89	1.82	1.80	1.80	1.80	1.80			1.81	1.80
12		1.77					1.70	1.70	1.70	1.71	1.73	1.70		1.71
13		1.63	1.61				1.62	1.62	1.62	1.61	1.64			1.65
14		1.56	1.54			1.57	1.57	1.56	1.55	1.56	1.56		1.56	
15		1.50	1.48	1.48	1.49	1.48	1.49	1.49	1.49	1.48	1.495		1.48	
16						1.43	1.43	1.41	1.41	1.41	1.42	1.43		1.42
17		1.37	1.36	1.34	1.33	1.33	1.33	1.33	1.33	1.33	1.31		1.33	140
18		1.25	1.25	1.26	1.26	1.25	1.25	1.26	1.25	1.25	1.245		1.26	
19		1.19	1.17	1.16	1.17	1.17	1.18	1.17	1.18	1.18	1.17		1.17	
20		1.14	1.14	1.13	1.12	1.15	1.14	1.15	1.15	1.15	1.155		1.15	1.145

Table 2 for the temperature range 335—365°C additional reflexes from the planes with $d = 4.65$; 4.11; 3.73 Å are observed at small angles.

According to calculations, the set of the diffraction lines observed corresponds to the formation at interaction of the layers of an ordered polycrystalline phase with the lattice of the γ-Ni_3Ga_2 type and of a

TABLE 2. Interplanar distances of phases formed in contacting Ni and GaAs films ($m_{Ni} = m_{GaAs}$) and calculated data on interplanar distances of some phases of binary Ni—Ga, Ni—As and Ga—As systems.

No.	Experimental values d, Å										Calculated values of d, Å			
	Temperature, °C													
	90—215	220—230	235—245	250—260	265—280	290—310	320	335—365	380—465	480	γ-Ni_3Ga_2	Ni_3Ga_4	NiAs	GaAs
1							3.42	3.44	3.45	3.43	3.47	3.44		
2		3.28	3.25	3.23	3.20	3.18	3.20	3.23	3.23	3.23		3.30		3.26
3										3.08	3.107		3.14	
4								2.80	2.80	2.80	2.84	2.86		
5		2.73	2.72	2.71	2.70	2.68	2.65	2.64	2.65	2.65	2.62	2.69	2.66	
6		2.51	2.51	2.51	2.49	2.48					2.48		2.52	
7	2.05	1.98	1.98	1.97	1.97	1.96	1.97	1.99	1.99	1.99	1.99	2.02	1.96	1.99
8							1.95	1.95	1.95	1.96	1.92	1.99		
9		1.90	1.89	1.90	1.86	1.84	1.84						1.81	
10	1.80				1.83	1.81	1.80	1.80	1.80	1.80	1.80	1.85		
11						1.68	1.68	1.69	1.69	1.69	1.69	1.72		1.70
12						1.63	1.62	1.63	1.63	1.63	1.63	1.65		
13		1.56	1.56	1.55	1.54	1.52	1.51						1.50	
14		1.48	1.48	1.48	1.47	1.47	1.47	1.47	1.48	1.48	1.49	1.50	1.47	
15							1.41	1.41	1.41	1.41	1.42	1.43		1.43
16		1.37	1.37	1.37	1.36	1.35	1.35					1.345		
17						1.34	1.34	1.33	1.33	1.33	1.34		1.33	
18		1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.26	1.26	1.25	1.28	1.28	
19		1.20	1.19	1.19	1.18	1.16	1.17	1.17	1.17	1.17	1.17	1.17	1.17	
20		1.16	1.17	1.16	1.16	1.14	1.15	1.15	1.14	1.14	1.14	1.16	1.15	

phase with cubic lattice having parameter $a = 11.30$ Å close to observed for the phase Ni_3Ga_4: $a = 11.414$ Å (Table 4).

For the composition $M = 2$ at the substrate temperature 420°C the formation of two phases is observed, namely: the nickel-arsenide type and a phase with a cubic lattice of the Ni_3Ga_4 type. Taking into ac-

TABLE 3. Interplanar distances of phases formed in contacting Ni and GaAs films ($m_{Ni} = 2m_{GaAs}$) and calculated data on interplanar distances of some phases of binary Ni—Ga, Ni—As and Ga—As systems.

No.	Experimental values d, Å										Indexes of planes		Calc. values of d, Å	
	Temperature, °C													
	170—190	205	220	240	265	290	330	370	420	500—540	γ-Ni_3Ga_2	Ni_3Ga_4	Ni_3Ga_4	Ni_5As_2
1									3.40			(311)	3.44	3.415
2	3.32	3.24	3.24	3.20	3.19	3.16			3.20		(100)	(222)	3.30	3.30
3							3.05	3.08	3.08	3.10		(320)	3.16	3.15
4	2.76	2.73	2.73	2.72	2.68	2.66		2.75	2.77		(101)	(410)	2.76	
5							2.64	2.64	2.64	2.64		(411)	2.69	2.65
6	2.48	2.48	2.47	2.50	2.39						(002)			
7	2.00	1.98	2.04	1.98	1.97	1.99		2.00	1.99	1.99	(102)	(440)	2.02	2.02
8	1.92	1.88	1.86	1.86	1.83	1.95	1.95	1.95	1.96	1.96	(110)	(522)	1.96	1.94
9						1.79	1.79	1.79	1.79	1.78		(620)	1.80	
10	1.57	1.56	1.56	1.53	1.53						(210)			
11	1.50		1.50								(112)			
12	1.47	1.48	1.48	1.47	1.47	1.47	1.47	1.47	1.47	1.48	(103)	(731)	1.49	1.48
13	1.38	1.38	1.37	1.34	1.34	1.32	1.40	1.32	1.32	1.32	(202)	(822)	1.345	1.32
14	1.25	1.24	1.24	1.25	1.25	1.24	1.25	1.25	1.25	1.24	(004)	(840)	1.28	
15			1.16	1.15			1.15	1.16	1.16		(104)	(932)	1.18	1.15
16	1.13	1.12	1.13			1.13		1.14	1.13	1.13	(300)	(940)	1.16	1.13
17	1.05	1.05	1.07			1.07	1.06	1.06	1.06		(114)	(871)	1.07	1.06
18	1.03	1.03	1.02	1.03		1.04		1.03	1.03	1.02	(203)	(954)	1.03	1.02

count (not shown in Table 3) the reflexes from the planes with d = = 4.38; 4.12 Å after indexation, the values of the crystal lattice parameters are equal: for the phase with cubic lattice a = 11.28 Å, for the phase with hexagonal lattice a = 3.57 Å, c = 5.00 Å. The formation of a phase with lattice of the Ni_5As_2 is not excluded either.

For the films with composition M = 1 an additional stabilising annealing for 1 h was used under conditions of the same temperature gradient. In this case, lowering of the temperature to 170°C occurs and

TABLE 4. Data on indexation of phases formed at interaction of the Ni and GaAs layers ($m_{Ni} = m_{GaAs}$) at 355°C and additional annealing at the same temperature for 1 h.

No.	*d*, Å	(*hkl*)	*a*, Å	(*hkl*)	*a*, Å	*c*, Å
1	4.65	211	11.39			
2	4.11	220	11.60	101		5.11
3	3.73	221	11.19			
4	3.45	311	11.44	200	7.96	
5	3.24	222	11.22			
6	3.10	320	11.17	111		4.95
7	2.65	330	11.24			
8	2.23	500	11.15			
9	1.99	440	11.26	220	7.96	
10	1.80	620	11.38	212		4.98
11	1.68	630	11.27	302		4.93
12	1.63	444	11.29	401	7.96	
13	1.55	720	11.28	222		4.95
14	1.33	822	11.24	330	7.95	
15	1.29	832	11.32	412	7.97	
16	1.26	840	11.27	421		4.95
17	1.17	932	11.30	332	7.96	
18	1.15	940	11.33	422	7.95	
19	1.08	952	11.33	521	7.97	
20	1.06	871	11.31			
21	1.03	954	11.32	611	7.93	
	Mean values		11.30		7.96	4.95

the interaction at this temperature leads to the formation of a polycrystalline hexagonal phase of the nickel-arsenide type.

Thus for all the films studied differing in the Ni and GaAs layer mass ratio at a substrate temperature up to 100—150°C the films have a mainly amorphous structure. At higher substrate temperatures, in spite of different composition, the phases of the nickel-arsenide type with variable parameter *a* and almost constant parameter *c* are formed in the films.

In parallel with a crystalline phase an amorphous phase is also pres-

ent. In all the cases the lattice parameter *a* decreases with a rise in the substrate temperature at nickel condensation. This may testify to a higher rate of the Ni and Ga interaction. The lowest-temperature phase of the Ni—Ga system, namely $NiGa_4$, is likely to be formed in this case, as described [2]. Further interaction leading to formation of the phases of the ternary system occurs, as it is assumed in [1], with participation of a liquid phase or involves formation of a thin amorphous layer at the metal—semiconductor boundary, as it is postulated by authors of reference [9]. This layer may play a part of a floating zone in the growth process of contacting layers. In this case one of the phases of the ternary Ni—Ga—As system is formed, in particular, a phase with the nickel-arsenide lattice similar to the lattices in the binary Ni—As and Ni—Ga systems. Change of the parameter a of the ternary system to decreasing is probably connected with substitution of stoichiometric vacancies and of a part of the gallium positions in the γ-Ni_3Ga_2 lattice by arsenic (covalent radii of arsenic and gallium are corresponding by 1.21 and 1.39 Å).

As it is seen from data of Tables 1—3, formation of the nickel-arsenide type phase in a broad range of the substrate temperature is observed for all the films studied with various nickel to gallium arsenide mass ratio. This is stipulated, probably, by features of the nickel-arsenide structure. Analysis of numerous specimens of the phases with the nickel-arsenide structure [10] has shown a lattice of this type is preserved not only in compounds AB but observed also at a shift of the composition both to A_2B (filling of interstitials) and to AB_2 (formation of vacant nodes). At this as it is shown in [10], number of atoms B per unit cell is constant and equal two, hence follows that atoms B form main lattice AB. So, for composition $A_{1.5}B$ (case of γ-Ni_3Ga_2) additional atoms fill up tetrahedric cavities.

Since at decreasing ratio of the lattice parameters c/a cavities of the nickel-arsenide lattice are enlarged, their filling in with nickel atoms become possible. A consequence of this feature of the nickel-arsenide structure is formation of a similar lattice in the ternary Ni—Ga—As system for all the compositions studied (5:4:4; 5:2:2; 5:1:1). Decrease of c/a ratio in the ternary system is stipulated by substitution of positions, usually occupied by Ga, by As atoms and this, in its turn, allows to change number of Ni atoms per unit cell.

3. CONCLUSION

Thus, the results obtained indicate the formation of phases of ternary Ni—Ga—As system at the interaction of the Ni layers with GaAs. The structure of these phases is similar to that of some phases of binary Ni—Ga and Ni—As systems.

The presence of particular phases is explained by an effect of the

heterophase fluctuations leading to the formation of nuclei, growing in a diffusion way (if their size is more than critical). But in the diffusion zone the nuclei are under conditions of the chemical potential gradient (gradient of concentration). They are adjacent to nuclei of other phases and to original materials. Their subsequent growth depends on diffusive interaction of adjacent nuclei of different phases. As a result, the growth of particular nuclei may suppress growth of nuclei of other types although it does not mean their actual absence. However the simultaneous suppression of growth of all the phases in the diffusion zone is impossible [11].

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