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Effect of condensation conditions on phase formation in thin two-layer Ni/GaAs films

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The temperature and structure state of substrate (NaCl poly- and single crystals) are shown to influence the structure of phases formed as a result of interaction between Ni and GaAs layers. In films on polycrystal substrates, polycrystal phases with structures similar to the γ-, γ'-, NiAs, Ni_3Ga_4 phases in Ni-Ga and Ni-As systems are formed besides the amorphous one. Single crystal substrate exerts an orienting influence resulting in the energetically favourable growth of the hexagonal phase of the triple system with parameters $a_{\gamma''} = a_{\gamma'}$, $c_{\gamma''} = 2c_{\gamma'}$.

Показано, что температура и структурное состояние подложки (поли- и монокристаллов NaCl) оказывает влияние на структуру фаз, образующихся при взаимодействии слоев Ni и GaAs. На поликристаллических подложках в пленках, наряду с аморфной, образуются поликристаллические фазы, структура которых подобна фазам γ-, γ'-, NiAs, Ni_3Ga_4, в системах Ni-Ga, Ni-As. Монокристаллическая подложка оказывает ориентирующее действе и приводит к энергетически более выгодному росту гексагональной фазы тройной системы с параметрами $a_{\gamma''} = a_{\gamma'}$, $c_{\gamma''} = 2c_{\gamma'}$.

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The growth of phases forming due to interaction between thin layers of distinct substances being in contact is known to be affected appreciably by temperature, material and structure state of the substrate (amorphous, poly- or single crystal) whereon those layers are deposited. In [1], the study of phase interaction between thin (30 nm) GaAs films and variable-thickness (from 3 to 50 nm) Ni ones is described. The substrate (polycrystalline NaCl film) temperature was 20 and 400 °C when GaAs was condensed and 400 °C when Ni was deposited. Various phases of the ternary Ni-Ga-As system similar to those of binary Ni-Ga and Ni-As ones were observed to be formed depending on the contacting GaAs and Ni layers thickness as well as on the substrate temperature during the condensation (20 or 400 °C).

Since the structure of forming phases may be influenced not only by the substrate temperature but also by its structure (single crystal or polycrystal), it is of interest to trace the phase growth in bilayer Ni/GaAs films depending on its structure state within a wide temperature interval. In this work, structures of above-mentioned bilayer films were studied on NaCl single crystal cleavages and on polycrystalline NaCl films at different temperatures.

The study procedure was as follows. The gallium arsenide film was condensed onto the substrate at room temperature; then, a temperature gradient (90–500 °C) was created along the elongated plate (substrate support) and Ni layer condensed. The evaporation and condensation were performed in oil-free vacuum 10^{-4} Pa. The mutual

arrangement of evaporators and substrate allowed to obtain bilayer films at the mass ratio $m_{Ni}:m_{GaAs}$ = 1:1 corresponding to the composition (atomic per cent) 55.2:22.4:22.4, that is, approximately $Ni_{2.5}GaAs$. Films cooled in vacuum down to room temperature were separated from the substrate and studied using transmitting electron diffraction method. Electron diffraction patterns from phases forming at the interaction were identified using standard methods as well as by comparison of experimental data with interplanar distances sets for known phases of double systems Ni-Ga, Ni-As, Ga-As. Nets of reciprocal lattice sites presented in [2] for variously oriented cubic and hexagonal crystals were used to identify point-type diffraction patterns.

Consideration of electron diffraction patterns from polycrystalline films corresponding to the composition $Ni_{2.5}GaAs$ show that at T = 100 to 150 °C those patterns contain strong halos from the amorphous phase and very blurred lines with d = 2.05 and 1.80 Å (for fcc Ni, d_{111} = 2.03 Å, d_{200} = 1.76 Å). At higher substrate temperatures, a set of lines is observed which are identified as those belonging to a hexagonal phase of Ni-As type. Therewith, the lattice parameter a of the ternary system hexagonal phase varies smoothly from 3.80 to 3.67 Å and the c/a ratio from 1.32 to 1.36 as the temperature elevates from 220 to 310 °C, the value of c lattice parameter remaining constant (c = 5.0 Å). In Ni-As and Ni-Ga systems, hexagonal phases with the same lattice types γ-Ni_3Ga_2 and NiAs have lattice parameters a_γ = 4.00 Å, c_γ = 4.98 Å, c_γ/a_γ = 1.25 and a_{NiAs} = 3.62 Å, c_{NiAs} = 5.03 Å, c_{NiAs}/a_{NiAs} = 1.39, respectively. Halos from the amorphous phase are present in diffraction patterns along with diffraction lines from hexagonal phases. The diffraction pattern undergoes substantial changes at the substrate temperatures from 320 to 500 °C. As calculations have shown, the diffraction lines set corresponds in this case to formation of a mixture of two phases: one with lattice parameters close to those of the ordered hexagonal γ'-Ni_3Ga_2 phase (a = 4.95 Å, c = 7.96 Å) and another cubic one with a = 11.30 Å that is close to the value for Ni_3Ga_4 (a = 11.414 Å) [3]; see Table 1.

Another situation is observed in films condensed on the single-crystal NaCl substrate. At T = 200 to 300 °C, a system of point reflections is observed positioned in vertices of rhombs with angles between

Table 1. Identification data for phases forming at Ni and GaAs layers interaction ($m_{Ni} = m_{GaAs}$) at 355 °C.

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	
Averaged values:			11.30		7.96	4.95

sides φ = 110°. Analysis of different nets of reciprocal lattice sites given in [2] shows that those reflections correspond to a single-crystalline phase with hexagonal lattice oriented by [121] direction along the electron beam, i.e. normal to the substrate plane. Plane indices corresponding to reflections on diffraction patterns are presented in Table 2. The crystal lattice parameters calculated using long-range reflections (taking into account the inaccuracy of the equation $rd = L\lambda$, where r is the reflection, d is the interplanar distance, $L\lambda$ is the instrument constant, L is the effective distance from the sample to the photography plate, λ is the wavelength), are found to be a = 4.11 Å, c = 10.09 Å.

Thus, if the hexagonal polycrystalline phase of ternary Ni-Ga-As system (on polycrystalline NaCl substrates) at 320–400 °C substrate temperatures has a structure similar to that of the ordered γ'-Ni_3Ga_2 ($a = 2a_\gamma$, $c = c_\gamma$), a reciprocal relationship between the parameters ($a_{\gamma''} = a_\gamma$, $c_{\gamma''} = 2c_\gamma$) is observed in the single-crystal phase deposited on NaCl

Table 2

d(Å)	(hkl)
3.39	$\bar{1}01$, $1\bar{1}1$, $10\bar{1}$, $\bar{1}1\bar{1}$
2.94	$0\bar{1}2$, $01\bar{2}$
1.77	$1\bar{2}3$, $\bar{1}23$
1.72	$\bar{2}02$, $2\bar{2}2$, $20\bar{2}$, $\bar{2}2\bar{2}$
1.47	$0\bar{2}4$, $02\bar{4}$
1.32	$3\bar{2}1$, $\bar{3}2\bar{1}$, $3\bar{1}1$, $\bar{3}11$
1.12	$\bar{1}2\bar{5}$, $12\bar{5}$
0.97	$0\bar{3}6$, $03\bar{6}$, $\bar{4}3\bar{2}$, $4\bar{3}2$

single crystal. Since all other conditions except for the substrate structure were the same, it is just the orienting action of the substrate (NaCl single crystals) that is like to be the reason for the growth of the phase with such parameters.

If the [121] direction is positioned along the normal to the substrate (cleavage plane (100) of NaCl), indices for the plane (hkl) of the hexagonal system parallel to the substrate one can be determined. In contrast to the cubic system, (hkl) plane indices in this case do not coincide with those of the normal to it, [uvw], and can be determined from equations pairs ($\boldsymbol{Cn}$) = 0 and ($\boldsymbol{Bn}$) = 0 where $\boldsymbol{n} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$ is the normal vector and vectors $\boldsymbol{C}$ and $\boldsymbol{B}$ lie in the perpendicular plane (hkl) and are equal to $\boldsymbol{C} = \boldsymbol{b}/k - \boldsymbol{a}/h$, $\boldsymbol{B} = \boldsymbol{c}/l - \boldsymbol{a}/h$ respectively. From two equations, ratios between indices $v{:}u$ and $w{:}u$ and indices of (hkl) plane perpendicular to them can be determined [4]. It follows from the relationship

$$u{:}v{:}w = |2h + k|{:}|h + 2k|{:}|3/2(a^2/c^2)l|$$

that $h = 2u - v$, $k = 2v - u$, $l = 2c/a^2$. In this case, [uvw] = [121], (c/a^2 = 6.02 and (hkl) = (014).

Let us consider the conjugation of hexagonal and cubic lattices in the direct and reciprocal spaces. The particles arrangement in the hexagonal lattice with a = 4.11 Å, c = 10.09 Å (i.e. when $a = a_\gamma$, $c = 2c_\gamma$, where γ-phase of Ni_3Ga_2 has a lattice of nickel arsenide type) is taken into account. If a plane (014) perpendicular to the [121] direction is arranged within a hexagonal lattice with doubled period along $\boldsymbol{c}$ axis, the shortest distances between atoms of the same kind in that plane positioned in [[010]] (1), [[001/4]] (2), [[110]] (3), [[101/4]] (4) sites, amount $|\boldsymbol{r}_{13}| = |\boldsymbol{r}_{24}| = a$, $|\boldsymbol{r}_{12}| = |\boldsymbol{r}_{34}| = |\boldsymbol{r}_{23}| = \sqrt{a^2 + (c/4)^2}$ and form a net of parallelograms with sides 4.82 Å and 4.11 Å, the angle between $\boldsymbol{r}_{12}$ and $\boldsymbol{a}$ being 64.76° (or a net of isosceles triangles). Corresponding nets for γ and γ′ phases consist of parallelograms with sides 4.0 and 6.38 Å, 7.98 and 21.38 Å and angles 71.79° and 79.25°, respectively. Therewith, the (001) plane in γ phase and (041) for γ′ one are perpendicular to [121] direction.

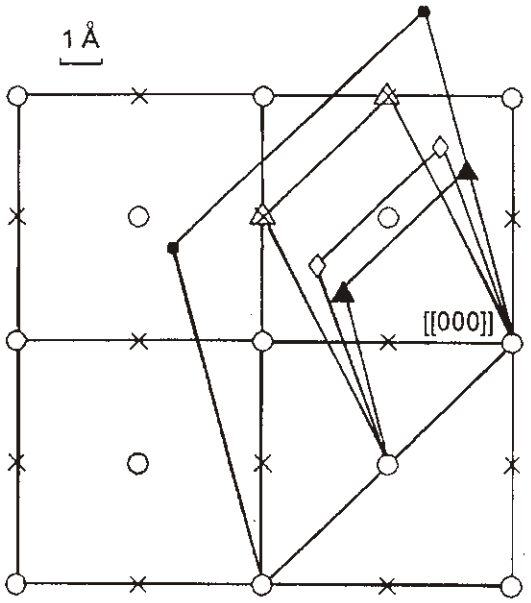

Fig.1. Scheme of lattices conjugation between cubic NaCl and hexagonal (γ, γ′, γ″) phases in the direct space: ○, × are Na^+, Cl^- ions in the plane perpendicular to [100] direction; △, ◇ are metal atoms in γ-Ni_3Ga_2 and γ″-$Ni_xGa_yAs_z$ lattices ([121]‖[100]); ▲, ● are metal atoms in γ-Ni_3Ga_2 and γ′-Ni_3Ga_2 lattices in the basal plane ([100]‖[100]).

Conjugation of nets in the direct space for NaCl, γ-phase of Ni_3Ga_2 γ′-phase, γ′-phase of the ternary system is presented in Fig. 1. When constructing the scheme, the most favoured particles arrangement is accounted for at the $\boldsymbol{a}$ (or $\boldsymbol{b}$) axis of the hexagonal lattice coincident with [110] direction of cubic NaCl crystal, because for NaCl $a\sqrt{2}/2$ = 3.99 Å what is close to the observed a parameter for γ, γ′, γ″ phases. The most unfavourable arrangement is characteristic for γ-Ni_3Ga_2 particles positioned over opposite-signed ions of NaCl. It follows from electron diffraction patterns identification that the growth of the γ″ phase of the ternary system is more energetically favourable. In this case, it coincident sites along [110] NaCl, particles of the growing phase distant at $|\boldsymbol{r}_1|$ = 4.82 Å from each

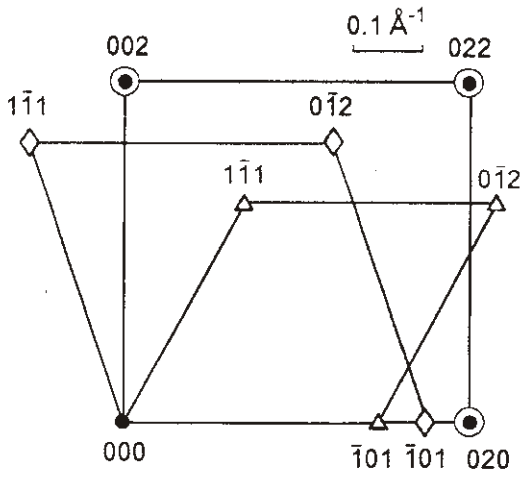

Fig.2. Scheme of lattices conjugation in the reciprocal space when [121] direction of hexagonal crystals is coincident with [100] of cubic ones: ● are NaCl, GaAs [100], ○ is γ-Ni_3Ga_2 [121], Δ is γ′-Ni_3Ga_2 [121], ◊ is γ″-Ni_3Ga_2 [121].

other are positioned in points halving approximately the distances along the facet diagonal. An arrangement similar to the above is observed for γ-Ni_3Ga_2 particles when its [001] is oriented along [001] NaCl.

Fig. 2 shows the conjugation of reciprocal lattices for γ-Ni_3Ga_2, γ′-phase, γ″-phase of the ternary system with reciprocal NaCl lattice when [121] of γ, γ′, γ″ phases is oriented parallel to [001] of NaCl. It is seen from the Figure that also in this case better conjugation conditions with NaCl substrate are observed for hexagonal γ″-phase of $Ni_xGa_yAs_z$ while they are ideal for γ-Ni_3Ga_2.

Experiments have shown however that effect of two factors, namely, a trend of γ-phase to the ordering at temperatures from 200 to 400 °C and an orienting action of NaCl substrate, result in that the γ″-phase growth is more energetically favourable as compared to that of γ′ phase in a bulk condition.

Thus, structure of phases forming at interaction of thin Ni and GaAs layers is affected both by the substrate temperature during the condensation and by its structure state (single- or polycrystalline NaCl). Polycrystalline films exhibit structures identical to those observed in binary systems γ-Ni_3Ga_2, NiAs, Ni_3Ga_4, depending on the substrate temperature. When the latter elevates, the growing polycrystalline phase of the ternary system shows a progressive variation of the c/a ratio from 1.32 to 1.36. At higher temperatures, an ordering is observed where $a = 2a_\gamma$, $c = c_\gamma$, similar to the binary Ni-Ga system. On single-crystalline substrates, a single crystal phase with parameters $a_{\gamma''} = a\gamma$, $c_{\gamma''} = 2c_\gamma$ is grown under the same conditions.

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Про вплив умов конденсації на фазоутворення в тонких двошарових плівках Ni/GaAs

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Показано, що температура і структурний стан підкладки (полі- та монокристалів NaCl) впливають на структуру фаз, що утворюються при взаємодії шарів Ni і GaAs. На полікристалічних підкладках в плівках, поряд з аморфною, утворюються полікристалічні фази, структура яких подібна до фаз γ-, γ′, NiAs, Ni_3Ga_4 в системах Ni–Ga, Ni–As. Монокристалічна підкладка проявляє орієнтуючу дію і приводить до енергетично більш вигідного росту гексагональної фази потрійної системи з параметрами $a_{\gamma''} = a_\gamma$, $c_{\gamma''} = 2c_\gamma$.