Functional materials, 1997, **4**, No. 3, 355–358

γ-phase structure in Ni-Ga-As thin film system

S.V. Dukarov

Kharkiv State University, 4 Svobody Sq., 310077 Kharkiv, Ukraine

Received February 5, 1997

When GaAs and Ni layers are deposited onto NaCl single crystals, a single crystal phase of the Ni-Ga-As ternary system is observed to grow. The presence of sites with a non-zero third index permits to determine the lattice parameters giving a'' = 4.11 Å, c'' = 10.90 Å as well as the angle between $[\bar{1}01]$ and $[\bar{1}1\bar{1}]$ vectors amounting 109°30'. Due to the orienting effect of the NaCl substrate, the growth of the γ''-phase of the ternary system with $a'' = a_\gamma$, $c'' = 2c_\gamma$, turns out to be more energetically favourable, while in massive specimens of the Ni—Ga binary system, the γ-phase ordering under annealing is accompanied by the γ'-phase growth with $a' = 2a_\gamma$, $c' = c_\gamma$.

При конденсации слоев GaAs и Ni на подогретые до температуры 200-400°C монокристаллы NaCl наблюдается рост монокристальной фазы тройной системы Ni-Ga-As. Наличие узлов с ненулевым третьим индексом дает возможность определить параметры решетки a'' = 4.11 Å, c'' = 10.90 Å, а также угол между векторами $[\bar{1}01]$и $[\bar{1}1\bar{1}]$, равный 109°30'. Благодаря ориентирующему влиянию NaCl-подложки энергетически более выгодным оказывается рост γ''-фазы тройной системы с параметрами $a'' = a_\gamma$, $c'' = 2c_\gamma$, в то время как в массивных образцах двойной системы Ni-Ga упорядочение γ-фазы при отжиге сопровождается ростом γ'-фазы с $a' = 2a_\gamma$, $c' = c_\gamma$.

Functional Materials 4, No.3 (1997)

γ-phase structure in Ni–Ga–As thin film system

S.V.Dukarov

Kharkiv State University, 4 Svobody Sq., 310077 Kharkiv, Ukraine

Received February 5, 1997

When GaAs and Ni layers are deposited onto NaCl single crystals, a single crystal phase of the Ni–Ga–As ternary system is observed to grow. The presence of sites with a non-zero third index permits to determine the lattice parameters giving $a'' = 4.11$ Å, $c'' = 10.90$ Å as well as the angle between $[\bar{1}01]$ and $[\bar{1}1\bar{1}]$ vectors amounting 109°30′. Due to the orienting effect of the NaCl substrate, the growth of the γ″-phase of the ternary system with $a'' = a_\gamma$, $c'' = 2c_\gamma$, turns out to be more energetically favourable, while in massive specimens of the Ni–Ga binary system, the γ-phase ordering under annealing is accompanied by the γ′-phase growth with $a' = 2a_\gamma$, $c' = c_\gamma$.

При конденсации слоев GaAs и Ni на подогретые до температуры 200–400 °C монокристаллы NaCl наблюдается рост монокристальной фазы тройной системы Ni–Ga–As. Наличие узлов с ненулевым третьим индексом дает возможность определить параметры решетки $a'' = 4.11$ Å, $c'' = 10.90$ Å, а также угол между векторами $[\bar{1}01]$ и $[\bar{1}1\bar{1}]$, равный 109°30′. Благодаря ориентирующему влиянию NaCl-подложки энергетически более выгодным оказывается рост γ″-фазы тройной системы с параметрами $a'' = a_\gamma$, $c'' = 2c_\gamma$, в то время как в массивных образцах двойной системы Ni–Ga упорядочение γ-фазы при отжиге сопровождается ростом γ′-фазы с $a' = 2a_\gamma$, $c' = c_\gamma$.

An ordering of both primary and secondary solid solutions is known to occur in many metallic systems at relatively low temperatures. So, in the nickel-gallium system, a variable composition phase γ-Ni_3Ga_2 is formed having a nickel-arsenide type structure with lattice parameters $a_\gamma = 3.992$ Å, $c_\gamma = 4.96$ Å, $c/a = 1.25$ at $T > 790$ °C [1]. At lower temperatures, the formation of a low-temperature phase is observed in these alloys [2], its structure is identified as that belonging to a superstructure — γ′-phase of Ni_3Ga_2 with parameters $a' = 2a_\gamma$, $c' = c_\gamma$ [3].

In [4], electron diffraction study results have been given for structure of phases forming due to the interaction of thin (about 10 nm) nickel and gallium arsenide films deposited onto the NaCl single crystal surface at two temperatures (room one and $T = 400$ °C) and with various thicknesses ratio values. Later, similar studies have been performed on phases forming at the interaction of nickel and gallium arsenide layers having a constant thickness under various temperature conditions in the course of nickel condensation. In both cases, a series of electron diffraction patterns contains a reflections system typical for a single crystal phase positioned in vertices of rhombs having the angle $\varphi = 110°$ between their sides. Site nets given in [5, 6] for reciprocal lattice planes in cubic and hexagonal crystals positioned in vertices of rhombs corresponding to various arrangements of the crystal planes with respect to the primary beam direction have been used to interpret the electron diffraction patterns obtained in above investigations. So, nets consisting of rhombs are observed for fcc crystals oriented with [110] and [111] directions along the primary beam or for bcc ones oriented with [111] along that beam. However, vertex angles of corresponding rhombs are 72°32′ and 60° for *fcc* crystals or 60° for *bcc*

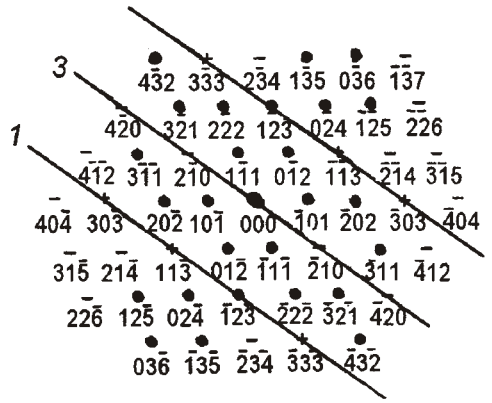

Fig.1. Sites (•) arrangement scheme in the reciprocal lattice plane of a hexagonal crystal perpendicular to [121] direction. Sites corresponding to the double diffraction [6] (+) are positioned along straight lines (1) and (2); reflections absent in the electron diffraction pattern ( ) are arranged along the line (3).

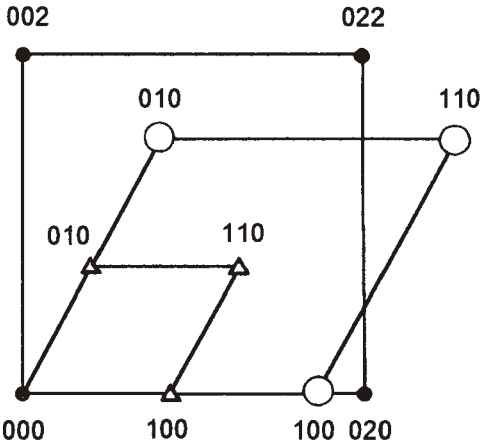

Fig.2. Lattices conjugation scheme in the reciprocal space when the [001] normal to the basis plane of a hexagonal crystal coincides with the [100] direction of cubic NaCl and GaAs crystals. • NaCl, GaAs [100], ° γ-Ni_3Ga_2 [001], Δ γ'-Ni_3Ga_2 [011].

ones, i.e. they differ from experimental data. Thus, it is unlikely that reflections on electron diffraction patterns obtained for double-layered Ni–GaAs films are related to diffraction on *fcc* or *bcc* lattices.

We have considered the reciprocal lattice site nets corresponding to experimentally observed reflections in vertices of rhombs and probable to exist in the case of hexagonal crystals. It is just the nets perpendicular to [011], [121], [211] directions that meet the above conditions. Rhombs are formed if $|\vec{h}_1|$ and $|\vec{h}_2|$ are chosen drawn from the reciprocal lattice coordinates origin to sites with indices $(0\bar{1}1)$, $(1\bar{1}1)$, $(\bar{1}01)$, $(\bar{1}0\bar{1})$, $(\bar{1}11)$, $(01\bar{1})$ for directions along the primary beam [011], [121], [211], respectively

Reflections nearest to the primary beam differing in interplanar distance values d_1 and d_2 (d_1 = 3.29 Å, d_1' = 3.39 Å and d_2 = 2.89 Å, d_2' = 2.94 Å for two sample series) have been used to determine the hexagonal lattice parameters ***a*** and ***c*** separately Indices were ascribed to those reflections according to ones given on nets for various reciprocal lattice planes [5], and then the hexagonal lattice parameters ***a*** and ***c*** have been determined and angles between rhomb sides have been calculated.

The results obtained for two sample series mentioned above are presented in Table 1. That is, d_1 and d_2 values are obtained by electron diffraction pattern processing for samples having a gradient of the Ni layer thickness along the substrate, the condensation being performed at the substrate temperature 400 °C. While d_1' and d_2' values are determined for films deposited on the substrate where a longitudinal temperature gradient from 100 to 500 °C was provided prior to the Ni layer condensation, layer thicknesses over the substrate length were approximately constant. Calculated values of angles φ between rhomb sides are also given in Table 1 Comparison of the observed and calculated data on those angles allows to conclude that they are related to films oriented with [121] direction (or with [211] one identical with the former) along the primary beam. Fig.1 shows the net of the reciprocal lattice sites positioned in the plane normal to [121] direction. A

Table 1

[*uvw*]	$(h_1k_1l_1)$	$(h_2k_2l_2)$	d_1 = 3.29 Å d_2 = 2.89 Å			d_1 = 3.39 Å d_2 = 2.94 Å		
			a(Å)	***c***(Å)	φ	***a***(Å)	***c***(Å)	φ
011	100	111	3.80	6.04	99 °	3.91	5.90	96°49'
121	101	012	4.00	10.40	110°30'	4.14	10.22	109°37'
211	102	011	4.00	10.40	110°30'	4.14	10.22	109°37'

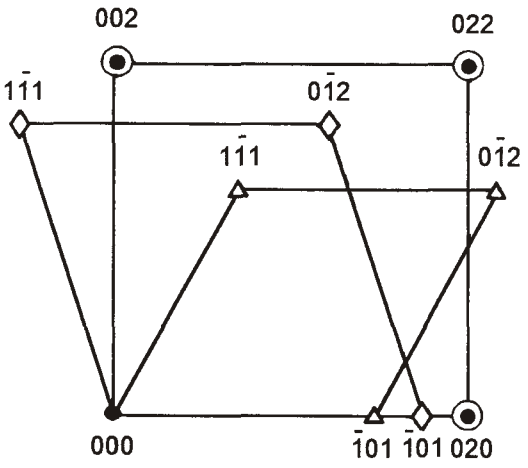

Fig.3. Lattices conjugation scheme in the reciprocal space when the [121] direction of hexagonal crystals coincides with the [100] one of cubic crystals. • NaCl, GaAs [100], ° γ-Ni_3Ga_2 [121], Δ γ'-Ni_3Ga_2 [121], ◊ γ'' $Ni_3(GaAs)_2$ [121].

more broad field of site indices is shown in this figure than in [5], allowing to give indices to all reflections on electron diffraction patterns obtained in this work. Indication data are summarized in Table 2.

The crystal lattice parameters have been refined using reflections from planes with large indices. Experimental values of distances R for long-range reflections were corrected for in accuracy of the formula $R'd = L\lambda(R' \approx R(1 - \Delta), \Delta = 3x^2/8, x = tg\ 2\theta = R/L$, $L = 860$mm, $2L\lambda = 66.54$ Å·mm). For (306) and (125) reflections, d values 1 12 and 0.97 Å have been obtained, respectively The following crystal lattice parameters values have been determined from the above data. $a = 4.11$ Å, $c = 10.09$ Å, $c/a = 2.46$, the angle φ between (101) and (111) planes is 109°30' The obtained a and c values are related to lattice parameters of Ni–Ga system γ-phase by ratios $a = a_\gamma$, $c = 2c_\gamma$. The calculated φ angle value coincides actually with that observed on diffraction patterns (see Table 1).

To explain a and c values obtained for the single crystal phase of the ternary system under consideration and the reasons of its growth with [121] direction perpendicular to (001) plane of the NaCl substrate, an orienting effect of the latter is to be accounted for The growth in [121] direction, in contrast to [001] one that is more typical for hexagonal crystals, might be associated with a smaller angular and linear misfit between lattices of the growing phase and of the substrate. Therewith, it is just the lattice dimension increase along the c axis that turns out to be more favourable energetically, in contrast to the increase along the a axis as it is the case in the course of γ'-phase ordering in a bulk Ni–Ga system [3], since the latter causes an increase of the size misfit between the growing phase lattice and the substrate one. This conclusion follows from the lattices conjugation schemes (see Figs.2 and 3) constructed using their reciprocal spaces oriented in a certain manner In Fig.2, vertex points of the square net belong to the reciprocal lattice sites of NaCl crystals when the [100] direction is perpendicular to the single crystal cleavage plane where GaAs and Ni layers are deposited. In the same scale, points designated as (•), (°) and (Δ) correspond to sites of the reciprocal lattice for GaAs (at the identical orientation), for γ and γ'-phases with NiAs type lattice ($c/a = 1\ 25$ for γ and 0 625 for γ') oriented with [100] direction normal to the substrate, respectively The reciprocal lattice sites for hexagonal phases form a rhombic system with the angle $\varphi = 60°$ between sides, no matter what is the c/a ratio. In those cases, the conjugation of hexagonal and cubic phase lattices seems to be very unfavourable. Fig.3 shows similar constructions in a reciprocal space when hexagonal γ and γ' lattices as well as γ'' one observed in this work are oriented with [121] direction parallel to [100] of NaCl and GaAs. Lattices of the hexagonal (γ-) phase and cubic (GaAs, NaCl) crystals turn out to be oriented in the best manner A calculation evidences that, if the c/a ratio is 1 25, the angle between $(\bar{1}01)$ and $(\bar{1}\bar{1}1)$ planes (i.e. between the reciprocal lattice vectors drawn to sites with the same indices) is 90.77° This results in an almost ideal con-

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	$12\bar{3}$, $\bar{1}23$
1 72	202, 222, $20\bar{2}$, $\bar{2}2\bar{2}$
1.47	$02\bar{4}$, 024
1.32	$32\bar{1}$, $\bar{3}2\bar{1}$, $3\bar{1}1$, $\bar{3}11$
1 12	$\bar{1}25$, $12\bar{5}$
0.97	$03\bar{6}$, 036, $\bar{4}3\bar{2}$, 432

jugation between the cubic lattice and the hexagonal one.

A different picture, however, is observed in experiment. In the ternary Ni–Ga–As system, the γ″ phase with a hexagonal lattice (c/a = 2.46) is formed rather than one based on the γ′-Ni_3Ga_2 lattice. It follows from Fig.3 that the conjugation of γ″ lattice and the cubic one is more favourable at [121]‖[100] than that of γ′ and the cubic (NaCl) one. Consequently, the growth of an ordered γ″ phase with a doubled period along c axis is more favourable energetically that that of γ′ one having the doubled period along a axis.

Thus, the hexagonal γ″-phase of Ni–Ga–As system with a gallium-arsenide type lattice having parameters a = 4.11 Å, c = 10.09 Å (c/a = 2.46) is observed to be formed under an interaction of GaAs and Ni layers deposited onto NaCl single crystals at the substrate temperatures from 200 to 400 °C.

References

1 M.Hansen, K.Anderko, Constitution of Binary Alloys, McGraw-Hill Book Company, Inc, New York (1958).

2. R.M.Barabash, Yu.N.Koval, Crystal Structure of Metals and Alloys, Naukova Dumka, Kiev (1986) [in Russian].

3. F.A.Shunk, Constitution of Binary Alloys, Second Supplement, McGraw-Hill Book Company, Inc, New York (1958).

4. N T.Gladkikh, I.P.Grebennik, S.V.Dukarov et al., *Metallofizika*, **14**, 66 (1992).

5. S.S.Gorelik, L.N.Rastorguev, Yu.A.Skakov, X-ray and Electron-Optical Analysis, Applications, Metallurgia, Moscow (1970) [in Russian].

6. L.M.Utevsky, Diffraction Electron Microscopy in Metals Science, Metallurgia, Moscow (1973) [in Russian].

Структура γ-фази в тонкоплівковій системі Ni–Ga–As

С.В.Дукаров

При конденсації шарів GaAs і Ni на підігріті до температури 200–400 °С монокристали NaCl спостерігається ріст монокристальної фази потрійної системи Ni–Ga–As. Наявність вузлів з ненульовим третім індексом дає можливість визначити параметри гратки a'' = 4.11 Å, c'' = 10.90 Å, а також кут між векторами $[\bar{1}01]$ і $[\bar{1}\bar{1}\bar{1}]$, який дорівнює 109°30′ Завдяки орієнтуючому впливу NaCl-підкладки енергетично більш вигідним виявляється ріст γ″-фази потрійної системи з параметрами $a'' = a_\gamma$, $c'' = 2c_\gamma$, в той час як у масивних зразках подвійної системи Ni–Ga впорядкування γ-фази при відпалі супроводжується ростом γ′-фази з параметрами $a' = 2a_\gamma$, $c' = c_\gamma$.