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## Peculiarities of nucleation at chemoepitaxy

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Because of of analysis of experimental data on 26 binary systems peculiarities the processes of nucleation are analysed at chemoepitaxy in film structures. In an outcome the insufficiency of criterions, defining conventional mechanisms of growth of recordings and some other character of the intermediate mechanism of growth was established. Is established, that this or that mechanism of growth of yields solid-phase of reaction is determined by a complex of parameters. Two-dimensional growth of films is most probable at small of supersaturation and difference of factors of thermal expansion of a substrate and accumulated phase, large difference of their modules of a shift and high firmness properties of a substrate in conditions average and force adhesion. Most favorable conditions three-dimensional of growth of such recordings are high of supersaturations and large discordance junction of lattices in conditions weak adhesion. The conclusion is made that the processes of twinning and shaping of habitus in increasing phases in conditions of a high entropy of melting, large difference of factors of thermal expansion, large of strain on the phase boundary and weak of adhesion are most probable. The probability of formation of the doubles at of crystals less of faces is great in conditions large of supersaturations and of strains on the phase boundary, high firmness performances of a substrate (parent phase) at average and force adhesion. The habitus of increasing phases is most swept up at a high entropy of melting, large difference of modules of a shift of a substrate and film and force adhesion.

**Keywords:** chemoepitaxy, supersaturation, mechanism, habitus, nucleation, twinning.

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The process of nucleation of recordings, as is known, can flow past on one of three mechanisms: to the mechanism Frank's and van der Merwe (two-dimensional growth), mechanism of a Volmer's-Weber's (three-dimensional growth) and mechanism Krastanov's -Stranskov's (intermediate growth) /1/. Interestingly to find out in what measure these mechanisms are realized at solid-phase of epitaxy and in particular at chemoepitaxy - oriented increase of yields of chemical interaction of substance acting from the outside, with substance of a substrate. With this purpose the experimental data, obtained by us, on chemoepitaxial to growth in 26 binary systems were analysed. A film it turned out by a method of vacuum evaporation, or method of

ionic-plasma sputtering on various single-crystal substrates. The experimental outcomes calculated datas are shown in a table, where an apart from of morphological performances contain: the mechanism of growth of a film, magnitude adhesion  $\sigma_{ad} = 2\sigma - \sigma_0$  (where  $\sigma_0 = \sigma + \sigma_1 - \sigma_{AB}$ ;  $\sigma$ ,  $\sigma_1$  and  $\sigma_{AB}$  - specific free energies on the boundary a substrate - nucleus of an increasing phase, nucleus - layer of an adsorption, substrate - layer of an adsorption accordingly), effective supersaturation  $P_{eff} = P_{a\beta}$  ( $P$ -supersaturation of a parent phase by a diffusing component,  $a_\beta$  - thermodynamic activity), difference of factors of thermal expansion  $\Delta\alpha$  and difference of modules of a shift  $\Delta G$  of a substrate and film (increasing  $\beta$  - phase), entropy melting  $S$  and magnitude of a

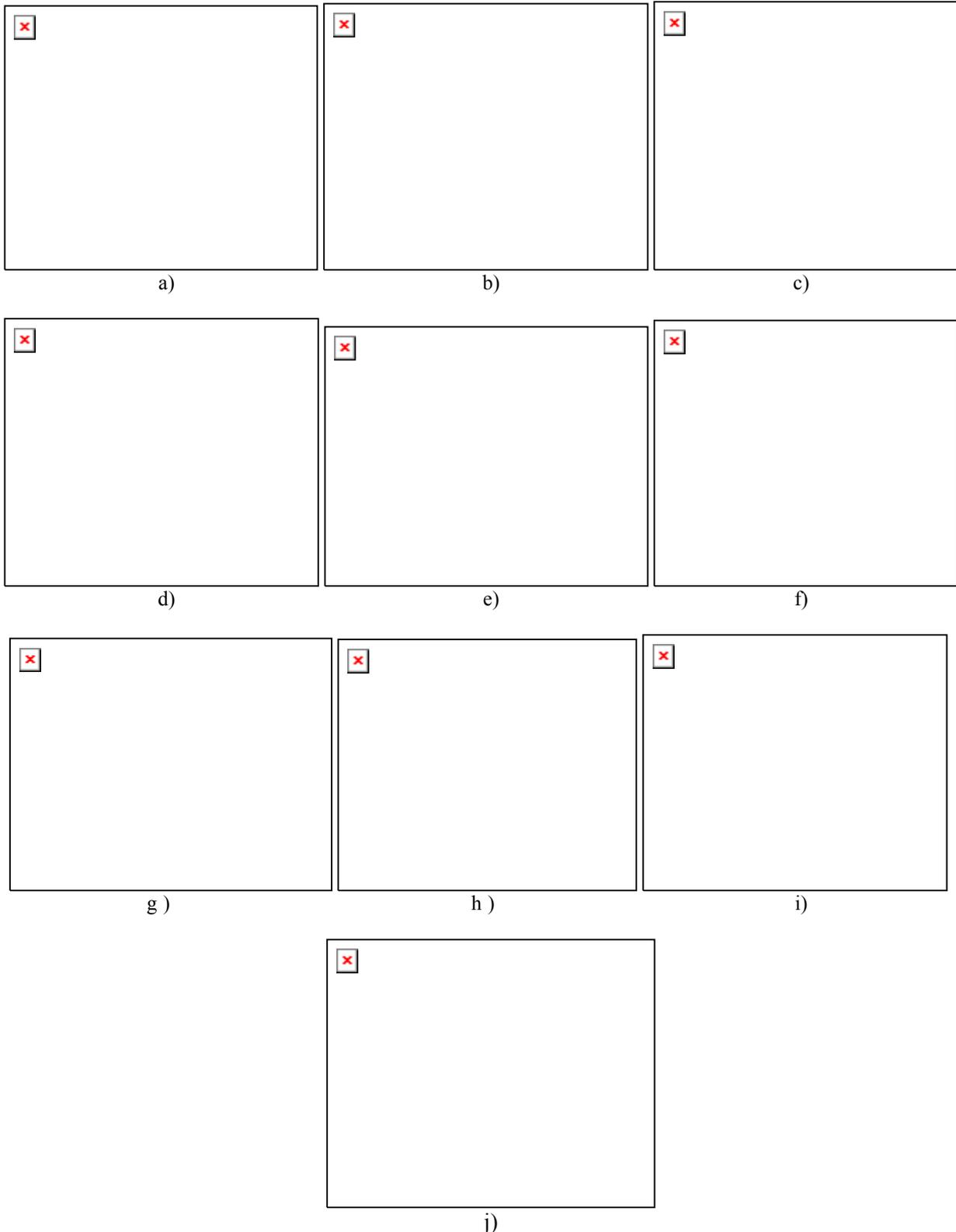


Fig.1. TEM micrograph snapshots of accumulated phases: CuZn (a), Sb<sub>2</sub>Te<sub>3</sub> (b), CrSi<sub>2</sub> on Ni (c), SiO<sub>2</sub> (d), Na<sub>3</sub>Sb (e), Zn<sub>2</sub>Mg (f), ZnSe (g), Sb<sub>2</sub>Se<sub>3</sub> (h), ZnTe (i), CrSi<sub>2</sub> on Ta (j).

discordance junction of lattices  $\Delta a/a$ .

From a table follows, that at chemoepitaxial origin and growth of product solid-phase of reactions on a crystalline substrate all above-

stated mechanisms of growth of recordings are observed. However conditions, at which these mechanisms a little are realized differ that take place at heteroepitaxy. For example, the two-

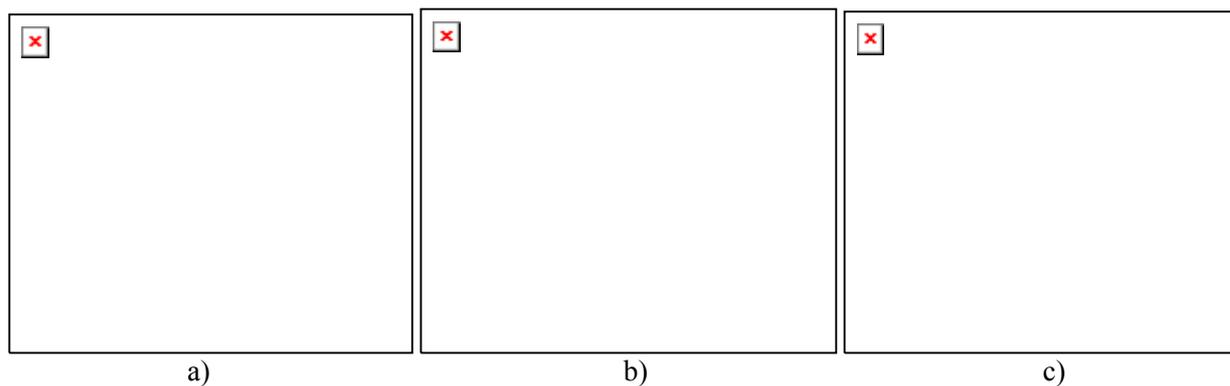


Fig.2. TEM micrograph snapshots of accumulated phases: K<sub>3</sub>Sb (a), ZnS (b), CrSi<sub>2</sub> on Si (c).

dimensional growth at heteroepitaxy is observed at large  $\sigma_{ad}$  (at force adhesion, when  $\sigma_o < 0$ ), the intermediate mechanism - at average  $\sigma_{ad}$  (at average adhesion, when  $\sigma_o \approx 0$ ) and three-dimensional - at small  $\sigma_{ad}$  (at weak adhesion, when  $\sigma_o > 0$  also is insignificant supersaturation) or two-dimensional growth at weak adhesion and high supersaturation /1/. At chemoepitaxy of a condition of a realization of that or other mechanism of growth of recordings noticeably become complicated and in it one of singularities nucleation of increasing film chemical junctions. In particular, at weak adhesion and small supersaturation can be observed and three-dimensional growth (phase Cu<sub>2</sub>Te, Sb<sub>2</sub>Te<sub>3</sub>, fig. 1, a, b), and two-dimensional growth (phase ZnSb, SiO<sub>2</sub> and CrSi<sub>2</sub> on Ni, fig. 1, c, d), and at higher supersaturation and intermediate mechanism of growth (phase Na<sub>3</sub>Sb, Cu<sub>2</sub>Sb, Ta<sub>2</sub>O<sub>5</sub>, Zn<sub>2</sub>Mg, NiO, Cr<sub>23</sub>C<sub>6</sub>, Ni<sub>2</sub>Si, fig. 1, e, f and fig. 2, c). Three-dimensional the growth has a place also at average adhesion (phase Sb<sub>2</sub>Se<sub>3</sub>, ZnSe, fig. 1, g, h). And nevertheless it is possible to state, that the two-dimensional growth of product solid-phase of a reactions on a crystalline substrate is most probable at small supersaturation and difference of factors of thermal expansion of a substrate and film, large difference of their modules of a shift and high performances of firmness of a substrate in conditions average and force of adhesion. The most favorable conditions three-dimensional of growth of such film yields are: high supersaturation and large magnitude of a discordance junction of lattices in conditions

weak adhesion.

The reason of change of the mechanism of growth of recordings can be different /2/, but all of them, by and large, call a modification of a relation of boundary free energies. It can be and supersaturation, and temperature of a substrate, and material of the substrate, and magnitude of the contribution of an energy solid-phase of reaction in a modification of Gibbs' potential at formation of nucleus of an increasing phase /3/ etc. For example, at a diminution of supersaturation three-dimensional the mechanism of growth can be replaced by the two-dimensional mechanism, that is observed at saturation of a copper substrate by pairs of zinc at first above zinc, and then above a  $\beta$ -brass.

From a table further follows, that the majority of analyzable recordings has noticeable habitus. And, crystallographic fasetion originating crystallites of an increasing phase is observed not only at high and average values of an entropy melting  $S$  (as it usually happens in a lack solid-phase of reactions), but also at low values  $S$  (phases Cu<sub>2</sub>Te, NiO, fig. 1, i and ZnS, fig. 2, b). In it other singularity chemoepitaxial of growth of substance consists.

As is known /1, 4/, at high values of an entropy melting the phase boundary appears atomic-smooth or contains steps, due to what the edges of a nucleus grow layerwise and remain thus flat, and the growth rates of different edges essentially differ. Therefore smooth phase boundary has the large anisotropy of growth rate, as stipulates shaping faceted of the forms crystallites. At small

Table

Performances of recordings and boundary a film-substrate

Substra- te/Filmt	Habi- tus	Twin- ning	Mec- hanis m	$\sigma_{ad}$ , mJ / m <sup>2</sup>	P <sub>eff</sub>	$\Delta\alpha \times 10^{-6}$ , K <sup>-1</sup>	$\Delta G$ , GPa	$\sigma_s$ , MPa	S	$\Delta a/a$ , %
Zn/ZnS	weak	-	Int	180	2.10 <sup>4</sup>	11	15	150	2,8	14,9
Zn/Zn <sub>2</sub> Mg	weak	-	Int	10	4.10 <sup>2</sup>	11	11	150	5,9	7,8
Ni/NiO	+	-	Int	0	90	2	21	280	3,2	5,9
Ta/CrSi <sub>2</sub>	+	-	Int	210	9.10 <sup>2</sup>	5,5	48	110	8,6	34,0
Cu/Cu <sub>2</sub> O	-	weak	Tw	450	10	1	66	250	4,5	15,3
Si/CrSi <sub>2</sub>	-	weak	Int	160	90	9,5	35	16	8,6	3,9
Cu/Cu <sub>2</sub> Sb	+	weak	Int	0	2.10 <sup>2</sup>	12,3	78	250	5,3	9,9
Ni/CrSi <sub>2</sub>	+	weak	Tw	60	90	2	50	280	8,6	12,9
Ni/SiO <sub>2</sub>	-	weak	Tw	160	40	2	60	280	0,7	5,3
Sb/K <sub>3</sub> Sb	weak	weak	Int	100	4.10 <sup>4</sup>	11,6	12	7	8,3	19,2
Si/Ni <sub>2</sub> Si	weak	weak	Int	0	190	9,5	34	16	3,8	9,9
Cu/Cu <sub>2</sub> Te	weak	+	Th	0	3.10 <sup>2</sup>	3	65	250	2,0	4,0
Cu/Cu <sub>2</sub> In	weak	+	Int	120	5	6,0	87	250	4,6	4,0
Ni/NiSe	weak	+	Tw	220	30	1,0	52	280	4,7	4,1
Cu/Cu <sub>3</sub> Sn	weak	+	Int	150	7.10 <sup>2</sup>	1,0	42	250	5,2	7,3
Sb/Na <sub>3</sub> Sb	weak	+	Int	20	4.10 <sup>2</sup>	22,6	1	7	8,3	5,5
Sb/CdSb	weak	+	Tw	160	9.10 <sup>2</sup>	10,6	10	7	5,8	5,6
Zn/ZnSe	-	+	Th	100	2.10 <sup>3</sup>	16	8	150	3,3	5,8
Cr/Cr <sub>23</sub> C <sub>6</sub>	-	+	Int	20	9.10 <sup>2</sup>	7	6	400	4,2	5,7
Cu/Cu <sub>2</sub> Cd	-	+	Int	270	2.10 <sup>2</sup>	13,3	90	250	2,7	3,0
Cu/CuZn	-	+	Th	140	3.10 <sup>2</sup>	2,0	65	250	2,2	3,5
Sb <sub>2</sub> Te <sub>3</sub>	+	+	Th	20	50	7,6	14	7	12,9	2,2
Sb <sub>2</sub> Se <sub>3</sub>	+	+	Th	160	10	14,6	8	7	7,3	8,7
Zn/ZnTe	+	+	Th	90	5.10 <sup>4</sup>	20	43	150	4,7	11,9
Sb/ZnSb	+	+	Tw	60	90	11,6	20	7	5,8	5,5
Ta/Ta <sub>2</sub> O <sub>5</sub>	+	+	Int	0	10 <sup>4</sup>	13,5	22	110	8,4	10,4

The note. S =  $\Delta H_m / RT_m$ ; the signs “+” and “-” mean accordingly presence or lack in a film of the doubles and of habitus; reductions: Th-three-dimehsional, Tw-two-dimensional, Int - intermediate.

values S the surface of the boundary is rough, therefore it can join particles of an increasing phase practically in any point, as stipulates almost identical growth rate in different directions and as a corllary - rounded the form of growing crystals.

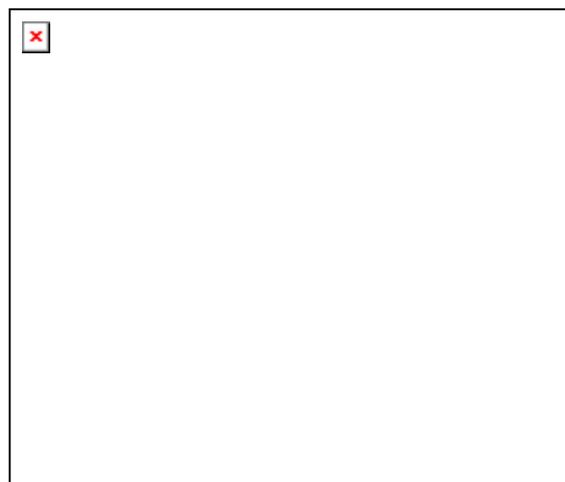
In our experiments was observed precisely expressed habitus (fig. 1, b, c, h) at nine phases, as a rule, at the large values of an entropy melting. The elemination is made by a phase NiO, formative on a substrate with high performances of firmness and elasticity. Poorly expressed facition of growing crystals was observed at an average and low value S, of an elemination of phases Zn<sub>2</sub>Mg, K<sub>3</sub>Sb, Cu<sub>3</sub>Sn

and CdSb (fig. 1, e, f, and fig. 2, b), at which weak of facition crystallites, probably, is stipulated by flowing past processes of twinning or high of supersaturation. Because of a low value S at phases ZnSe, Cr<sub>23</sub>C<sub>6</sub>, Cu<sub>2</sub>Cd, CuZn and Cu<sub>2</sub>O habitus is absent (fig 1, a, g ). The elemination is made by a phase CrSi<sub>2</sub>, growing on a silicon substrate, at which facition of crystals is not observed (fig. 1, d), probably, from of intensively flowing past processes of twinning.

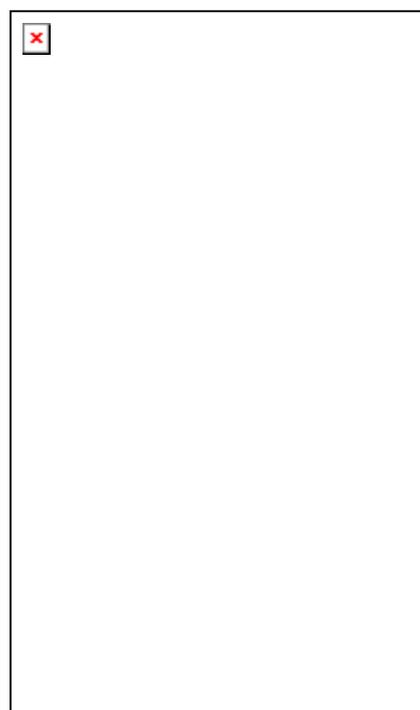
The third singularity of nucleation at chemoepitaxy is, that in an outcome of coherent reorganization of a lattice of a parent phase in affiliated processes of twinning

intensively flow past. On TEM micrograph the doubles are visible as dark or light plates or edges in twin a position (fig. 1, f, g, h and fig. 2, c) ; on electron diffraction pattern they call emerging additional reflexes (fig. 3 ), and in a case textured of recordings on X-rays - and electron diffraction pattern - decomposition textured of maximas in azimuth direction (fig.4). From the fig. 4, and is visible, that the decomposition of maximas on X-rays pattern is connected to decomposition of a zone of positions on an orb of projections, which, being intersected with a circle of a reflection, gives some poles (on figure two) instead of one diffusion.

The reduced table testifies that of twinning of products solid-phase of a reaction the place in majority of investigated pairs a substrate - film has. Most intensively the twinning flows past in systems, where the large difference of factors of thermal expansion and rather high supersaturation is observed. In these conditions the probability of formation of a defective structure in an accumulated phase (and in a substrate) and large interior strains of a discordance and thermal, and also concentration and diffusion strains due to presence of diffusion zone /5/ is high. The defect of a structure and relaxation of interior strains reduce in processes of twinning. And twinning is observed not only in hexagonal and cubic crystals, but also in rhombic and trigonal structures, for which are characteristic low (80-250 C) epitaxial of temperature (CdSb, Sb<sub>2</sub>Te<sub>3</sub>, ZnSb, NiSe etc.). The association of morphology of an increasing phase from a material of a substrate is remarked also force. So, silicone of chromium CrSi<sub>2</sub> at of growth on a silicon substrate practically does not contain the doubles of growth and has not of habitus, at growth on a substrate of tantalum still does not contain the doubles, but has the habitus and at growth on a substrate of nickel contains and habitus and doubles, though the entropy of melting in all three cases is identical. This distinction in morphology of recordings silicone of chromium a, apparently, is connected, according to a table, to a various value  $\Delta\alpha$ , with different firmness and elastic properties of substance of substructures or with different magnitude adhesion and also



a)



b)

Fig.3. Electron diffraction pattern of the Na<sub>3</sub>Sb (a) and schematic explaining splittings in the diffraction pattern (b).

discordance or junction of lattices.

At last from a table follows, that the intermediate mechanism of growth of recordings has a place not only at average adhesion and effective of supersaturation, but at weak adhesion and small of supersaturations (Na<sub>3</sub>Sb, Ta<sub>2</sub>O<sub>5</sub>, Zn<sub>2</sub>Mg, NiO, Ni<sub>2</sub>Si and others, fig. 1, e, f and fig. 2, b). Thus, in “pure” an aspect this mechanism is exhibited seldom. Usually on a surface of a substrate simultaneously are formed and the two-

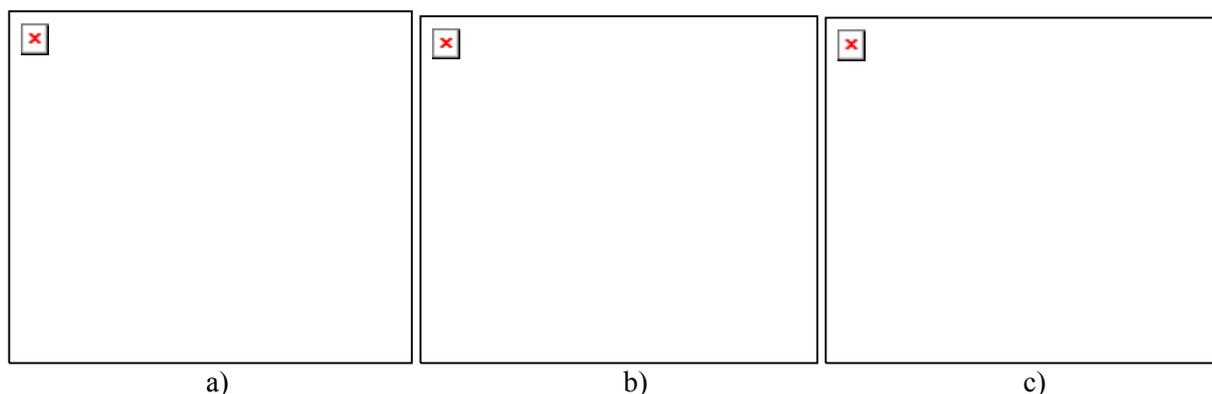


Fig.4. Splitting of reflections due to twinning (a), X-rays pattern of a phase  $\text{Cr}_{23}\text{C}_6$  (b) and electron diffraction pattern of a phase  $\text{CrSi}_2$  (c).

dimensional and three-dimensional germs of an increasing phase all this and makes the fourth singularity of nucleation at chemoepitaxy.

In whole all above-stated singularities, under our judgement, are connected to the contribution to processes of nucleations of an energy of solid-phase a reaction, which stipulates formation of larger critical nucleus of increasing phases in conditions smaller of supersaturations rather than at heteroepitaxy and with coherent reorganization of a lattice of a parent phase in a lattice of an increasing phase.

Thus, the criterions of mechanisms of growth of phases, fair at usual nucleation, appear insufficient at chemoepitaxial of growth of substance. Only on magnitude adhesion and supersaturation in a concrete binary system it is impossible univalently to predict this or that mechanism of chemoepitaxial of growth of a film, so also morphology of increasing phases. , for these parameters are determined by a complex of performances, and also their mutual influence. For example, the probability of formation of the doubles and of habitus in increasing phases

is greatest first of all at high values of an entropy of melting and difference of factors of thermal expansion of a substrate and film in conditions weak and average adhesion, and also large interior of strain. The probability of formation of the doubles in of crystals less crystal of plane of increasing phases is great at rather high of supersaturations, high performances of elasticity and firmness of a substrate in conditions average both force adhesion and high interior of strains. (mainly concentration and diffusion) on the phase boundary. Further, the probability of formation of crystals with of plane without the doubles is greatest at a high value of an entropy of melting, high difference of modules of a shift of a substrate and film in conditions, as a rule, weak adhesion. Other performances of a system a film - substrate (type juncture of lattices, kinetics of growth of recordings, relation of diffusivities of cooperating components and others) play, on our sight, the minor role in processes of nucleation. Is necessary all this for taking into account at deriving film yields solid-phase of reactions with a necessary structure and properties.

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## Особливості зародження при хемоепітаксії

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На основі аналізу експериментальних даних 26 подвійних систем вивлені особливості процесів зародження при хемоепітаксії в плівкових структурах. Встановлено недостатність критеріїв, що визначають загальновідомі механізми росту плівок та характер проміжного механізму росту. Показано, що той чи інший механізм росту продуктів твердофазних реакцій визначається комплексом параметрів. Двовірний ріст найбільш можливий при малих пересиченнях та різниці коефіцієнтів термічного розширення підкладки і наростаючої фази. Найбільш сприятливими умовами трьохмірного росту плівок є високі перенасичення та велика невідповідність суміжних ґраток в умовах слабкої адгезії. Змінюються і умови формування габітуса плівок хімічних сполук, а також умови протікання в них процесів двійникування та формування габітуса в наростаючих фазах при високій ентропії плавлення, великій різниці коефіцієнтів термічного розширення, великих напругах на фазовій межі та слабкій адгезії. Можливість утворення двійників у негранних кристалів особливо значна в умовах великих пересичень та напруг на фазовій межі, високих міцнісних властивостей підкладки (материнської фази) при середній та сильній адгезії. Габітус плівок найбільш помітний при високому значенні ентропії плавлення, значній різниці модулів пружності підкладки та плівки, і сильній адгезії.

**Ключові слова:** хемоепітаксія, пересичення, механізм, габітус, зародження, двійникування.