P.I. Ignatenko*, D.N. Terpiy**, A.A. Goncharov**, M.A. Muza*, N.A. Vasilenko***

Disperse of increasing films chemical compounds

*Donetsk National university, ** Donbass machine-building Academy,
*** Severodonetsk an institute of technology
83015, Donetsk, (062) 3384673, E-mail:volya@abc.donbass.com

On a base of the theory and analysis of experimental datas on 35 chemical compounds, increasing on crystalline substrates with the help of jet raising dust, the dependence of a disperse of their structure on a supersaturation of a mother phase by a diffusing componentr, temperature of increase , value of mismatch of conjugated crystal lattices, resilient constants of an increasing phase and specific free boundary energy is detected.

The common legitimacy is placed: with augmentation of an odds of products $R_v \, T \, lnP_{eff}$ and $0,5 \, (\Delta a/a)^2 \, E/\nu$ the dimensions of critical nuclei (especialy twodimensional) of increasing chemical compounds are reduced.

The disperse of films estimated on a base of datas on the dimensions of critical nuclei of increasing phases. The dimensions of nuclei of compounds are in an interval 0,5 - 57 nm. The compounds with a low and high disperse are detected and the pathes of achievement of a required disperse increasing phases are defined

Key words: disperse, dimensions of nuclei, supersaturation, temperature, boundary free energy.

It is well-known, that the disperse of a stuff essentially influences his physical, physico-chemical and mechanical characteristics. In is considered, that the defining role in a disperse of material is played by a supersaturation of a mother phase by a diffusing component. In particular, at high supersaturations the structure is formed highdisperse. Howerer, as display researches, including ours, this factor completely not definited a degree of dispersion of material; series of other factors react also.

In the given work all major factors influential in a disperse of products solid-phase of a reaction as films on crystalline substrates are parsed. It is done on a base of experimental datas on 35 binary systems and in correspondence with theoretical performances [1-3]. Thus the disperse of films estimated on the dimensions of critical nuclei of increasing phases, as was exhibited [4], that the nucleation kinetics essentially predetermine kinetics of continuous layer of a film, since both they are characterized by such common parameters, as energy of formation of critical nuclei (ΔG^*_i), activation energy of a diffusion etc. The evaluation of the critical dimensions twodimensional (r^*_2) and threedimensional (r^*_3) of nuclei of increasing phases and work of their formation was spent under the formulas [2]:

$$r*_2 = \frac{2\sigma_1}{z - \sigma_0/h} \; ; \qquad r*_3 = \frac{2p}{3z} \; ; \qquad \Delta G*_2 = \frac{4\sigma_1 h}{z - \sigma_0/h} \; ; \qquad \Delta G*_3 = \frac{4p^3}{27z^2} \; , \qquad (1),$$

Where $\sigma_0 = \sigma + \sigma_1 - \sigma_{AB}$ (σ, σ_1, σ_{AB} — specific free energies respectively on boundary a substrate (A) – nucleus of an increasing phase (β), nucleus - layer of an adsorption (B) and substrate - layer of an adsorption); h-height of twodimensional nuclei; $p = 4\sigma_1 + \sigma_0$;

$z = R_v T \ln P_{eff} - L$ ($P_{eff} = P \times a_\beta$ i.e. represents product of a relative supersaturation of a mother phase (A) diffusing atoms and thermodynamic activity); T-absolute temperature of increase; $R_v = R/V_m$, i.e. is equal to the attitude of a gas constant and molar volume of an increasing phase; $L = 0,5\{(x-x_1)/x\}^2 (E/\nu)$, where $(x-x_1)/x$ – the value of mismatch of crystal lattices mother and increasing of phases; E – Young's modulus, ν – Poisson`s ratio.

In the table the necessary datas and calculared value of twodimensional and three-dimensional critical nuclei for increasing phases and energy of nucleating are reduced.

The tabulared datas direct that is true in series of cases at high supersaturations will be formated of a film with highdisperse by structure (CuZn, Cu_2Al, CdTe). However, at such supersaturations can be formated middledisperse (ZnTe, CdSb, InSb) and even lowdisperse of compounds (Ta_2O_5, K_3Sb, Na_3Sb, $Cr_{23}C_6$, Al_2O_3), but thus, as a rule, should be high value $_1$ and T and small L. And on the contrary, at a low supersaturation can be formated not only lowdisperse of structure , but also middle- and highdisperse of compounds (Cu_2Mg, Cu_2Cd, SiO_2, Sb_2Se_3, CdSe, Sb_2Te_3), but thus should be small value σ_1 and T.

From the table follows, that lowdisperses such phases, as Ni_2Si, Na_3Sb, $Cr_{23}O_6$, Ta_2O_5, Cr_2O_3, $MgZn_2$, Al_2O_3., Cu_3Sn, Cu_2O, Cu_2Te, CdO, TiO_2, Nb_2O_5 , NiO, CoO should form. Thus, as a rule, $r*_2 < r*_3$ and $\Delta G*_2 < \Delta G*_3$, that [1-3] agrees favours to the oriented increase ε_{eff}: of phases. In this case value z (i.e. the odds between product $R_v T \ln P_{eff}$ and L) minimumly or has average value in conditions of a small

effective supersaturation and major value σ_1. The fact of a low disperse the above-stated
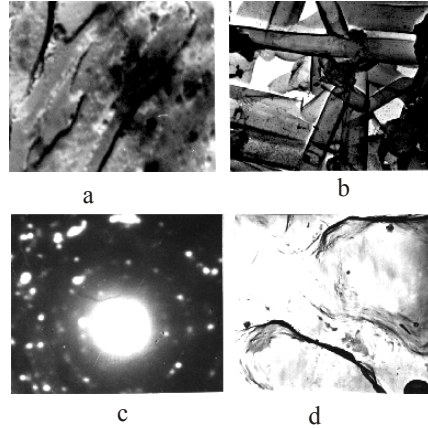

Fig. 1. Electron-optical patterns lowdisperse increasing of compounds : Ni_2Si (a), Na_3Sb (b, c) $MgZn_2$ (d). x 10000.

phases confirms experimentally (rice 1). Thus the crystallites of phases Na_3Sb and $MgZn_2$ have cigar the form, that testifies [5] to presence of set of steps on vicinal of surface of substrates Zn and Sb. The dimensions of critical nuclei oscillate in limens 10-57 nm.

At high values z or at average z, but high supersaturation and small σ_1 the dimensions of critical nuclei become small and the creation
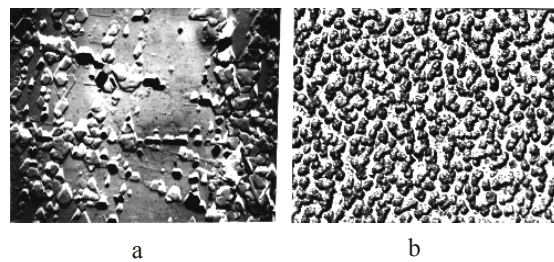

Fig. 2. TEM patterns of highdisperse increasing of compounds: SB_2Te_3 (a), SiO_2 (b). x 20000.

highdisperse of compounds (rice 2) with the dimensions of nuclei from 0,5 up to 3 nm is supervised. It falls into to such phases, as CuZn, CdTe, Cu_2Mg, CdSe, SiO_2, Cu_2Al, Cu_2Sb, Cu_2Cd, Sb_2Te_3, Sb_2Se_3 and ZnSb. The remaining increasing phases have middledisperse structure (rice 3) with the dimensions of critical nuclei from 3 up to 10 nm.

Table

Datas for calculation of the dimensions of critical nuclei of increasing phases

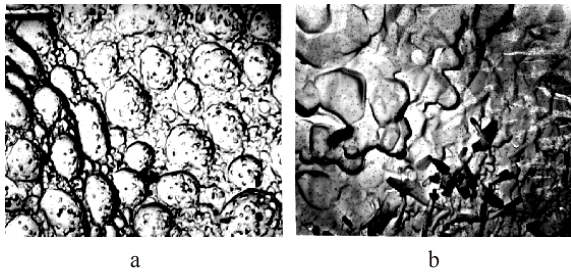| Phases	σ_1, J/m²	σ_o, J/m²	h, nm	R_v, MJ/m³K	L, MPa	$\ln P_{eff}$	T, K	z- $-\sigma_o/h$ MPa	r*$_2$, nm	r*$_3$, nm	ΔG^*, J
CuZn	0,07	0	0,29	0,55	2300	4,5	953	58,7	2,4	3,2	0,096
Cu$_3$Sn	0,08	0	3,82	0,24	586	3,4	723	4	40,3	24,6	25
Cu$_2$Mg	0,02	0	0,7	0,31	672	2,8	823	42	0,95	1,2	0,03
Cu$_2$Al	0,02	0	0,5	0,38	3990	12,2	873	57,2	0,7	0,9	0,014
Cu$_2$Sb	0,01	0,03	0,6	0,28	760	5,3	573	44	0,7	1,4	0,01
Cu$_2$Te	0,04	0,08	0,7	0,24	230	2,3	423	2,4	33,3	46	1,9
Cu$_2$Cd	0,02	0	1,6	0,31	230	2,8	323	49,4	0,8	1,1	0,05
Ta$_2$O$_5$	0,37	0	0,4	0,16	473	9,1	663	24,9	29,7	9,6	8,6
SiO$_2$	0,08	0	0,4	0,37	844	2,7	923	78	2,0	2,7	0,13
Sb$_2$Se$_3$	0,05	0	0,4	0,1	221	2,5	1073	47	2,1	4	0,08
Cu$_2$O	0,3	0	0,43	0,35	780	1,9	1273	31,5	19	8,1	4,9
CrSi$_2$	0,05	0,34	0,64	0,31	1825	4,5	1323	14,7	6,8	18	0,43
ZnSe	0,22	0,35	0,57	0,3	754	7,5	373	23,7	18,6	9,8	8,0
ZnTe	0,13	0,27	0,61	0,24	1366	11,5	523	55	4,9	6,97	0,8
K$_3$Sb	0,12	0	0,11	0,08	800	10,6	973	25	10,8	12,8	0,25
CdSb	0,08	0	0,85	0,24	910	6,8	573	25,1	6,4	8,5	0,87
ZnSb	0,03	0	0,82	0,29	1020	4,5	823	54	1,1	1,5	0,05
NiSe	0,28	0,04	0,53	0,51	1085	5,4	423	72,9	7,7	9,6	2,3
Ni$_2$Si	0,33	0,06	0,49	0,38	1130	2,9	1073	41,9	15,7	16,7	5,1
CdTe	0,04	0	0,65	0,2	810	7,7	573	59,4	1,3	2,2	0,07
CdSe	0,12	0,28	0,6	0,25	48	1,1	673	90,3	2,6	3,7	0,38
CdO	0,22	0,3	0,47	0,53	1260	2,9	873	18	24,4	9,6	5
Na$_3$Sb	0,16	0	0,95	0,12	902	8	973	31,8	10	13,4	3
Sb$_2$Te$_3$	0,01	0,06	3,04	0,09	133	2,9	673	43,2	0,46	0,62	0,03
InSb	0,17	0,04	0,65	0,2	1390	9,6	773	67,3	5,2	5,2	1,2
Cr$_{23}$C$_6$	0,6	0,34	1,07	0,05	403	6,9	1373	39	30,7	30,9	26,1
Cr$_2$O$_3$	0,41	0,34	1,37	0,28	1754	5,1	1273	39	20,8	20,5	23
NiO	0,4	0,2	0,42	0,83	2780	4,5	773	60	13,3	11,2	4,5
CoO	0,4	0,27	0,42	0,66	650	1,1	1073	14	57,1	11,4	2,8
ZnO	0,16	0,12	0,52	0,58	730	1,8	773	54	5,9	6,6	0,98
MgZn$_2$	0,11	0,21	0,85	0,31	555	5,9	323	10,9	20,2	12,2	3,8
TiO$_2$	0,3	0,15	0,48	0,44	72	0,3	1473	18	24,4	9,6	5
Al$_2$O$_3$	0,28	0,28	1,3	0,32	3150	6,4	1573	50	11,4	13,2	8,4
Nb$_2$O$_5$	0,26	0	2,1	0,15	500	2,4	1473	30,3	17,5	23,3	19
Si$_3$N$_4$	0,12	0	0,56	0,4	454	4,5	623	78,7	3,2	4,2	0,4

The note: 1 a (атто) = 10^{-18}

Fig. 3. TEM patterns of middldisperse increasing of compounds : ZnSe (a), ZnTe (b). x 10000

By results of tabulared datas the graph of dependence of twodimensional of critical nuclei from value z (rice 4) is constructed, from which
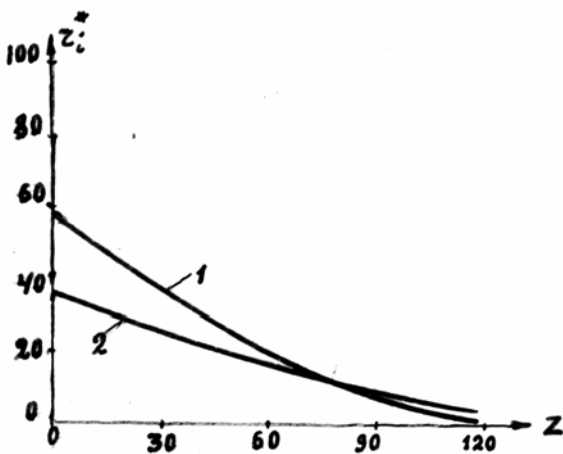

Fig. 4. Dependence of dimention of cristal nuclei r^*_I on value z: two-dimentional (curve 1) and three-dimentional (curve 2).

follows (with a correlation coefficient equal 0,68), that with augmentation z the dimensions of nuclei diminish, that is acorded with theoretical reviewing (according f.(1)). For three-dimensional critical nuclei data dependence under is rexpresed. From the theory

follows, further, that at a strong adhesion ($\sigma_o \leq 0$) $r^*_2 \leq r^*_3$, and at a weak adhesion ($\sigma_o > 0$) - on the contrary, that with rare exception, confirms experimentally. From the theory also follows, that with other things being equal disperse of compounds should be lower than a disperse of components, from which they will be derivated, that too discovers experimental confirmation.

At last, from the table implies, that for many compounds $\Delta G^*_2 \ll \Delta G^*_3$, that directs [1-3] favourable conditions chemoepitaxial of a nucleation and growth of phases. At $\Delta G^*_2 \geq \Delta G^*_3$ the probability of the oriented increase of films of chemical compounds appears low. The phases concern to such compounds: InSb, CdO, Cu_2Mg, Cu_2Al, Cu_2Sb, Si_3N_4, and Sb_2Se_3.

Thus, varying such parameters as P_{eff}, T, $\Delta a/a$ and σ_i (last two parameters can be changed with help of an alloy building of a substrate or the plottings on her of a thin layer of other material) can be gained of films of chemical compounds of a different degree of dispersion and structural perfection. In particular, to receive highdisperse structure it is necessary to spend jet raising dust at a high effective supersaturation, small value of a specific free energy on boundary between a substrate and increasing phase and, as a rule, at a major odds of products $R_v T \ln P_{eff}$ and $0,5\,(\Delta a/a)^2 \times E/v$.

[1] P.I. Ignatenko. Thermodynamic analysis chemoepitaxial of growth of a new phase during a reactionary diffusion // *Izv.AN SSSR.Metals*, **4**, pp. 54-59 (1979).
[2] P.I. Ignatenko. Thermodynamic-kinetic theory of epitaxy // *Physics and engineering of high pressures*, **9(4)**, pp. 111-118 (1999).
[3] P.I. Ignatenko. Contribution of an energy of a chemical reaction on phase boundary in a common change of a potential of Gibbs' at formation of nucleus during a reactionary diffusion // *Mag. of physical chemistry,* **78(10)**, pp. 2579-2581 (1984).
[4] P.I. Ignatenko. Kinetics chemoepitaxial of growth of a new phase at a reactionary diffusion // *Izv. AN SSSR.Metals*, **2**, pp. 167-171 (1982).
[5] S.A. Kukushkin, A.V.Osipov. Thermodynamics and kinetics of phase changes of the first sort on a surface of solids // *Chemical physics*, **15(9)**, pp. 5-104 (1996).

П.І. Ігнатенко, Д.Н Терпій, А.А. Гончаров,
М.А. Муза, Н.А. Василенко

Дисперсність нарощуваних плівок хімічних сполук

Інститут фізики напівпровідників НАН України,
пр. Науки, 45, Київ, 03028

На основі аналізу теоретичних та єкспериментальних даних по 35 хімічних сполуках, що нарощуються на кристалічних підкладках за допомогою реактивного напилювання виявлена залежність дисперсності їхньої структури від пересичення материнської фази компонентом, що дифундує, температури напилювання, величини невідповідності сполучуваних кристалічних граток, пружних констант наростаючої фази і питомої вільної граничної енергії.

Дисперсність плівок оцінювалася на основі даних по розмірах критичних зародків наростаючих фаз. Розміри зародків з'єднань знаходяться в інтервалі 0,5 - 57 нм.

Теоретично та експериментально показано, що з ростом різниці множень зменшуються розміри критичних зародків (особливо двомірних).

Відзначено з'єднання з низькою та високою дисперсністю й зазначені шляхи досягнення необхідної дисперсності фаз, що нарощуються.