ISSN 1027-5495. Functional Materials, 25, No.4 (2018), p. 780-787.
doi:https://doi.org/10.15407/fm25.04.780

Properties of the volume phase in the layerwise growth. Case of origin of new phase above phase boundary at previous layer

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Received May 21, 2018

In present work it was studied the formation of transparent "windows" in a layered-grown sample, each layer of which consists of a basic opaque phase and an additional transparent one, in the case when the "islets" of an additional phase in a new layer originate above the phase boundary in the previous layer. Also, for this case, the law of changing the fraction σ_i of the area of the layer occupied by the transparent phase with the layer number i is studied. Distribution densities of "windows" over the area and their asymptotics in small- and large-scale areas are obtained. The existence of qualitatively different forms of the dependence of σ_i on the number of the layer as a function of the intensity parameter of formation of "islets" is shown. This parameter is the value of the average number n of new "islets" per one "islet" (the length of the boundary of one "islet") in the previous layer.
Keywords: Layerwise, origin above boundary, windows of transparensy.

Изучено образование прозрачных "окон" в послойно выращенном образце, каждый слой которого состоит из основной непрозрачной фазы и дополнительной прозрачной, в случае, когда "островки" дополнительной фазы в новом слое зарождаются над границей фаз в предыдущем слое. Изучен для данного случая закон изменения доли σ_i площади слоя, занятой прозрачной фазой, с номером слоя i. Получены плотности распределения "окон" по площади и их асимптотики в мелко- и крупномасштабной областях. Показано существование качественно разных форм зависимости σ_i от номера слоя в зависимости от параметра интенсивности образования "островков" — величины среднего числа n новых "островков", приходящихся на один "островок" (длину границы одного "островка") в предыдущем слое.

Властивості об'ємної фази при пошаровому зростанні. Випадок формування нової фази над межею фаз у попередньому шарі. *Р.Є.Бродський*.
Вивчено формування прозорих "вікон" у пошарово вирощеному зразку, кожен шар якого складається з основної непрозорої фази і додаткової прозорої, у разі, коли "острівці" додаткової фази у новому шарі зароджуються над межею фаз у попередньому шарі. Вивчено для даного випадку закон зміни частки σ_i площі шару, зайнятої прозорою фазою, з номером шару i. Отримані густини розподілу "вікон" за площею і їх асимптотики у дрібно- і великомасштабній областях. Показано існування якісно різних форм залежності σ_i від номера шару в залежності від параметра інтенсивності утворення "острівців" — величини середнього числа n нових "острівців", що припадають на один "острівець" (довжину межі одного "острівця") у попередньому шарі.

1. Introduction

In the case of layer-by-layer formation of a sample whose layers consist of the main phase of a material with inclusions of another, "new" phase, such inclusions in adjacent layers can contact each other [1–4], forming volume inclusions. These volume inclusions can be completely within the sample or come out on the end surfaces. In particular, they can permeate through the entire sample. In this case, the sample can acquire new properties, for example, if the main phase is insulating, while the additional is conducting one, then in case of a volumetric inclusion come out on both surfaces, the sample will become conductive.

Another example is a transparent new phase in an opaque sample. In the case of a through inclusion, if the projections of inclusions in all layers on one plane that is parallel to the layers have an intersection area, a transparent "window" will appear in the sample. The formation of such "windows" is studied in this paper.

The probability of the appearance of a "window" and the distribution of "windows" over the area depends on how the new phase is formed in separate layers. In [5], the case of independent formation of a new phase in layers was studied, in [6] — the case of the nucleation of "islets" of a new phase strictly above a new phase in the previous layer. Another common case is the case of the nucleation of a new phase above the phase boundary. The results of the investigation of this case are presented in this paper.

2. Statement of the problem.

Let us consider a layerwise forming sample. We assume that all the layers have the form of a circle of radius R. The layers consist of a basic opaque phase with inclusions of an additional transparent one. The number of layers is N. The inclusions of the new phase consist of round "islets" of radius r. "Islets" of this form are obtained in the case when the "islet" originates at one point and then grows isotropically. The radii of all "islets" will coincide if the nucleation of all "islets" occurs at the same time (for example, at the start time of the layer formation) and all "islets" grow up the same time — until the end of the layer formation.

We will investigate the case when the nucleation points of the "islets" are located strictly above the boundary of the phases in the previous layer. The points of nucleation of "islets" in the initial, zero layer will be assumed to be uniformly distributed over the layer. The number of "islets" in the zero layer is n_0.

Let us introduce the characteristics of the random process of nucleation of "islets". We will do this in a form convenient for both analytical research and numerical modeling. For this, we break the boundary of the phases of the preceding layer into cells of length $\lambda << \tilde{l}$, where $\tilde{l} = 2\pi r$ is the length of the boundary of one "islet". We choose λ so that Δl, $\lambda << \Delta l << \tilde{l}$ can be introduced to proceed to the continuous case. Suppose that one and only one "islet" can originate (or not) with probability $p = \lambda/\tilde{l} \cdot n$ over each cell of length λ in a new layer. The number $n \le \tilde{l}/\lambda$ has the meaning of the average number of "islets" in the new layer to one "islet" (the length of the boundary of one "islet") of the previous layer. (In the numerical experiment, $n > \tilde{l}/\lambda$ can be taken, but this means simply a mandatory nucleation in each cell and is equivalent to $n = \tilde{l}/\lambda$). The numerical modeling of the system will be constructed following this way. The transition to the continuous case in the limit $\lambda \to 0$ is a transition to a Poisson process. We choose a segment of the boundary with length Δl such that $\lambda << \Delta l << \tilde{l}$, including $\kappa = \Delta l/\lambda$ cells. The probability p_k of the formation of exactly k "islets" over the interval Δl is

$$\mathrm{FP_k} = p^k(1-p)^{(\kappa-k)} \cdot \frac{\kappa!}{k!(\kappa-k)!}.$$

At $\lambda \to 0$ we obtain the Poisson distribution

$$p_k \to \frac{p^k}{k!} e^{-\frac{\Delta l}{\tilde{l}} n} \left(\frac{\Delta l}{\lambda}\right)^k = \frac{\left(\frac{\Delta l}{\tilde{l}} \cdot n\right)^k}{k!} e^{-\frac{\Delta l}{\tilde{l}} n}. \quad (1)$$

It is easy to see that for this expression the normalization condition $\sum_{k=0}^{\infty} p_k = 1$ is satisfied.

The average number of new "islets" over Δl

$$\sum_{k=0}^{\infty} k \cdot p_k = \sum_{k=1}^{\infty} k \cdot \frac{\left(\frac{\Delta l}{\tilde{l}} \cdot n\right)^k}{k!} e^{-\frac{\Delta l}{\tilde{l}} n} = \frac{\Delta l}{\tilde{l}} \cdot n$$

has a physically understandable meaning — i.e. "islets" are generated along the entire boundary uniformly, the average number of new "islets" over Δl is proportional to the average number n of "islets" over $\tilde{l}$ with a coefficient $\Delta l/\tilde{l}$.

The purpose of this paper is, at first, to obtain the law of change of the layer filling with a transparent phase along the layer number and, secondly, to obtain the distribution of the "windows" of transparency over the area in the finished sample when the "islets" of the transparent phase are generated above the phase boundary. By filling it is meant the fraction of the area of the layer occupied by the new phase.

Area change of the transparent phase in successive layers.

We introduce S_i — the area of the transparent phase in the layer i. Depending on the average number n of new "islets" on one "islet" of the previous layer, the number of "islets" in the layer and the area S_i may increase, decrease or remain constant with the layer number. Note that since we are talking about a random process, the statements about the increase and decrease are meaningful on average for many experiments. The value n_e such that for $n < n_e$ the area S_i will decrease with the layer number, with $n > n_e$ — increase and for $n = n_e$ will not, on average, change, we will call the "equilibrium" value of n.

If the "islets" inside the layer did not intersect, the equilibrium value of n would be unity. However, since intersections "absorb" part of the phase boundary in the layer, the actual value of n_e will be somewhat larger.

The number of "islets" in the zero layer, in the general case, should be considered small, $S_0 << S_L$, where $S_L = \pi R^2$ — layer area.

In this case, at $n < n_e$, the area of the transparent phase will decrease rapidly with the layer number (starting from the already small value) to zero, so that layers with relatively small numbers will contain only the basic, opaque phase. The "windows" of transparency will not be formed at this case.

Let's consider case $n > n_e$.

Let us study the variation of S in several first layers. For sufficiently large n new "islets" over each separate "islet" of the previous layer will form a circle of radius $2r$, similarly to [6], as shown in Fig. 1.

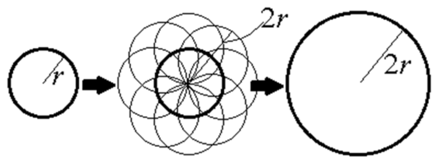

Fig. 1. Quadratic growth of the area of the transparent phase over one separate "islet", the first step.

Let us suppose that n is not as large, and this circle is not completely filled. In the case of the formation of "islets" over the new phase (rather than the boundary) studied in [6], part of the centers of the new "islets" lay not on the boundary, but inside the initial "islet", so that the increment of the area of the new phase $S_1 - S_0$ in the case [6] was less than in the one considered here. Thus, in the first step, we should observe, on average, a larger increase in the area of the new phase in comparison with [6] for the same n.

The boundary of these new "islets" will consist of, firstly, a part roughly coinciding with a circle of radius $2r$ and, secondly, from a small section near the center of the initial "islet", in the limiting case $n \to \infty$ — from a single point in the center. Hence, depending on whether the "islet" is born on this inner site, in the second step will form either a circle of a new phase of radius $3r$ (with an additional boundary line along the circle of radius r), or a ring with an outer radius $3r$ and an internal r (Fig. 2).

This distinction is important from the point of view of forming a "window". In the first case, we get a "window" that coincides with the original "islet"; in the second case, we do not get a "window" at all. The reali-

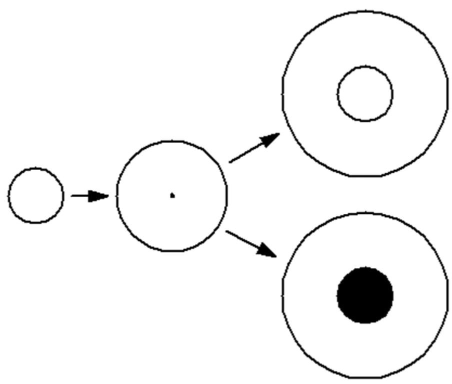

Fig. 2. The first two steps of a transparent phase formation over one separate "islet" for large n. The lines show the phase boundaries.

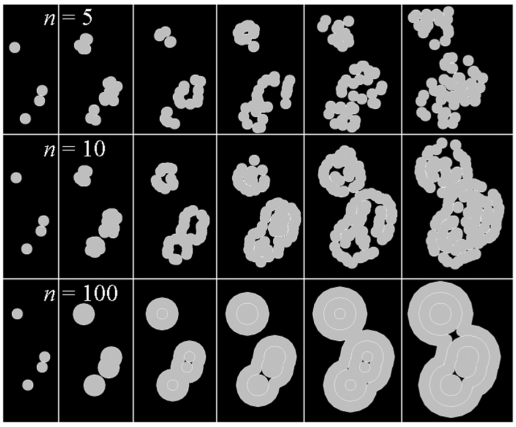

Fig. 3. The image of filling six consecutive layers, starting with the original, by transparent phase, is depicted. A selected area containing several "islets" in the source layer is shown. The average number of new "islets" per one "islet" of the previous layer is $n = 5$, 10, 100.

zation of the first case should obviously be expected for very large n, the second case for slightly smaller but still large enough for the "islets" of the new phase to be joined at the second step into a solid ring without the main phase (and the boundary line) inside, which would be observed for small n.

On the next layers, in analogous way, either new-phase circles with linearly increasing radii, similarly to [6], or concentric rings will arise. The critical value n separating the cases of a circle and rings is denoted by n_c. In either case, the area of the new phase will approximately quadratically increase.

When $n \geq n_c$, over each "islet" of the source layer circular regions of a transparent phase of radius $(i + 1)r$, where i is the layer number (the initial layer is assumed to be zero) will be formed in successive layers. So if the regions do not intersect, the total area occupied by the transparent phase will change with the layer number as $\pi((i + 1)r)^2$ and the filling of the layer with the transparent phase will be equal to

$$\frac{S_i}{S_L} = \left(\frac{r}{R}\right)^2 (i + 1)^2. \quad (2)$$

In Fig. 3 shown a characteristic view of the covering of the first several layers by "islets" is presented. A small area is shown on which several "islets" were located in the initial layer for $n = 5$, 10, 100, the transparent phase is shown in light gray, the border is white. The radius of the "islet" in this experiment was chosen to be $r = 15$ elementary cells (cells of length λ in the description above). From here and further on in numerical experiments we suppose that $R = 500$.

The image of the third layer for $n = 5$ and $n = 10$ shows the formation of "rings", in Fig. 3 for $n = 100$ continuous circles are observed. We note that the case of $n = 100$ corresponds in the given experiment to the necessary nucleation of an "islet" at each "point" — the boundary cell, since the total number of cells of the boundary of one "islet", equal to $2\pi r \approx 94$, is less than n here.

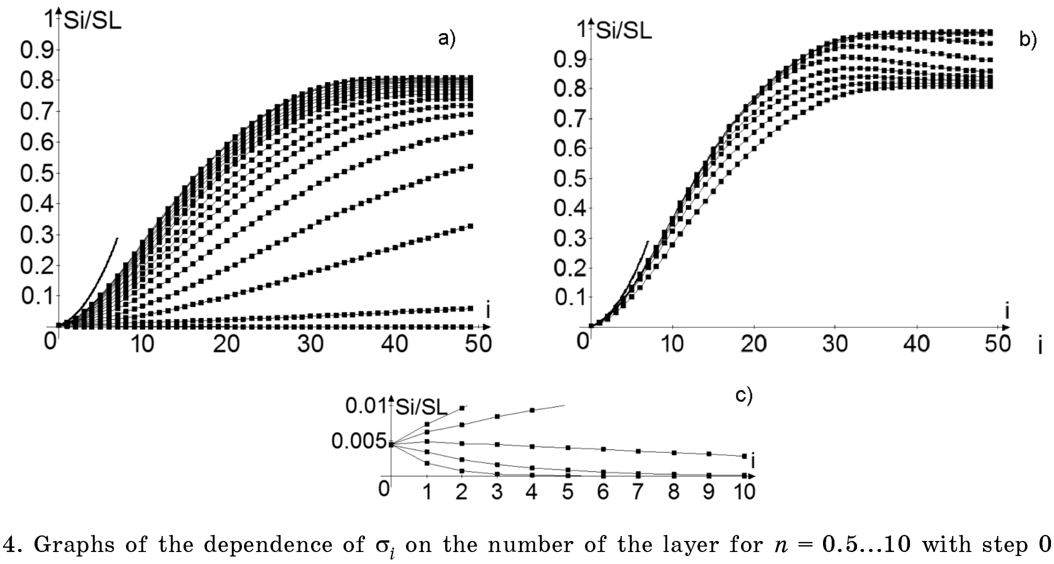

Fig. 4. Graphs of the dependence of σ_i on the number of the layer for $n = 0.5...10$ with step 0.5 on the left and $n = 10...100$ with step 10 on the right are presented. Graphs with large n are located higher. The initial sections of the parabolic law (2) are also shown. (4c) graphs of the dependence of σ_i on the number of the layer i, the initial region are shows on image bottom. The graphs for $n = 0.5$; 1; 1.5; 2; 2.5 (from the lower graph to the upper one) are shown.

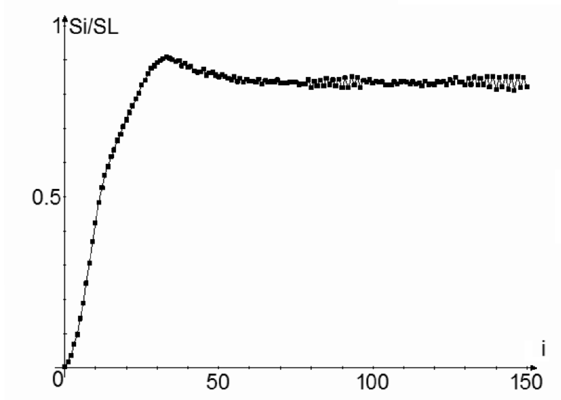

Fig. 5. Graph of the dependence of σ_i on the number of the layer, $n = 50$, $r = 15$. Number of layers $N = 150$.

Fig. 4 shows the graphs of the dependence of the filling $\sigma_i = S_i/S_L$ from the layer number for $n = 0$, 5...10 with step 0.5 (4a) and $n = 10...100$ with step 10 (4b), averaged over a large number of numerical experiments. The position of the graph corresponding to some n is getting up with the higher n. We averaged over 300 experiments for each n. It is seen that in the region of the first numbers of the layers at $n = 100$, the observed dependence is close to the quadratic law (2) (shown by a solid line). Such a law occurs when the outer boundary of the transparent region is completely covered by the "islets" of transparency and the entire internal area is transparent at each step. This is so for $n = 100$, because such a value of n exceeds the number of points of the boundary of one "islet" in a given numerical experiment. For $n = 0$, 5...10, the graph is sufficiently far from the quadratic law, and for $n \le n_e$ the value of S_i/S_L decreases with the number of the layer (see the enlarged initial section in Fig. 4a). As can be seen $1.5 < n_e < 2$, this value is close to 1.5.

In Fig. 4 it is demonstrated that for small n the filling of the layer goes to a constant value immediately after the growth region, while at large n it can have a maximum at some layer number.

Beginning with a certain layer, the "islet" clusters formed around one initial "islet" in the zero layer will begin to unite, and then penetrate to the boundary of the layer. This leads, similarly to [6], to the appearance of one or several linear sections on the graphs σ_i for individual experiments. On the graphs averaged over many experiments, linear sections will be blurred.

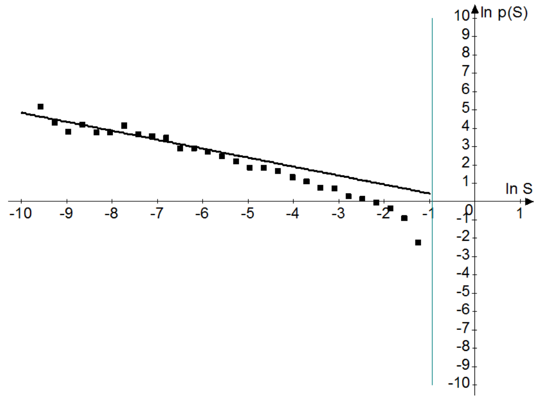

Fig. 6. The density of distribution of "windows" of transparency over the area and its small-scale asymptotics in the case of one and only one "islet" in the layer.

The area of the layer S_L is the upper limit of the possible values of the area of the new phase S_i in the layer, so that S_i with increasing of layer number will be saturating, or oscillating within a certain value less than S_L.

On the graph for $n = 50$, $r = 15$ in Fig. 5 two linear sections are presented, corresponding to two stages of growth of clusters of the transparent phase. Such steps may correspond, for example, to the following. The first stage could be the growth of large cluster after uniting clusters over individual islets, while the second one could be the output of the cluster to the boundary of the layer and, correspondingly, to the cutting off of its part by this boundary [6].

4. "Windows" of transparency, the case of one "islet" per layer.

Consider the process of formation of "windows" of transparency when "islets" are born only at the boundary of the phases in the case when there is one and only one "islet" in each layer. The distribution density of the "windows" given from the numerical experiment and its small-scale asymptotic behavior are shown in Fig. 6, the graph in a double logarithmic scale. The area of the "window" is given as a part of the area of the "islet".

The vertical line shows the maximum possible area of the "window". This area corresponds to the lenticular "window" shown in Fig. 7 and is equal to the area of intersection of two circles, the centers of which are at a distance $d = r$ from each other. Such a "window" is formed in the

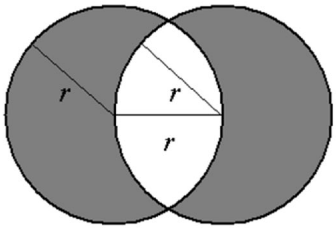

Fig. 7. Lenticular "window", formed in the case when "islets" in layers through one are strictly above each other.

limiting case, when "islets" in layers through one are strictly above each other

$$S_{\max} = 2r^2\left(\arccos\frac{d}{2r} - \frac{d}{2r}\sqrt{1 - \left(\frac{d}{2r}\right)^2}\right) \quad (3)$$

with $d = r$, where r is the radius of the islet. Taking into account the above $\pi r^2 = 1$,

$S_{max} = 2/\pi(\pi/3 - 1/2\sqrt{3}/2 \approx 0.391$ and $\ln S_{max} \approx -0.939$.

The angular coefficient of the small-scale asymptotics obtained in the numerical experiment is −0.489, i.e. close to −0.5,

$$p_S(S) \propto \frac{1}{\sqrt{S}}. \quad (4)$$

5. The "windows" of transparency, the case of many "islets" in the layer.

Let us pass to the study of the "windows" of transparency that are formed in the sample for the general case of many "islets" in the layer. This case will be studied using numerical simulation.

In Fig. 8 the distribution density of the "windows" over the area in a double logarithmic scale for $n = 1...10$, (the larger is n, the higher is the graph) is presented. The value of the area (horizontal axis) is taken relative to the area of the "islet", so the zero of the axis corresponds to the area of one "islet". The number of layers is $N = 7$, the number of "islets" in the first layer $n_0 = 10$, the radius of the "islet" $r = 50$. With this set of parameters, "windows" are formed in a wide range of areas and shapes. The graphs are based on the results of 1000 experiments.

It can be seen that the graphs have three sections. The extreme left section, up to values of $\ln S/S_L \approx -7$, corresponds to "windows" of up to 7 "cells", used in numeric modeling. In this area the influence of numerical errors is very large, that's why we will discuss the following two sections. The section in the middle part will be called the small-scale region; the extreme right-hand side is large-scale.

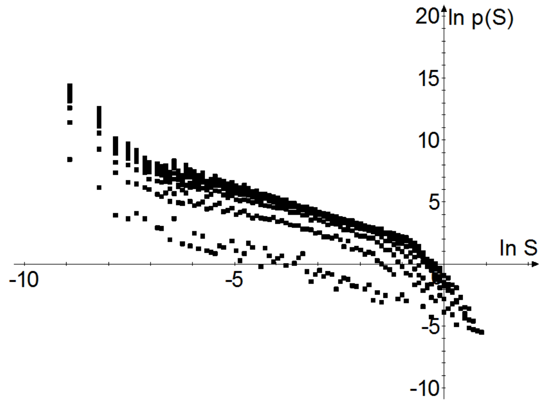

Fig. 8. Density of distribution of "windows" by area for $n = 1...10$ with $N = 7$, $n_0 = 10$, $r = 50$.

It can be seen that the graphs in the small-scale region are well approximated by straight lines, almost parallel to each other. Those, the corresponding form of the density is described by universal law, and does not depend on n. The presence of linear approximation means that in this region the distribution density is power, where $p \propto S^{\kappa}$, and κ is the slope of the approximating lines. The values of κ for different n are shown in Fig. 9.

As can be seen, the values of κ are close to −1, so the distribution density of the "windows" over the area in this region has the fo

$$p(S) \propto S^{-1}. \quad (5)$$

Note that this type of distribution is retained within a wide range of parameter variation. For example, in Fig. 10 there are presented the graphs of the distribution density of the "windows" over the area for the $N = 20$ layers with $n_0 = 20$ "islets" in the initial layer, the radii of the "islets" $r = 30$. Each graph was constructed from the results of 1000 experiments. As above, $n = 1...10$.

The angular coefficient of a straight line approximating of the graph in a small-scale region for large n is also close to −1, but we note that since with an increase in the number of layers, the number of "windows" decreases rapidly, with small values of n deviations from this regularity occur because of a small sample. At $n = 1$ in this case, "windows" are not formed at all, with $n = 2$

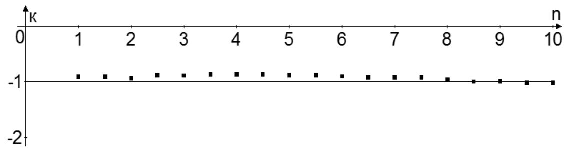

Fig. 9. Angular coefficients of linear approximation of the small-scale region of the distribution density of "windows" over the area.

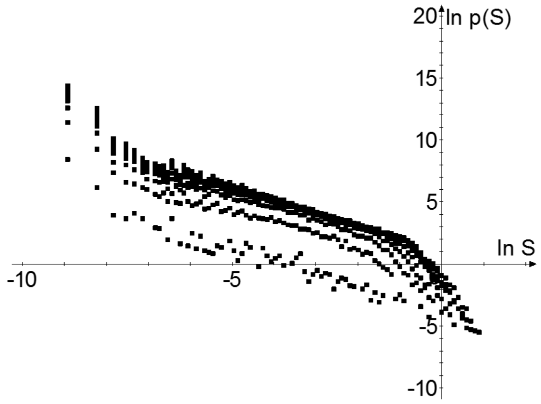

Fig. 10. Density of distribution of "windows" by area for $n = 1...10$ with $N = 20$, $n_0 = 20$, $r = 30$.

only 38 windows were obtained for 1000 experiments. For the same reason, the boundaries between small- and large-scale regions are more blurred.

If n is very large, the "windows" coincide with the "islets" in the source layer and their area distribution coincides with the distribution of the area of transparent regions in the source layer. In Fig. 11 it is shown the distribution density of the "windows" over the area for $n = 100$. The horizontal axis here is linear, the values of the area itself (related to the area of one "islet") are plotted, not the logarithm. The vertical axis is logarithmic.

A sharp peak is seen in the area of the "window", equal to the area of one "islet" $S = S_L$. Such a "window" is formed in the case when there is an isolated "islet" in the source layer, and in all the next layers above it there is a transparent phase. Also there is a peak near $S = 2S_L$.

All "windows" larger in area than one "islet" are formed by merging several "islets" in the source layer into one transparent region. In the next layers above such a region there can be both a transparent phase and elements of the opaque phase, which will lead to a "cutting out" of the part of the original area from the resulting "window".

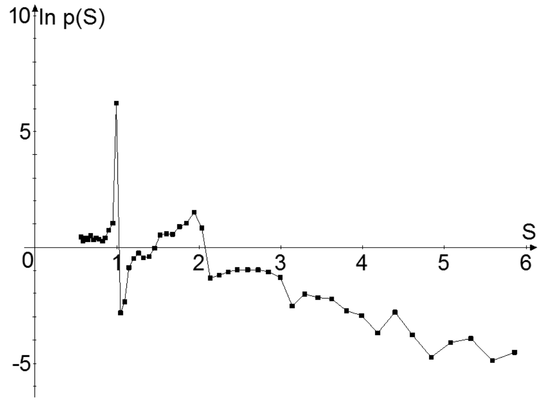

Fig. 11. Distribution density of "windows" over the area for $n = 100$.

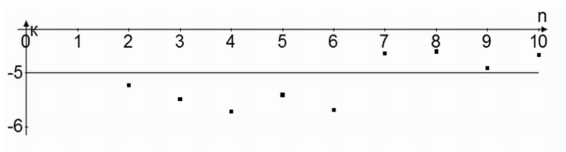

Fig. 12. Angular coefficients of linear approximation of a large-scale region of the distribution density of "windows" over the area.

Let us return to a series of experiments for $N = 7$. In a large-scale region, the graphs of the distribution density can also be aroximated by straight lines, with much smaller (larger modulo) κ than in the small-scale region.

The values of κ in a large-scale region for a series of experiments with $N = 7$ are given for $n = 1...10$ in Fig. 12.

The values of κ lie in the range (−6, −4) and have a much larger scatter than in the case of a small-scale region, which is apparently connected with a much smaller sample.

Note that the term "large-scale region" in the case of many "islets" in the layer has a different meaning than in the case of one "islet" per layer. The small-scale region turns into a large-scale one in case of many "islets", as can be seen from the graphs, at values of $\ln S/S_L$ about −0.9, The physical meaning of this value of bound S is the following. This is the maximum possible value of the area of the "window" generated over one separate "islet" when the "islets" begin to appear on the phase boundary (Fig. 10).

The area of such a "window" is, as indicated above, $S_m = 2r^2(\arccos 1/2 - 1/2\sqrt{3/4})$. The logarithm of this quantity, related to the area of the "islet" is approximately equal to $\ln S_{max} \approx -0.939$.

That is, if a large-scale region in the case of one "islet" in a layer is a region of "windows" areas, slightly smaller than S_m, then the large-scale region in the case of many "islets" in the layer is the region of the areas of "windows", larger then S_m. This region of the windows formed by the overlap of regions consisting of several merged "islets" in consecutive layers.

6. Conclusions

The formation of volume inclusions of an additional transparent phase and the formation of transparent "windows" in the sample are considered in the case of layer-by-layer growth of the sample. The case of nucleation of "islets" of a new phase over the phase boundary of the previous layer was studied.

– It is shown that the law of variation of $\sigma_i = S_i/S_L$ filling of the layer with a transparent phase has a quadratic region in the region of small numbers of layers and, with a further increase in the number of the layer, one or several linear sections, as in the case of [6] (Figs. 4, 5). A quadratic region is clearly visible for large $n \sim 100$ and less noticeable for smaller n.

The appearance of this region is practically independent of the location of the "islets" in the original layer in a separate experiment, so the quadratic section is present on the graphs averaged over many experiments.

Line segments are clearly visible in the graphs of σ_i for individual numerical experiments (Fig. 5), but when averaged, these sections are not visible, because the position of the beginning and the end of each linear section depends on the location of the "islets" in the source layer.

The dependences of the layer filling on the layer number are obtained for $n = 0.5 - 100$ (Fig. 4,). It is shown that the filling decreases with the number of the layer for small n and increases for larger values. The boundary value is $n_e \approx 1.5$.

– The density of the distribution of "windows" of transparency over the area for the case of one "islet" on the layer has a small-scale asymptotic form

$$p_S(S) \propto \frac{1}{\sqrt{S}}.$$

The maximum possible value of the "window" area with a single "islet" in the layer corresponds to the limiting case of the location of "islets" in the layers through one strictly above one another. In this case, a lenticular "window" is formed within area $S_{max} \approx 0.391 \cdot S_L$, where S_L is the area of the "islet".

– The density of distribution of "windows" of transparency over the area in the case of many "islets" in the layer has the same form in a wide range of parameters. The density has a small-scale power-law asymptotics

$$p(S) \propto S^{-1}.$$

In a large-scale region, the density can also be approximated by a power function with exponent in the range of $(-6, -4)$.

– The boundary value of the "window" area separating the small-scale region from the large-scale one in the case of many "islets" in the layer corresponds to the area S_{max} of the largest possible "window" formed over one separate "islet" of the initial layer (Fig. 10). That is, the formation of "windows" in a large-scale region, in contrast to a small-scale one, is not due to the covering of separate "islets" in consecutive layers, but to the overlap of transparent regions formed by the fusion of several "islets" into one common transparent region in each layer.

– With a very large number of "islets" in the layer n ($n \sim 100$), the distribution density of the "windows" coincides with the density of the distribution over the area of the regions of the transparent phase in the initial layer. This density has a sharp peak at $S = S_L$, and a smaller peak at $S = 2S_L$.

Acknowledgements. The author is grateful to Prof. V.V.Yanovsky for numerous valuable recommendations received during the discussion of the work and during the writing of the article. The author would like to thank the senior researcher Dr. A.G.Doroshenko, who drew the author's attention to the physical significance of the investigation of the case of the nucleation of a new phase in a layer at the boundary of phases.

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