

Surface Nanostructure of Layers from Water Solutions after Sedimentation

L.A. Bulavin, Yu.F. Zabashta, L.Yu. Vergun, O.S. Svechnikova, S.R. Bobrovnik

T. Shevchenko National University of Kyiv, Faculty of Physics, 64/13, Volodymyrska St., 01601 Kyiv, Ukraine

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The question of mechanisms of sedimentation on a substrate of a substance from water solutions is considered. The surface structure of layers obtained by sedimentation of water solutions of two types is investigated. For the first type (an aqueous solution of glucose with a concentration of 40 %), the formation of hydrogen bonds of the dissolved substance with water molecules is characteristic. In the formation of the second type of crystals (aqueous NaCl solution with a concentration of 0.9 %), such bonds are not formed. An analysis of the images obtained using the Integra atomic force microscope revealed the difference between the surface structure of the layers obtained for these types of solutions. Using the histogram of the distribution of surface relief, a method for processing experimental data is proposed. According to this method, the surface is described using a traditional continuum model. When applying this model, the vertical displacement of the points of the surface from the plane is described by a random field. In addition, it is assumed that the projections on the surface are of the same shape and are arranged at the same distance from each other. For the averaged model, the density function is a deterministic periodic function. It is established that for the first type of aqueous solution, the smoothed histogram contains maxima, and for the second type – the absence of minima is observed in the smoothed histogram.

It is taken into account that in the aqueous solution of the first type there are clusters containing both the particles of the dissolved substance and the molecules, and in the solution of the second type in the direction of the substrate, not the clusters but separate particles of the dissolved substance (ions) diffuse. It is shown that in the solution of the first type, the clusters diffuse to the substrate and deposit on it, forming an epitaxial layer consisting of areas with a horizontal surface separated by projections with substantially vertical walls and a depth of about the thickness of the layer. At the same time, the process of subsidence is realized, which is accompanied by the greatest decrease in the energy of the system. This process is achieved in the case when the largest contact area between the cluster and the substrate is ensured, if possible. In the second case, the layer is formed as a result of settling on the substrate of particles of the dissolved substance, which creates conditions for smoothing out the protrusions inherent in the substrate and smoothly changing the angle of inclination of the surface of the layer.

Keywords: Epitaxial growth of crystals, Atomic force microscopy, Hydrogen bonds.

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1. INTRODUCTION

Prospects for the application of nanoscale-modified multilayer films in the electronics industry are commonly known. One of the methods for making such films is precipitation on the substrate of the solution from the solution.

A large number of works are devoted to the study of the structure of the layers obtained by sedimentation of water solutions (see, for example, [1-2], etc.). A well-known head factor that determines the behavior of water is the presence of hydrogen bonds. Will this factor affect epitaxy from aqueous solutions? In this article, we will try to answer this question by putting the next experiment. We shall study the growth of crystals on the same substrate of solutions of two types. For the first type of a particle of dissolved wine, they can form hydrogen bonds with molecules of water, for the second one – such connections are impossible. As we know, in this formulation, this question was not studied in the literary tour.

The surface in our study will be described using a traditional continual model, according to which the vertical displacements of the points on the plane from above $\bar{Z} = 0$ are described by a random field

$$\bar{Z} = \bar{Z}(\vec{r}), \quad (1)$$

where $\vec{r}\{x, y\}$ is the radius vector that determines the position of the projection of the points of the surface on the plane $\bar{Z} = 0$.

This field is characterized by a function

$$N = N(\bar{Z}), \quad (2)$$

where N is the number of cases for which this value is observed. It is called a density distribution histogram Z .

2. METHOD AND EXPERIMENTAL RESULTS

The surfaces of the layers formed on the glass substrate (Microscope slides, Cat.NO.7102) were investigated as a result of the epitaxial growth of crystals from the solution. According to the tasks set forth in the introduction in the production of samples, we must use solutions of two types, for which the particles of the dispersed substance form and do not form hydrogen bonds with water molecules. As representatives of these types, we have chosen respectively an aqueous solution of glucose (concentration of 40 %) and aqueous NaCl solution (with a concentration of 0.9 %).

Two types of solutions were used for making samples: aqueous solutions of glucose and water solutions of NaCl. On the polished glass plates, these solutions were applied at a temperature of 293 K and then dried

for 48 hours at a temperature of 293 K. Let us take the following designations: glass is the system *A*, glass + glucose is the system *B*, glass + NaCl is the system *C*. The samples produced by the above-mentioned method were assembled with the aid of the atomic force microscope "Integra". The results of this study are shown in Fig. 1a, Fig. 2a, Fig. 3a, representing the depictions of the structures obtained with the help of the aforementioned microscope, as well as in Fig. 1b, Fig. 2b, Fig. 3b, where the histograms $N(\bar{Z})$ corresponding to the indicated structures are shown.

According to Fig. 1, Fig. 2b, Fig. 3b, the $N(\bar{Z})$ histogram can be represented as a sum

$$N(\bar{Z}) = n(\bar{Z}) + n'(\bar{Z}), \quad (3)$$

where $n(\bar{Z})$ is the slowly changing function and $n'(\bar{Z})$ is the rapidly changing function with variable Z .

Functions $n(\bar{Z})$, which will be agreed upon to be called smoothed histograms, are shown in Fig. 4. Their significance is determined by the error $\pm \Delta n$, (Δn is the amplitude of the rapidly fluctuating function).

As can be seen from Fig. 4a, smoothed histograms for systems A contain four maxima. This fact will allow to consider the indicated histograms as the result of overlaying of the four histograms, the position of which in Fig. 4 is marked with a dotted line. By definition, each histogram is associated with some random magnitude. Accordingly, our breakdown of the output histogram means that now the offset \underline{Z} is considered as the sum of random variables:

$$\underline{Z} = \underline{Z}_a + \underline{Z}_b + \underline{Z}_c + \underline{Z}_d, \quad (4)$$

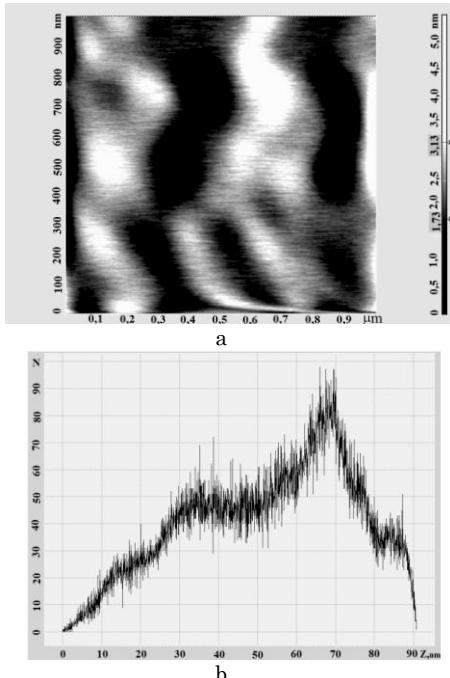


Fig. 1 – The structure of the system's surface A (a); histogram of the distribution of the relief of the system's surface A (b)

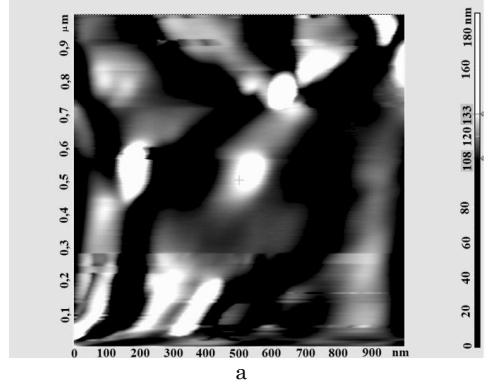


Fig. 2 – Structure of the system's surface B (a); histogram of the relief distribution of the system's surface B (b)

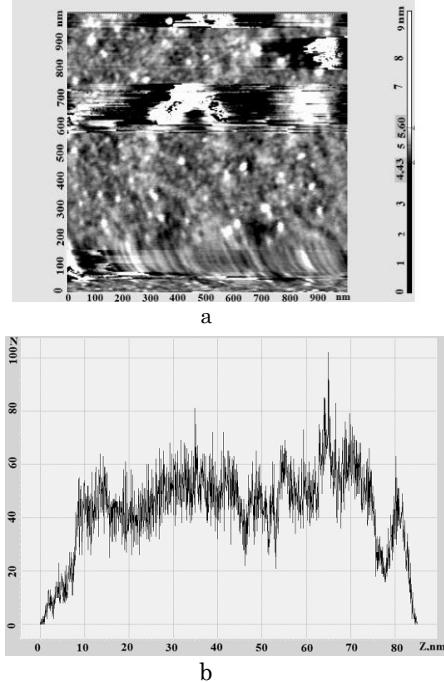


Fig. 3 – Surface structure of system C (a), histogram of the relief distribution of the system C (b)

From histograms we pass to probabilistic distributions writing the latter for a random variable Z_a in the form

$$W(\bar{Z}_a) = \frac{n(\bar{Z}_a)}{\sum_i n(\bar{Z}_{ai})}. \quad (5)$$

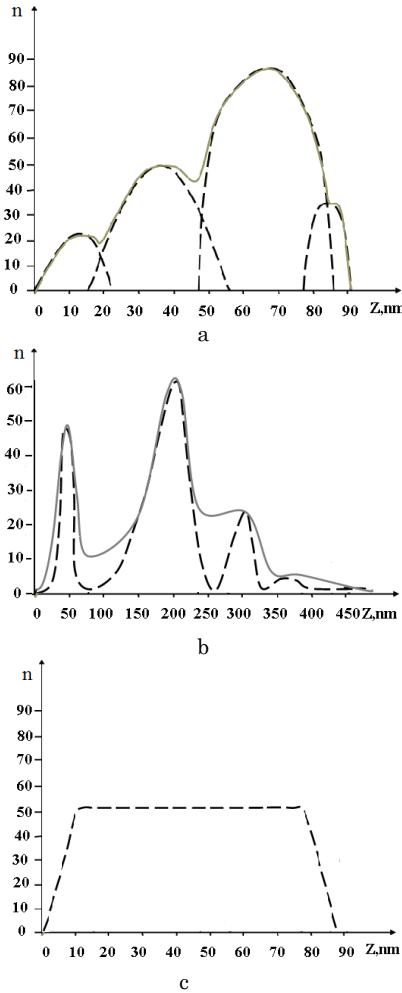


Fig. 4 – Smoothed displacement density histograms: for system A (a), for system B (b), for system C (c)

Using expression (5), we calculate the mathematical expectation

$$h_a = \sum_i \bar{Z}_{ai} W(\bar{Z}_{ai}) \quad (6)$$

and centered dispersion

$$D_a = \sum_i (\bar{Z}_{ai} - h_a)^2 W(\bar{Z}_{ai}). \quad (7)$$

As is commonly accepted, the value of Δh_a is considered as an error

$$\Delta h_a = D_a^{1/2} \quad (8)$$

Formulas similar to equations (5)-(8) retain their force also for random variables Z_b , Z_c , Z_d . The values of calculated mathematical expectations and their errors are given in Table 1.

We introduce into the consideration the value of P_a , which is the probability of realization in this test of any meaning Z .

$$P_a = \frac{\sum_i n(Z_{ai})}{\sum_i n(Z_{ai}) + \sum_i n(Z_{bi}) + \sum_i n(Z_{ci}) + \sum_i n(Z_{di})}. \quad (9)$$

Equalities for the values of P_b , P_c , P_d have a similar form. The meaning of all these probabilities is also given in Table 1.

According to Fig. 4b, for the system *B*, the smoothed histogram contains three maxima. After calculating the formulas similar to (2)-(9), we obtain the characteristics of random variables Z_a , Z_b , Z_d corresponding to the mentioned maxima (see Table 1).

From Fig. 4c, it follows that for the system *C* the smoothed histogram is practically aligned. For this system the smoothed histogram can be described by the formula

$$N(Z) \approx \text{const}. \quad (10)$$

3. AVERAGE RELIEF SURFACE

Simplifying the situation, we introduce into the consideration the average surface model, according to which the projections on the top have the same shape and are located at the same distance from each other.

For such a model, a function Z is a deterministic periodic function, its period is denoted by B . Correspondingly, the values Z_a , Z_b , Z_c , Z_d for the system *A* lose their accidental character. The latter are replaced by their mathematical expectations, and we assert that the value of Z is a vertical displacement, which can only take four discrete values, namely h_a , h_b , h_c , h_d .

From the periodicity of the idealized structure chosen by us, it follows that these values should be repeated with the period B . This means that the bias reception has all four values that should have been implemented within one period. And now, when the accidental character of the surface structure is ignored, the values P_a , P_b , P_c , P_d acquire another meaning. For the first of them, for example, we can write

$$P_a = \frac{b_a}{B}, \quad (11)$$

where b_a is the length of the interval, during which the value is observed. Similar expressions are true for values P_b , P_c and P_d .

Calculated by the formula (11), the meaning of values b_a , b_b , b_c and b_d is given in Table 1. In calculating these values we used $B = 400$ nm taken from the image of the structure in Fig. 1a.

Thus, the change of the considered idealized structure during the period is characterized for the system by four pairs of values h_a , b_a ; h_b , b_b ; h_c , b_c and h_d , b_d .

The smallest quantity, namely, h_a determines the position of the bottom of the depth relative to the plane $Z = 0$, and the value b_a is the width of this depth.

The fact that several pairs of linear sizes (h_b , b_b ; h_c , b_c ; h_d , b_d) remain means that in the averaged model adopted by us, the surface of the projection is stair-shaped.

Similar considerations about the values b_a , b_b and b_c preserve, obviously, their force and for the system *B*. The values of the parameters calculated by the formula (11) are given in Table 1.

We will mentally divide the average model of the system *B* through normal to the plane $Z = 0$. Built according to Table 1, this section is depicted in Fig. 5. In this figure, the part of the shaded section, occupied by the pad (system *A*), also with the average surface relief.

As can be seen from the given considerations, the presence of maxima on smoothed histograms means that there are horizontal sections with width b at the height h of the surface. The absence of such maxima on the smoothed histogram of the system C means that the surface of this system without such sections.

Accordingly, the section, similar to the section of Fig. 5, in this case will have the form shown in Fig. 6.

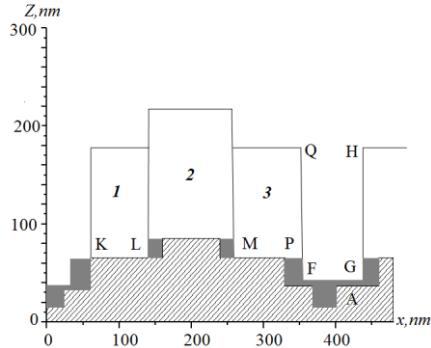


Fig. 5 – The structure of the layer of system B

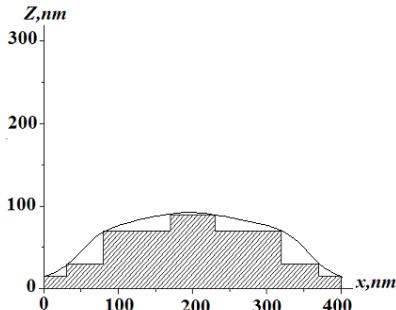


Fig. 6 – The structure of the layer of system C

4. MECHANISM OF EPITACIAL GROWTH

As can be seen from Fig. 5 and Fig. 6, the structure of the epitaxial layer for systems B and C is significantly different. For the system C the epitaxy tends to align the inequalities inherent in the surface of the substratum, resulting in the surface of the epitaxial layer being smoother (less rough) than the surface of the pad. For the system B , the epitaxial layer turns out to be cut by the pits with a depth equal to approximately the thickness of the layer.

In our opinion, the reason for this difference in the structure of the epitaxial layers is that in an aqueous solution of glucose, which serves as an initial material for the system B , the occurrence of hydrogen bonds between the particles of the dissolved substance (glucose molecules) and water molecules is observed. In the solution of NaCl (system C), there are no similar connections between the ions and the water molecules.

Let us consider what happens to the water glucose, when the latter comes in contact with the solid substrate, and the thermodynamic conditions for the crystallization of glucose on the substrate are created. In these conditions, molecules of glucose will aim to move from solution to the surface of the substrate. However, the situation is complicated by the fact that due to the possibility for molecules of glucose to form a hydrogen bond with molecules of water, the clusters appear in

the solution. These clusters are long-acting aggregates consisting of glucose and water molecules. As shown by experiments on dynamic light scattering [3], the size of such clusters is about 100 nm, and there is a significant part of the dispersed substance in clusters [4].

We denote by the τ a lifetime of the cluster, through τ_D the characteristic time of the cluster diffusion, which is determined by the formula

$$\tau_D = \frac{L^2}{D}, \quad (12)$$

where L is the characteristic size of the area occupied by the solution, D is the coefficient of diffusion of clusters.

When performing inequality

$$\tau \gg \tau_D, \quad (13)$$

the aspiration of glucose molecules located on the substrate surface caused by the corresponding thermodynamic conditions, will mainly be realized in the form of the diffusion motion of the clusters in the direction of the substrate. This movement ends with the laying of clusters on the lining. At the same time, this process of subsidence is realized, which is accompanied by the greatest decrease in the energy of the system. This decrease is achieved in the event that the largest contact area between the cluster and the substrate is ensured. We can say on this subject that the cluster "searches" on the substrate for itself the smoothest areas. Such areas are (see Fig. 5) the platforms KL, LM, and MP, in which clusters 1, 2, 3, divided into 5 by dotted lines, are placed. As can be seen from this figure, the size of these clusters is of the order of 100 nm. It is confirmed by the experimental data from [3, 4]. The location of the clusters, corresponding to the minimum of energy, has the consequence of the occurrence of deeps in the epitaxial layer, which was discussed above. One of these deeps (QFGH) is shown in Fig. 5.

The area of the layer, not occupied by clusters, is filled with glucose molecules. These are crystalline regions (in Fig. 5 they are obscured).

As already noted, clusters, together with molecules of glucose, also contain water. Therefore, for some time since the contact of the cluster with the pad, part of the layer formed by the clusters (regions 1, 2, 3 in Fig. 5) naturally also contains a certain amount of water. Only after drying the system, the specified part acquires a crystalline structure.

A different picture is observed at the formation of a layer for the system C . Here, in the direction of the pad, not clusters, but separate particles of a dissolved substance (ions) diffuse, and this radically changes the mechanism of formation of the epitaxial layer.

The growth of this layer begins with the fact that the first particle stays on the substrate surface (Fig. 7a). Conditionally we will attribute a particle shape to a cube. On the surface of the substrate, the particle "chooses" for itself such a place that after placing there, its energy has the least value. To do this, in contact with the substrate, it is necessary to enter the maximum possible number of faces of the cube. Therefore, the mentioned particle is located in the corner at the intersection of the vertical and horizontal surfaces of the substrate surface. At the same time, two borders touch the surface of the substrate.

Accordingly, the binding energy decreases by $2u$, where u is the energy of the interaction of the ion with the substrate atoms. The second particle in the same corner joins the first one. With this connection, the energy of the system decreases by the value $2u + u_1$, where u_1 is the binding energy between the bound particles.

The third particle takes a similar place, etc. In the corner, there is a series of particles as shown in Fig. 7b.

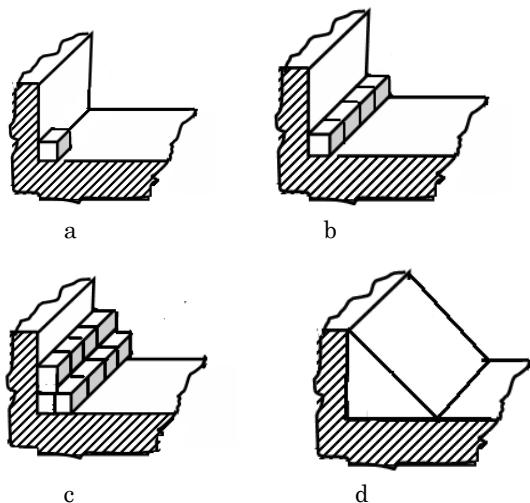


Fig. 7 – Mechanism of the formation of a layer for system C

Table 1 – Parameters characterizing the surface

Name of parameter (displacement components)	Mathematical expectation, h (nm)		Error, Δh (nm)		Probability, P		Half-width horizontal section, $b/2$ (nm)	
	System A	System B	System A	System B	System A	System B	System A	System B
Z_a	15.1	38.8	1.7	5.6	0.13	0.2	26.0	40.0
Z_b	36.4	165.5	4.7	18.4	0.21	0.53	42.0	106.0
Z_c	65.4	229.2	6.7	10.7	0.44	0.27	88.0	54.0
Z_d	85.6	299.5	1.7	4.9	0.22	–	44.0	–

REFERENCES

1. A. Fontcuberta i Morral, C. Colombo, G. Abstreiter, *Appl. Phys. Lett.* **92**, 063112 (2008).
2. Albert Queralto, Maria de la Mata, Jordi Arbiol, Xavier Obradors, *Adv. Mater Interface.* **3**, 160392 (2016).
3. L.A. Bulavin, Yu.F. Zabashta, E.O. Teliman, L.Yu. Vergun, *Colloid J.* **77**, 1 (2015).
4. T.S. Vlasenko, Yu.F. Zabashta, V.M. Sysoev, *Russ. J. Phys. Chem.* **88**, 1361 (2014).

Поверхнева наноструктура шарів, отриманих осадженням із водних розчинів

Л.А. Булавін, Ю.Ф. Забашта, Л.Ю. Вергун, О.С. Свєчнікова, С.Р. Бобровник

Київський національний університет ім. Т. Шевченка, фізичний факультет, вул. Володимирська, 64/13, 01601 Київ, Україна,

Розглядається питання щодо механізмів осадження на підкладці речовини із розчинів. Досліджується поверхнева структура шарів, отриманих осадженням водних розчинів двох типів. Для першого типу (водний розчин глукози з концентрацією 40 %) характерне утворення водневих зв'язків розчиненої речовини з молекулами води. При утворенні кристалів другого типу (водний розчин NaCl з концентрацією 0.9 %) такі зв'язки не утворюються. Аналіз зображень, отриманих за допомогою атомно-силового мікроскопа "Integra", виявив різницю між поверхневою структурою шарів, отриманих для цих типів розчинів. Використовуючи гістограми розподілу рельєфу поверхні, запропоновано методику обробки експериментальних даних. Згідно з цією методикою, поверхня описується при використанні традиційної континуальної моделі. При застосуванні цієї моделі вертикальне зміщення точок поверхні від площини описується випадковим полем. Крім того, приймається, що виступи на поверхні мають

однакову форму і розташовуються на однаковій відстані одна від одної. Для усередненої моделі функція густини є детермінованою періодичною функцією. Встановлено, що для первого типу водного розчину згладжена гістограма містить максимуми, а для другого типу – спостерігається їх відсутність.

Враховано, що у водному розчині первого типу виникають кластери, що містять як частки розчиненої речовини, так і молекули, а в розчині другого типу в напрямку підкладки дифундують не кластери, а окремі частинки розчиненої речовини (іони). Показано, що в розчині первого типу кластери дифундують до підкладки та осідають на ній, утворюючи епітаксіальний шар, який складається з обlastей з горизонтальною поверхнею, розділених виступами з практично вертикальними стінками і глибиною близько товщини шару. При цьому реалізується такий процес осідання, який супроводжується найбільшим зниженням енергії системи. Останнє досягається в разі, коли забезпечується за можливості найбільша площа контакту між кластером і підкладкою. У другому випадку шар утворюється в результаті осідання на підкладці частинок розчиненої речовини, що створює умови для згладжування виступів, властивих підкладці і плавної зміни кута нахилу поверхні шару.

Ключові слова: Епітаксіальний ріст кристалів, Атомно-силова мікроскопія, Водневі зв'язки.