

Evolution of Growth Processes of Paraphase Nanostructures of Lead Telluride

D.M. Freik*, Ya.P. Saliy, I.M. Lishchynskyy, V.V. Bachuk, N.Ya. Stefaniv

Vasyl Stefanyk Precarpathian University, 57, Shevchenko Str., 76000 Ivano-Frankivsk, Ukraine

(Received 05 November 2011; published online 08 May 2012)

On the basis of AFM images of PbTe/(111) BaF₂ nanostructures obtained from the vapor phase, the distribution of the surface relief heights is derived. Shown, that it has an asymmetric nature and is approximated by the sum of three Gaussians. It was established that the dependence of the most probable height of the main component on the deposition temperature has an activation character, and magnitude of the activation energy is less than the energy of one of the twelve bonds of crystal molecules. The growth mechanisms of the nanostructures are proposed. The surface relief of the nanostructures is adequately modeled by the cellular automata method.

Keywords: Nanostructures, Lead telluride, Growth mechanisms, Paraphase methods.

PACS numbers: 61.05.Cp, 68.37.Hk, 73.40.Lg, 79.61.G

1. INTRODUCTION

Lead chalcogenides which belong to the narrow-gap semiconductor compounds are promising materials for the production of sources and sensors of infrared radiation of the optical spectrum, as well as thermoelectric devices operating inside the temperature range of 200-500 °C [1-5]. The achieved success in thin film and nanostructure technologies opens new possibilities of their application through manifestation of the quantum-size effects [6]. In this case, the questions connected with the initiation and growth mechanisms, as well as nanostructure topology, come to the foreground.

It is established for nanostructures based on lead chalcogenides obtained by the molecular beam epitaxy method that self-organization processes are connected with the anisotropy of elastic strain, and their formation is realized by the Stranski-Krastanov mechanism when the transition of two-dimensional system to three-dimensional islands occurs [7-9]. During deposition of lead telluride from the vapor phase by the methods of hot wall on fresh cleavages of (111) BaF₂ crystals at the temperature change in the growth chamber, one can realize different growth mechanisms of lead telluride: three-dimensional islands (Volmer-Weber mechanism), combined growth of two-dimensional layer (Frank-van der Merwe mechanism), and three-dimensional islands [10]. In this case, change in the temperature modes of growth and deposited mass of the compound influence both the shape and sizes of nanostructures. However, the authors of the mentioned works have not analyzed the energy characteristics of the formation process of nanostructures and have not proposed the modeling techniques of their growth.

In the present work, based on the approximation by Gaussians of the investigation results by atomic-force microscopy (AFM), we have determined the activation energies of the growth processes of PbTe/(111) BaF₂ nanostructures and have modeled their surface relief.

2. EXPERIMENTAL TECHNIQUE AND RESULTS

Nanocrystalline PbTe structures were obtained by the deposition of the vapor of the synthesized compound in vacuum on fresh cleavages (111) of BaF₂ crystals. Experiments are carried out for different evaporation temperatures of the sample $T_e = 650-800$ °C, substrate temperatures $T_s = 50-250$ °C, and deposition times $\tau = 15, 30,$ and 60 min which determined the condensate thickness.

Obtained nanostructures were studied by the AFM methods Nanoscope 3a Dimension 3000 (Digital Instruments USA) in the periodic contact mode. Measurements are performed in the central part of the samples using serial silicon probes NSG-11 with nominal rounded radius of the probe point up to 10 nm (NTOMDT, Russia). Based on the results of AFM investigations of the surface topology, we have obtained the histograms of heights of this surface.

Approximation of the height z distribution of nanostructures with the size of $1 \times 1 \mu\text{m}^2$ was performed by the sum of three Gaussians of the f -type

$$N = a_1 \cdot \exp\left[-\frac{(z-h_1)^2}{s_1^2}\right] + a_2 \cdot \exp\left[-\frac{(z-h_2)^2}{s_2^2}\right] + a_3 \cdot \exp\left[-\frac{(z-h_3)^2}{s_3^2}\right]. \quad (1)$$

Here a_i are the amplitude values of the height distribution; h_i are the most probable values of heights in Gaussians, respectively; s_i are the values of the dispersion of height distribution.

Analysis of the results of AFM investigations indicates that the evaporation (sample) T_e and deposition (substrate) T_s temperatures, as well as the condensate mass (deposition time τ) are important technological factors which define the growth mechanism of PbTe nanocrystals on (111) BaF₂ cleavages during deposition of the vapor in an open vacuum.

* freik@pu.if.ua

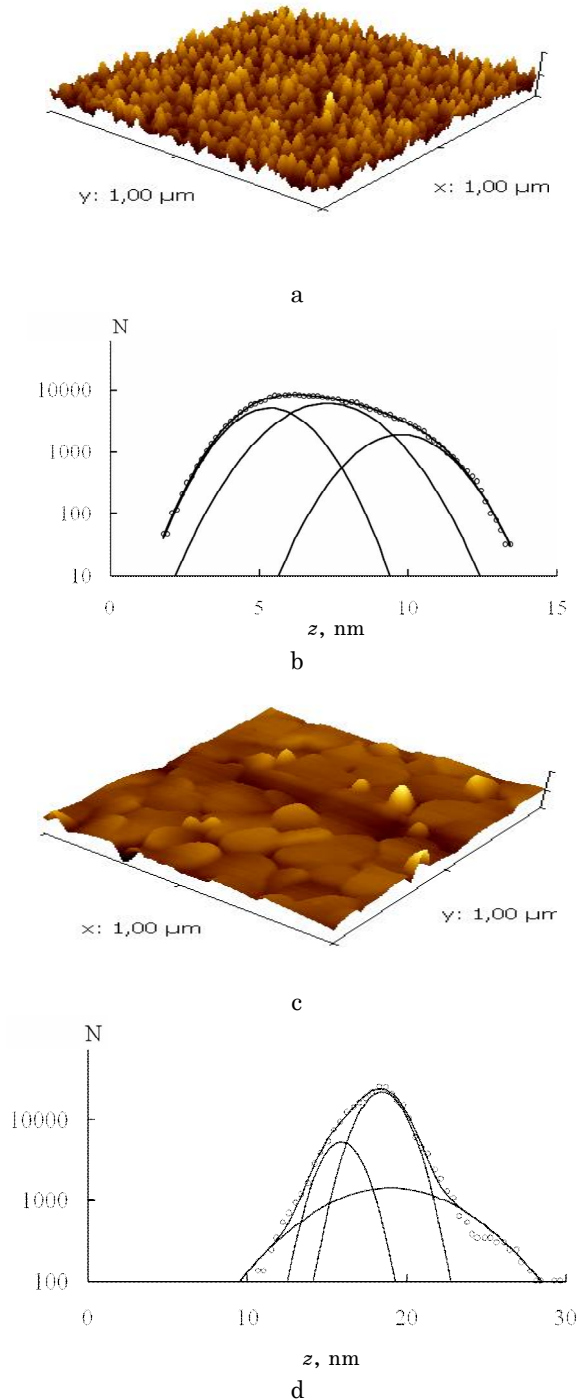


Fig. 1 – The AFM images (a, c) and height distribution (b, d) of PbTe nanostructures on (111) BaF₂ cleavages for deposition time $\tau = 60$ min. Evaporation temperature is $T_e = 700$ °C and substrate temperature is $T_s = 200$ °C

Formation of three-dimensional nucleuses according to the Volmer-Weber mechanism is the common feature for the chosen technological factors of the nanostructure growth. In this case, structures in the form of pyramidal trihedral formations with prevalence of vertical or lateral growth depending on the technological growth factors are the dominant ones (Fig. 1). Increase in the evaporation temperature of the sample T_e conditions considerable increase of their sizes. Mean height of nanostructures is changed from some nanometers

(3-4 nm) at $T_e = 650$ °C to some tens (40-60 nm) at the temperature of $T_e = 800$ °C under the condition of constant substrate temperature ($T_s = 50$ °C) and deposition time ($\tau = 30$ min). The same results are also obtained for other conditions ($\tau = 15$ and 60 min).

Temperature T_s influences dynamically the structural characteristics of the condensate. Thus, in particular, for all evaporation temperatures $T_s = 650-800$ °C, four deposition temperature ranges can be separated: I – $T_s = 20-50$ °C; II – $T_s = 60-110$ °C; III – $T_s = 110-200$ °C; IV – $T_s = 210-250$ °C. If at low T_s (I regime) the pyramidal structures (30-40 nm) are formed, at further increase in the deposition temperature up to the value of $T_s = 100$ °C (II regime), their sizes are significantly decreased. At the evaporation temperature $T_e = 650$ °C and deposition time $\tau = 60$ min they are equal to 20 nm and 2-5 nm, respectively. Essentially another character of the nanostructure formation takes place in the third range of the substrate temperatures – closely packed “parquet-like” formations with the size of 30-60 nm and insignificant roughness. Vertical column-like pyramidal structures with considerable heights (15-30 nm) grow again at higher temperatures (IV regime).

Increase in the mass of condensed matter (deposition time), in general case, leads to the same changes as deposition temperature does: changes in the surface topology, nanocrystalline shape, and sizes take place (see Fig. 1).

3. DISCUSSION OF THE INVESTIGATION RESULTS

Analysis of the approximating Gaussians (Fig. 1b, d) has shown that one of the peaks has, as a rule, large dispersion and it is a background for two other peaks, its amplitude value did not exceed 10% from the maximum amplitude a_1 , and h_3 was maximum in a general case. Relief with a large spread of heights (see Fig. 1c) corresponds to this distribution.

In Fig. 2 we show the dependences of heights h_1 and h_2 , respectively, on the deposition temperature. Height h_1 corresponds to the peak with the maximum amplitude in the distribution, and height h_2 – to the next value; amplitudes of the distribution components are ordered $a_1 > a_2 > a_3$. If dispersion of the main peak is small, a sufficiently smooth surface corresponds to it.

Experimental data (Fig. 2) is approximated by the exponential dependences of the following form:

$$h = h_\infty \cdot \exp(-E_a/kT), \quad (2)$$

where E_a are the activation energies of the process of peak formation with height h . These approximating dependences go into root-mean-square deviation from the most probable value. For the growth times of 15, 30, and 60 min E_a is equal to $-0,053$, $0,059$ and $0,203$ eV, and $h_\infty - 0,96$, 32 , and 3200 nm. The value of energy obtained during approximation for the growth time of 60 min is about $0,194$ eV which is 1/12 of the molecule binding energy in a solid.

For the growth times of 15, 30, and 60 min (Fig. 2b) E_a takes the values of $-0,058$, $-0,098$, and $0,063$ eV, and $h_\infty - 1,3$, $0,5$, and 73 nm. We have to note that for the second (by the amplitude) peak activation energy for

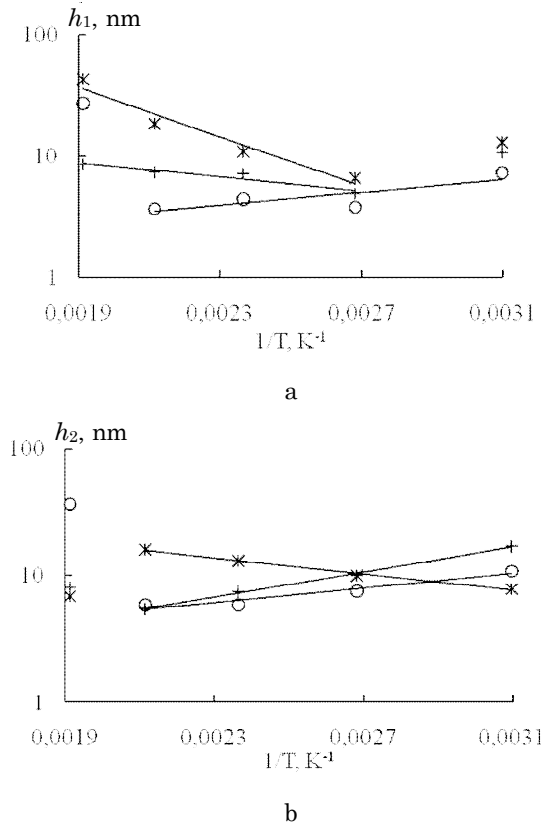


Fig. 2 – Dependence of the most probable height (by the amplitude) of the main h_1 (a) and the second h_2 (b) components in the height distribution of PbTe/(111) BaF₂ nanoformations versus the temperature for different deposition times τ , min: 15 (o); 30 (+); 60 (*)

the growth time of 15 min remains almost constant, for the time of 30 min – 2-fold increase in its magnitude and a sign change are observed, for the time of 60 min – almost 3-fold decrease in the value of activation energy takes place, i.e. for the time of 15 min both dependences are parallel with the temperature, for 30 min behavior of the dependences is opposite, and for 60 min – codirectional with the slope which differs 3 times.

Difference in the temperature trends of the most probable heights for different deposition times can indicate the presence, as minimum, of two different formation mechanisms of the surface relief, and difference in the temperature trends for two main components in the height distribution – the presence of two typical shapes in the surface relief. We note that in Fig. 2a, b there are points on the edges of the temperature range, which do not go into the dependence for the majority of points, that implies the change of the dominating mechanism of surface formation in this temperature range at the change of the deposition temperature.

Table 1 – Position of the maximum h_1 and roof-mean-square deviation s_1 in monomolecular layers for the direction [111] $h_1(s_1)$ for PbTe/(111) BaF₂ nanostructures at different deposition conditions

t , min \ T_s , °C	50	100	150	200	250
15	21(7)	9(3)	12(3)	11(4)	72(11)
30	28(5)	12(3)	20(2)	14(3)	22(3)
60	29(9)	16(4)	30(8)	48(3)	113(21)

As an alternative approximation, we have used the sum of three Poisson distributions, for which dispersion and mathematical expectation are equal. For such approximation heights were measured in molecular layers b along the direction [111]: $b = \sqrt{a/3} = 0,3725$ nm, where a is the lattice constant. It was revealed that the present data sets are badly approximated by this sum.

However, the idea of representation of the heights in dimensional units led to some conclusions. It is established that there is a correlation dependence between the roof-mean-square deviation s and the most probable value $s \sim h^{1.25}$ for heights h higher than 10 nm; for lower heights – $s \sim h$. We should also note that for all 15 analyzed distributions (see Table 1) peaks with typical heights appear among the main peaks: 10 layers – appear 4 times; 20 layers – 3 times; 30 layers – 3 times; 15 layers – 2 times. Other three heights appear once.

Height distributions with large h_1/s_1 ratio are responsible for smooth surfaces – cut pyramids, and with small ratio – for rough surfaces (needle-like). In Fig. 1a, 1b and Fig. 2c, 2d we represent the AFM images which correspond to two ratios ~ 5 and 16, respectively. Uniform height distribution describes atom deposition and attachment in an arbitrary place, and a highly fractal surface is formed in this case. Normal distribution is responsible for the deposition in specific places which provide a sufficient amount of atomic bindings.

We note that according to the theory laid down in the works of Ostwald [12], Lifshitz and Slezov [13], and Wagner [14], one distinguishes diffusion growth mechanism of clusters and mechanism controlled by the rate of chemical bonds on the cluster surface – the so-called Wagner mechanism [15]. Formation of chemical bonds is the electronic process, and classical diffusion is the atomic activation one with another time scale. These two processes can compete, i.e. be realized simultaneously under the condition that electronic processes of formation of chemical bonds are activation, and activation energies of both processes – electronic and diffusion – are comparable.

Based on the above mentioned features of the growth of nanoformations one can suggest that in our case of the deposition of lead telluride, two processes compete simultaneously: the diffusion and chemical interaction. Here, with the increase in the deposition time τ , electronic processes connected with the formation of chemical bonds become substituting ones; activation energy of the most probable height of nanostructures of the main (by amplitude) component of the Gaussian increases (see Fig. 2a). For different deposition times τ , i.e. sizes and masses of nanocrystallites, in the studied range of the substrate temperatures T_s , change in the mechanisms of their growth takes place that is indicated by the change in the angular slope coefficient of the curves (Fig. 2).

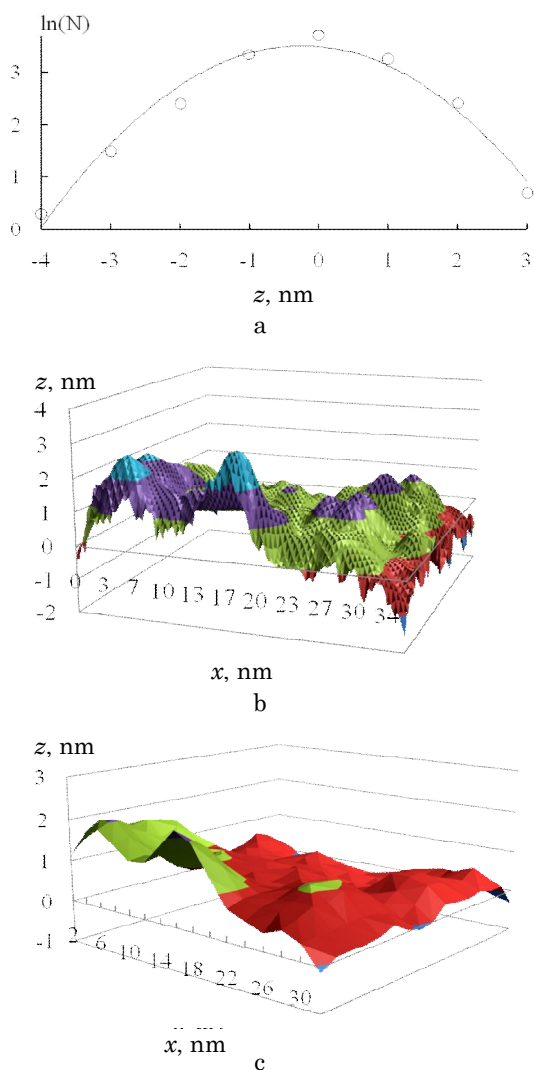


Fig. 3 – Normal distribution of the heights (a) and surfaces modeled by the method of cellular automata without thinning (b) and with thinning (c) for agreement with the AFM images

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Surface of nanostructure whose deposition is modeled by the method of cellular automata and height distribution are represented in Fig. 3. Atoms were deposited equiprobably, but fastened to the field surface of the size of 100×100 cells at the presence of, at least, one of four side neighbors. It is seen that height distribution is really normal: natural logarithm of the number of heights is presented along the ordinate axis, and approximation curve is parabola (Fig. 3).

Comparison of the modeled and real surfaces indicates the adequacy of the proposed deposition mechanism of PbTe/(111) BaF₂ nanostructure (Fig. 1a, c; 3c). We should note that to improve the comparison between modeled surface and its AFM image we have leaved one of twenty five points.

4. CONCLUSIONS

1. It is proposed to use the height distribution of the surface relief to analyze the AFM images.

2. It is shown that the height distribution has an asymmetrical behavior and is well approximated by the sum of three Gaussians.

3. It is established that the dependence of the most probable height of the main component on the deposition temperature has an activation character, and the value of activation energy is less than the energy of one of twelve molecular bonds.

4. It is shown that increase in the condensate mass conditions the dominance of the growth processes of nanostructures due to the formation of chemical bonds.

5. Relief of the film surface is sufficiently modeled by the cellular automata method.

ACKNOWLEDGEMENTS

The work has been performed under partial financial support of the Ministry of Education and Science, Youth and Sport of Ukraine (state registration number 0111U001766) and of the State Fund for Fundamental Researches of Ukraine (0110U07674).