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THREE-DIMENSIONAL NANOOBJECTS IN THE LAYERED DISSIPATIVE ENVIRONMENTS OF $A_2^V B_3^{VI}$

Comparison nanostructured Sb_2Te_3, Bi_2Te_3 crystals surface morphology and natural structures educed in them geometrically similar elements type of Benard cells, "bee honeycombs", some forms of hexahedral nanoobjects in the layered crystals were the example of dissipative structures. Self-organization processes in such systems results in forming of hexahedral structures on different hierarchical levels. Three-dimensional nanoobjects are similar to the structures of "bee honeycombs" and Benard cells hexahedral forms on the van der Waals surface of crystals of Sb_2Te_3, Bi_2Te_3 attributed to the interlayer structures - patterns. Similarity of such forms testifies to the single mechanism of the self-similar solid patterns formed by self-organization.

Key words: morphology, surface, dissipative structures, dislocations, nanostructuring.

Introduction

The emergence of dissipative structures is extremely important for the development of new processes of formation nanostructured materials. This, it belongs for example, the formation of hexagonal annular structures gold nanoparticles on a smooth substrate, and other pseudocrystal and hierarchically ordered structures. In [1-3], such systems are called "organized" and "structured". External flows of matter keep them in a steady state and does not allow move to equilibrium state. It is necessary to consider a number of approaches leading to spontaneous emergence of structures and their self-reproduction. This ability is related to the mechanism of appearance structures (localization processes factor) and spontaneous decay and diffusion in complex systems. This can manifest by examining fractals of different scales [4-6].

Shortest length of a circle of all the figures is a hexagon. Built at the same space on the hexagons requires less material than into squares or triangles. For example, consider a layered graphite and graphene. Ideal graphene consists exclusively of hexagonal cells. The presence of five and heptagonal cells will result to cuts in atomic plane in the cone. Another example – Benard cells. The emergence of Benard cells is a classic example of the spatial order of the structure. All the above are given in detail in the various published articles and monographs (e.g. [7-13]).

Depending on the concentration of embedded impurities in layered crystals $A_2^V B_3^{VI}$ <impurity> can be localized in the interlayer space and penetrate into the crystalline layers [10-11]. Purposeful introduction into layered semiconductors 3*d*-transition elements allows create structures with alternating, magnetic and semiconducting layers. Their thickness is several nanometers and, accordingly, a semiconductor material in which the combined magnetic and other properties. In studied $A_2^V B_3^{VI}$ single crystals is Predominant defects are dislocations located in the basal plane (0001). Hexagonal grid of dislocations and parallel rows presence found. Possible reactions occurring during the formation of the hexagonal mesh Sb_2Te_3 in similar reactions and are presented in [10]. Interest in the study of physical processes in the interlayer islet systems supported mainly by the fact that they are a source of important information about the nature of the interaction between atoms migrate across the surface of the crystal structure and elements of the real patterns.

In terms of effects of interest are two fundamentally different situations: when all the islands in the ensemble at rest, or when for various reasons they can move across the substrate surface. In the first situation, the diffusion fluxes can cause transformation of resting forms islands and atom- wise diffusion transport of matter from island to island. In the second situation, against the background of these processes may also occur, mutual collisions of islands, accompanied by their diffusion merger. Both situations are carried out in real conditions [14-15].

In this works, an analysis of known natural dissipative structures, nanostructured crystalline samples and similar objects identified by atomic force microscopy (AFM) on the van der Waals surface of the crystal type $A_2^VB_3^{VI}$ (for example Sb_2Te_3, Bi_2Te_3).

Experimental results and discussion

Concepts and the experimental results describing processes of new phase origin and its subsequent evolution [4, 14-15] are used for surface nanoobjects growth mechanism analysis. The statement of material is carried out from positions of the classical approach allowing from uniform point of view to analysis of processes (0001) $A_2^VB_3^{VI}$ occurring on surface at self-intercalation and intercalation due to Ostwald ripening. For confirmation of conclusions used a dome-shaped and pyramidal forms nanoislands (NI) fragments AFM-images in $A_2^VB_3^{VI}$ <*Se, Zn*> made on various growth phase. Electron microscopic images were obtained with a scanning probe microscope (SPM) brand Solver Next.

In $Te^{(1)}$-$Te^{(1)}$ environments of $A_2^VB_3^{VI}$ by intercalation atoms between telluride quintets Benard cells formed when a temperature gradient is not only perpendicular to the plane (0001) Sb_2Te_3, but also along the plane. The experimental results are shown in Figs 1-4. Figure1 shows a hexagonal honeycomb-known; obtained Sb_2Te_3 AFM image (Fig.1.) clear evidence that these objects are very close in form.

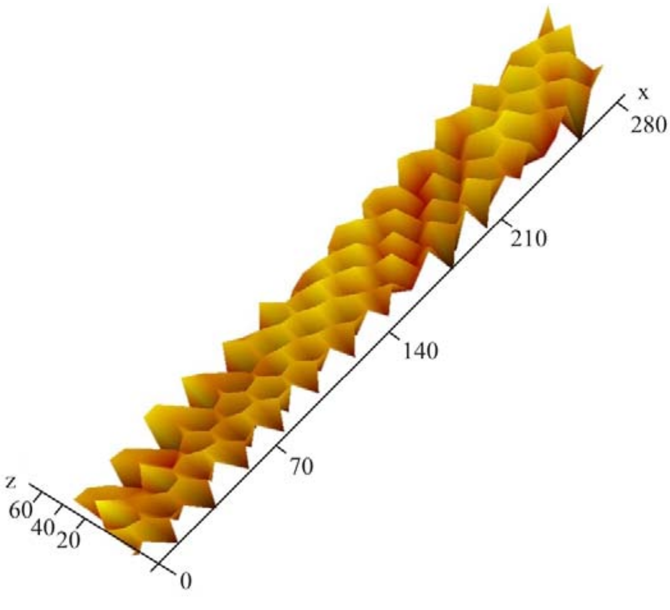


Fig.1. Photo of "bee honeycombs" in 3D scale on van der Waals surface.

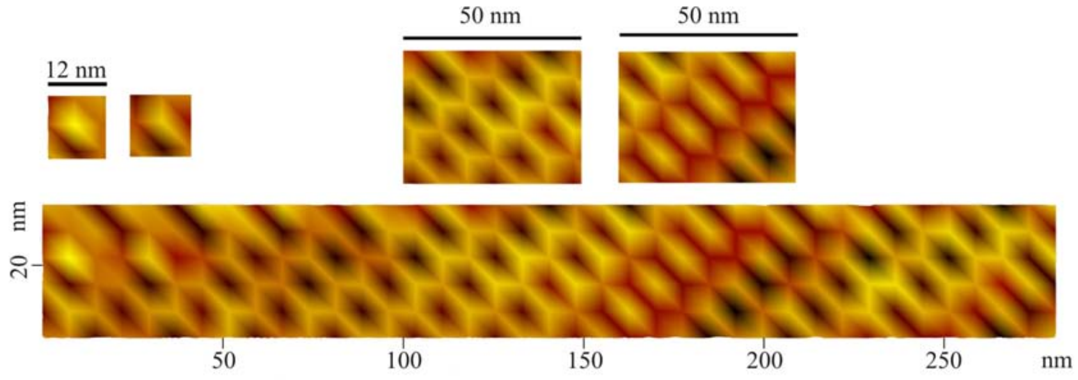


Fig.2. 2D AFM image of nanoobjects such "honeycomb of bees" in Sb_2Te_3:
in box at the top left are fragments of Benard cells images;
Upstairs, there are 2D- image (scan in 50×50nm) nanoforms such Benard cells.

In the middle of the top rate allocated hex (~ 50 nm) have the form of a grid similar to graphite; separate fragment in 3D- scale "bee cell" in the interlayer space Sb_2Te_3 given in Fig. 3.

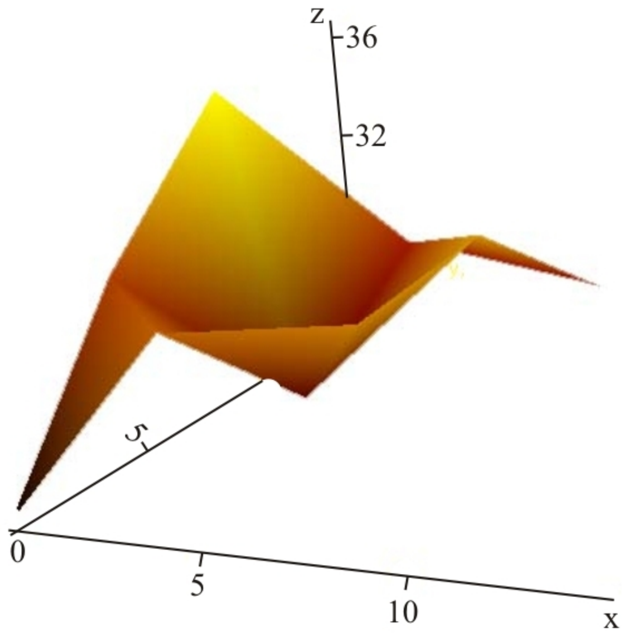
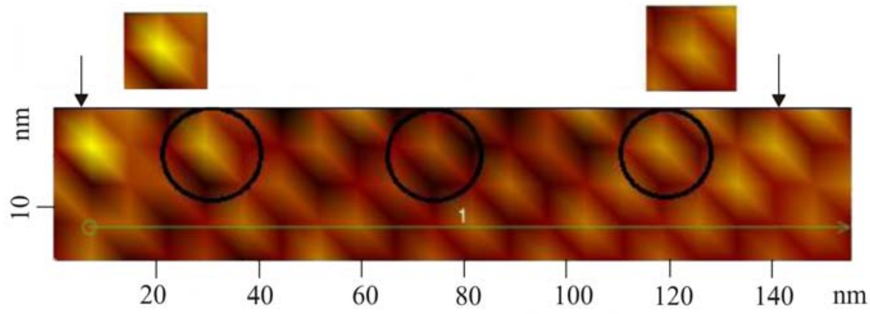


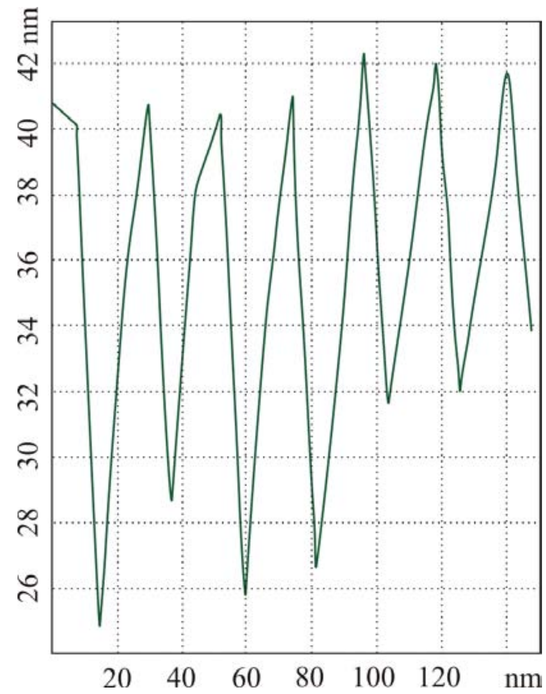
Fig.3. Separate three-dimensional fragment of " bee honeycomb" in Sb_2Te_3.

From profilograms (along the line 1 Fig. 4a), shown in Fig.4b seen that the height of the interlayer Benard cells ranges 12-16 nm, width has a size of about 10 nm. These structures are ordered and formed in the process of self-organization as well as other dissipative structure.

Highly ordered self-organizing structures in studied systems which far from equilibrium, have a certain shape and size of the spatial-time characteristic, they are stable against small perturbations. The most important characteristics of such dissipative structures is the localization region and the fractal dimension.



a)



b)

Fig.4. a) – 3D Benard's cells in Sb_2Te_3; b) – a profilogram along the line given in Fig.4a.

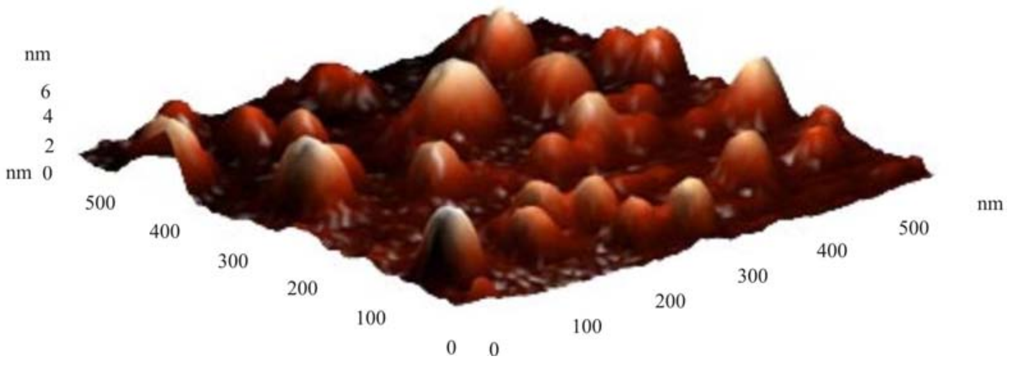
Complex systems are possible due to the hierarchical organization of systemic levels of complexity. It is obvious relationship between the phase transitions in the system state and abrupt changes of parameters. All phenomena occurring in nature (including in solids), in varying degrees, are interconnected. In considering the different scales of natural and man-made structures can be observed microlevel and macrolevel communication in the system hierarchy. In considering forms of seeming chaotic formations can detect the laws of growth of fractal forms [4-5, 11]. Given our experimental figures indicate not only fractality of natural processes, but also distributing them on nano-objects formed in layered systems (see Fig. 1-3, 5). These structures are identical to those obtained by modeling diffusion limited clustering hexagonal lattice "honeycomb" type [8, 12-13].

It is possible to distinguish three necessary (but not always sufficient) self-organization conditions in open systems with formation of dissipative structures:

– deviation from equilibrium has to exceed critical value, i.e. the system has to be in area of existence of bifurcations;

– volume of system has to be rather great and surpass some critical volume in which there is a necessary number undamped fluctuations; interaction of these fluctuations creates streamlining in system;

– existence of positive feedback.



a)

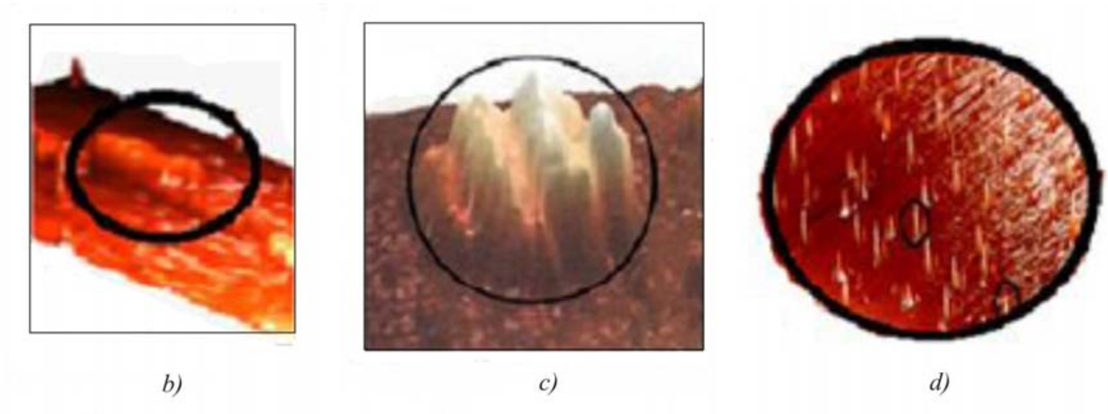


Fig.5. Forms of interlayer patterns in $A_2^VB_3^{VI}$ <impurity>:
a) – dome-shaped don't facetted nanoislands (Bi_2Te_3 <Cu>); b) – facetted nanoislandsNI (Bi_2Te_3 <Zn>);c) – localized patterns - (Sb_2Te_3); d) – don't facetted nanoislands (Bi_2Te_3 <Se>).

Self-organization of interlayer structures patterns in thermoelectric systems

We presented researches results of three-dimensional nanoobjects similar to "bee honeycombs" and hexagonal shape on van der Waals surface of Sb_2Te_3, Bi_2Te_3 crystals. Questions are considered of self-organization and formation of structures – patterns in crystalline solids. They are related with the concepts of dissipation associated with damping of various kinds of motions and the need for forming predictably repeating patterns in open systems.

In Fig.5 presents various forms of patterns grown in environs $Te^{(1)}$-$Te^{(1)}$ $A_2^VB_3^{VI}$ <impurity> . Determined their classification associated with localized spatial ordering, the sustainability of existing in conservative dissipative nonequilibrium environments.

The term "dissipative structures" unites all types of patterns. Concept of a pattern we applied to solid-state structures of various sizes.

It was analyzed solid-state conservative dissipative patterns in nanostructured $A_2^VB_3^{VI}$ crystals and similar natural objects patterns are revealed. The experimental testify not only fractal similarity of natural macroobjects but also about dissemination of them on the nanoobjects formed in the crystals of $A_2^VB_3^{VI}$.

Nanoobjects in Fig.5 are received by various methods. They are interesting to that are natural and regular (their single fragments repeat). In literature they are called nanoparticles, nanoislands (NI), clusters depending on their structure and the function which is carried out by them.

Numerous experiments on growth of nanoobjects show that the form of germs on a surface changed in the course of their growth. Either it is facetted, or, on the contrary, becomes unstable or dendritic. This fact significantly influences a stage of Ostwald ripening and respectively their structure. Despite these changes as we see from Fig. 6, the created nanofragments in interlayer space have forms of don't facetted nanoislands. These structures are formed at self-intercalation of copper in space $Te^{(1)}$-$Te^{(1)}$ Bi_2Te_3- thus arise up don't facetted fragments. The faceted nanofragments are formed at intercalation of atoms on a surface (0001) of layered crystals. Growth of these islets occurs due diffusion in the space $Te^{(1)}$-$Te^{(1)}$ of $A_2^VB_3^{VI}$ <*Se, Zn*> and due to the mechanism of Ostwald ripening [14].

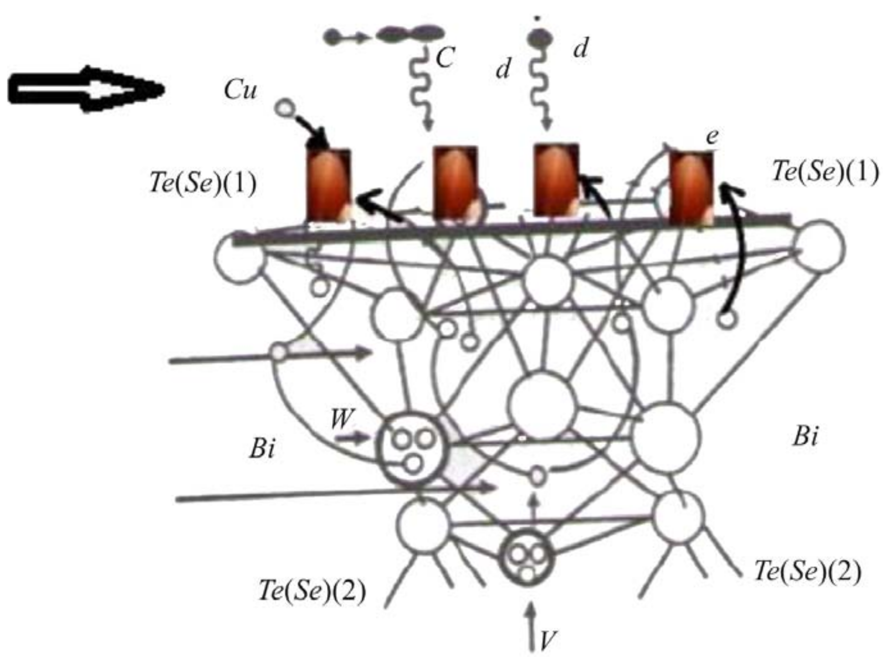


Fig. 6. Allocation scheme don't facetted NI on the van der Waals surface (0001) of Bi_2Te_3<Cu>, formed in the process of self-intercalation.

In both cases, the main mechanism for the growth faceted and don't faceted islets when limiting stage is the stage of the final surface diffusion and Ostwald ripening process.

We can say that the presented templates structures is followed particulars in clearly patterns; being between quintets $Te^{(1)}$-$Te^{(1)}$ $A_2^VB_3^{VI}$ these patterns move apart of quintets and actively participate in the scattering of electrons and phonons, which is manifested in a decrease lattice thermal conductivity in Bi_2Te_3 <*In, Se*> to K_L=5·10^2 W/cm·K at a total thermal conductivity K_t = 13.4·10^2 W/cm·K. In principle emergence of patterns in matter structure not a new phenomenon. Patterns in the world of particles can be similar to patterns not only in the world of atoms, but to those in solid-state structures. Except the given structures (Fig. 5) it is possible to review examples of patterns in composites, in multiphase eutectic systems.

Conclusion

Comparing the surface morphology of natural structures and morphology of nanostructured Sb_2Te_3 (Bi_2Te_3) crystals revealed geometrically similar elements. Benard cells, "bee honeycombs", some form of hexagonal nano-objects on the van der Waals surface of layered crystals were an example of conservative and dissipative self-organization. In such systems, self-organization processes in the $A_2^VB_3^{VI}$ interlayer space leads to the formation of hexagonal structures and nanoislets at various hierarchical levels.

Formation mechanisms of NI on a surface (0001) Bi_2Te_3<Cu> at self-intercalation and intercalations analized on the basis models of atoms condensation processes at a stage of Ostwald ripening that were convenient model for studying of forming processes self-organized nanoobjects on (0001) surface of layered structures.At self-intercalation of copper from layers and vacant sites on a telluride surface (0001) Bi_2Te_3 where the rate-limiting step is process of condensation of *Cu* atoms, by a mechanism Ostwald ripening formed domed don't facetted nanoislets.

In the process of directed diffusion of atoms *Se, Zn* intercalation in the space $Te^{(1)}$-$Te^{(1)}$ on the (0001) surface self-organized nanostructures faceted pyramidal shapes in the Bi_2Te_3<Se>, and in Bi_2Te_3<Zn> faceted NI formed due to coalescence of small NI.

In the deformed layered crystals in $Te^{(1)}$-$Te^{(1)}$ interlayers are created dissipative systems. Along with microdeformation in deformable crystals of $A_2^VB_3^{VI}$ there is a macroplastic current in which three-dimensional structural elements in combination with processes of the accelerated migration and coalescence participated. Dissipative structures in playing a role of macrodefects reduce the general heat conductivity of a crystal and by that increase its thermoelectric efficiency.

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