FORMATION OF NANO-LAYERED FRAGMENTS ON SURFACE (0001) HETEROGENEITIES IN BISMUTH TELLURIDE

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In the work it is shown that the defects of crystalline structure take part into formation of fractal aggregates on surface (0001) in unalloyed Bi_2Te_3 and Bi_2Te_3<Cu,Ni> except impurities. The analysis has revealed the interaction between dislocations and aggregation of impurity complexes, leading to fixing of dislocation fractal rings.

Introduction

The real fractal formations by the type of dislocation structures, fractal aggregations of microcracks, nano-objects in crystal interlayers of $A_2^V B_3^{VI}$ type and dichalcogenides of transition metals have become the objects of special attention of investigators of solid-state physics. The peculiarity of these structural systems consists in the fact that their fractal structure reveals only at joint resolution of several levels. The effects, leading to introduction of new structural levels reveal at plastic deformation. Its carriers form the fractal clusters (FC), the compactness of which further leads to design of super-defects, being the structural elements on the new level. The description of the given systems is achieved in the limits of both mono-fractal and multi-fractal representations [1-4]. The fractal conceptions in the case of irregular functions are considered in them.

The consideration of processes, leading to formation of dislocation aggregations, forming the cell walls with fractal structure presents interest. Thus, the confirming main evolution stages of dislocation ensemble of high density are presented in the work [1]; firstly their distribution is homogeneous one, further, the aggregations in the form of balls and loose cell walls appear and finally the clearly defined cellular structure forms. The reasons, leading to local formation of dislocation clusters are considered in [6]. The given investigations can be propogated on the other solid-body objects.

The perceptions about dislocation phenomenon, described here, can play the definite role in FC formation processes in layered crystals, which are Bi_2Te_3. Not only dislocations, situated perpendicular to "C" plane, but lying on it (forming etch grooves) are revealed on the surface (0001) cleavage in Bi_2Te_3 [7].

As a whole it is very difficult to interpret the experimental results, connected with alloyed systems on the base of bismuth chalcogenide. The pictures of hexagonal and parallel dislocation lines in bismuth telluride are given in monograph [8]. The cleavage plane (0001) in bismuth telluride coincides with crystal basal plane and is the main glide plane simultaneously. This allows us to directly observe the dislocation picture of this plane in the field of electron microscope.

Let's give investigation results of crystalline structure defects and dislocation structure of surface (0001) Bi_2Te_3, taken from [9]. The dislocations, which are heterogeneous ones in distribution, are the dominant type. It is shown, that interaction of two dislocations leads to formation of new dislocation, gliding in plane (0001) and it is responsible for dislocation branching and formation of dislocation grids in basal plane [9]. The presence of both hexagonal grids of dislocations and parallel rows of dislocations (in nano-scales ≈500 nm) has been established. The contrast analysis [8] shows the presence of stacking faults, situated parallel to basal plane and very small dislocation loops. The dislocation picture in the volume of Bi_2Te_3 crystal is more complex; than it can be concluded from study of only etch pits. These defects can be the places of "fixing" and origin of impurity fractal clusters.

The dislocations, going on three crystallographic directions, forming grids and rings, appear simultaneously in Bi_2Te_3 (fig.1) [10].

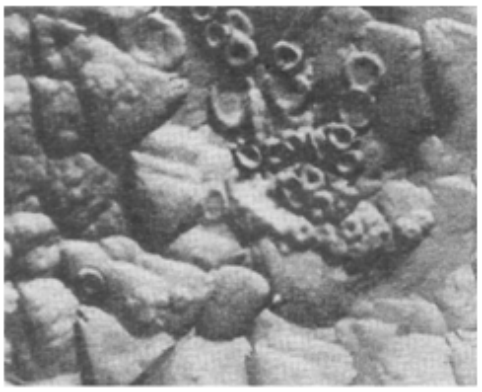

Fig.1. The dislocations and vacancy rings in Bi_2Te_3 [10].

Authors of work [11] suppose that chemical heterogeneities of composition $(Bi, Sb)_2(SeTe)_3$ with high density of dislocations in these samples, heterogeneously observable lead to the formation of domain microstructure, caused by the fields of elastic voltages with average sizes of domain 8-10 nm in Bi_2Te_3 of both *p*- and *n*-type. The observable deformation field is caused by the separate dislocations, which are situated in dipole form, distant from each other on 5 nm. In the work [12] it is shown on interaction between dislocation and comparably large aggregations of impurity complexes, this leads to fixing of defects and dislocations by impurity atoms. Thus, the favorable conditions for formation of both impurity nano-fragments and fractal formations on the base of dislocation grids, vacansion rings and point defects are formed in the growth process of Bi_2Te_3 crystal towards with impurities, including in the layers.

The above mentioned experimental facts lead us to the next work aim, connected with formation of nano-fractal objects with participation of aggregations of dislocations and

vacancies on the surface (0001) between $T_e^{(1)}$-$T_e^{(1)}$ in Bi_2Te_3, alloyed by easily-diffused impurities (Cu and Ni).

Experimental results and investigation technique

The Bi_2Te_3 compound is obtained by thermal synthesis at 900-950^{0}K, which usually is carried out in quartz ampoules, when Bi, Te and impurities (*Ni* or *Cu*) in necessary relation are loaded. After alloy synthesis it is loaded into graphitized ampoules (by sizes 8-10 nm), alloy it over again and further the monocrystalline ingots at temperature gradient $\Delta T=100^0$ and crystallization velocity lower than 1cm/h are obtained by Bridgman method or vertical directed crystallization. The nano-fragments are studied in such crystals. This process can hardly be considered as intercalation of layered matrix Bi_2Te_3. However, Bi_2Te_3-Me can be considered as intercalated ones, i.e. the layers of matrix-master and –guest (Ni, Cu and Ag) can be emphasized in them. Here the increase of interlayer distance at penetration of metal atoms in interlayer spaces is character because of the weak chemical bond between $T_e^{(1)}$-$T_e^{(1)}$.

The intercalation of Cu and Ni atoms and diffusion at different temperatures from 400^0 up to 500^{0}K is carried out as separate experiment.

Electron-microscope images are obtained on atom-force microscope (AFM) of NC-AFM trend. X-ray diffraction investigations are carried out on the installation of Philips Panalytical trend (X-ray diffractometer). The preparation of atomically clean surface is carried out by the way of crystal cleavage along basal plane on the air before experiment carrying out.

The result discussion.

The guest atoms (Vu, Ni, Ag…) in bismuth telluride localize in Van der Waals spaces, formed by atoms of neighbor layers-quintets, perpendicular to symmetry axis of third order (C axis in hexagonal lattice). There are three such quintets in hexagonal cell, the number of atoms of which in elementary cell is equal to 15. Each quintet consists of five simple layers (fig.2) [8].

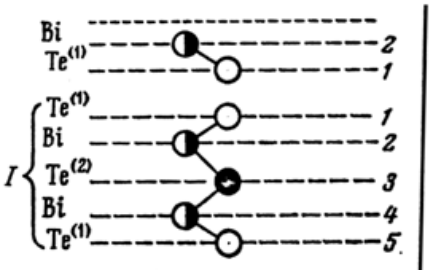

Fig.2. The atom distribution in lattice quintet of bismuth telluride [8].

The atoms of separate layer are similar and form the plane hexagonal lattice. The atoms of each next layer are under centers of triangles, formed by atoms of previous layer. Atoms $T_e^{(1)}$ have three atoms from each adjacent layer in the capacity of close neighbors (6 Bi atoms). $T_e^{(1)}$ is connected from the one side with three Bi atoms, and from another one it is connected with three of $T_e^{(1)}$ atoms, i.e. there are two essentially different places for Te atoms [8] in the lattice.

The scheme of atoms $T_e^{(II)} - Bi - T_e^{(1)} - T_e^{(1)} - Bi - T_e^{(II)}$ position in crystal lattice Bi_2Te_3, in which the nano-layers are in the form of fractal formations of impurities and other defect structures between atoms, $T_e^{(1)}$-$T_e^{(1)}$, is given on the fig.3.

Moreover, we must tell the difference the bonds between quintets and bonds inside quintets. This creates the real situations for position of impurity nano-layers in this almost "free" space between $T_e^{(1)}$-$T_e^{(1)}$ round dislocations and on vacancies of essential atom quantities. We already have given the experimental facts about existence of dislocations and different defect types on the surface (0001) from the works [7-10]. The vacancies from under *Te* on the complexes by the type " vacancy-impurity atom" can be the more probable places of aggregation and formation of nano-fragments (including FC) on the base of Cu, Ag, Ni. The places round dislocation pits [1-6] and other extensive defects [7-8], boundaries of blocks and grains, micro-cracks [5], concentration heterogeneities and micro-segregation phenomenon [8] can be the most difficult places for nano-fractals.

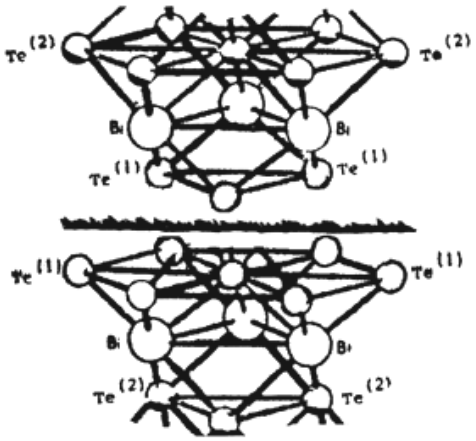

Fig.3. The scheme of crystalline structure Bi_2Te_3 with nano-fragments situated between $T_e^{(1)}$-$T_e^{(1)}$.

Firstly let's give the experimental data on the example of Bi_2Te_3<Cu> system. From the fig.4-5 it is seen which nano-crystal formations appear on the surface (0001) at intercalation by cuprum and at synthesis of bismuth telluride towards with Cu with further crystallization. The cuprum at lowered temperatures: 400 and 500^{0}K penetrates into layers as in nano-container, not interacting with superstoichiometric of Bi_2Te_3 components: tellurium and bismuth. The X-ray diffraction peaks from cuprum nano-particles evidence about this (fig.4). X-ray diffractograms (fig.5) of non-intercalated samples Bi_2Te_3<Cu>, (obtained in the crystal growing process) show the peaks mainly on CuTe and nano-particles with excess Cu and $Cu_{0,647}$ $Te_{0,353}$. Here the space $T_e^{(1)}$-$T_e^{(1)}$ Bi_2Te_3 plays the role of nano-reactor, in which CuTe and $Cu_{0,647}$ $Te_{0,353}$ form. The morphology of surface (0001)

Bi_2Te_3<Cu> at intercalation by cuprum is presented on the fig.6; the fractal structure here consist mainly of the cuprum, Bi_4Te_3 and nano-crystals (NC) of Bi_2Te_3 itself. AFM-images of surface in three-dimensional scale (3D) for Bi_2Te_3<Cu> with obtained nano-particles in the growth process are given on the fig.7.

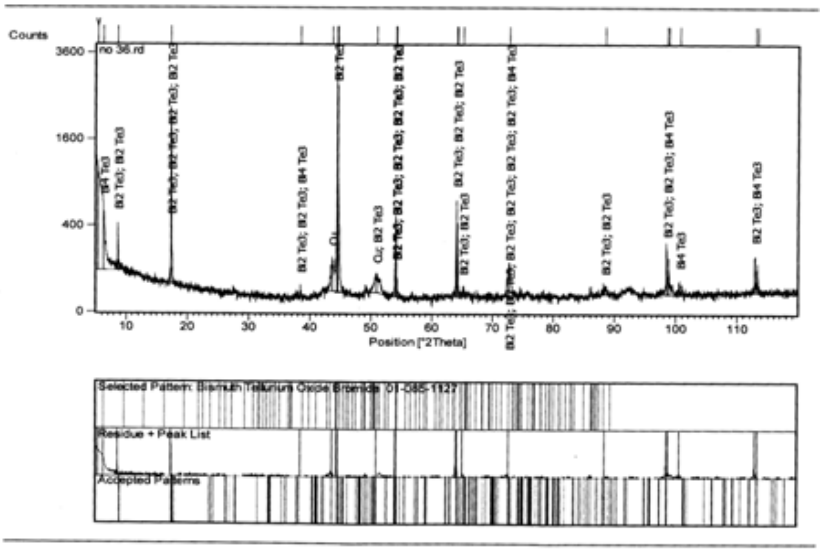

Fig.4. X-ray diffraction picture of bismuth telluride surface (0001) intercalated by cuprum.

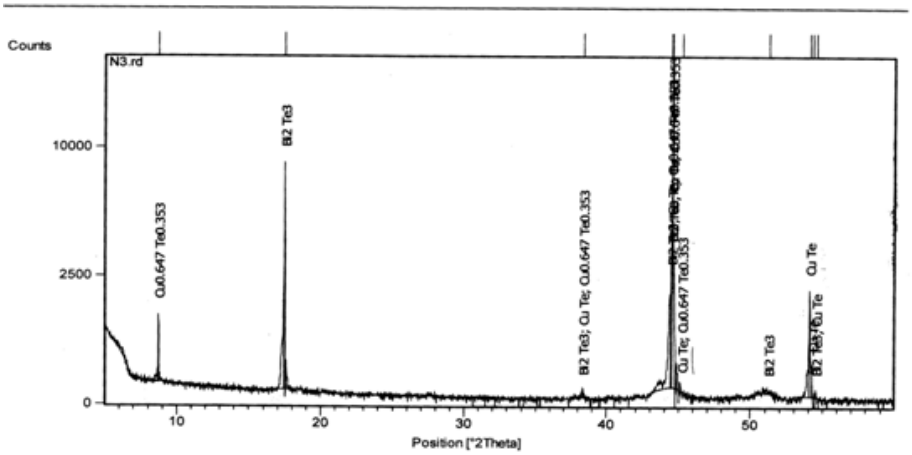

Fig.5. X-ray diffraction photo of Bi_2Te_3 monocrystal surface (0001) alloyed by cuprum.

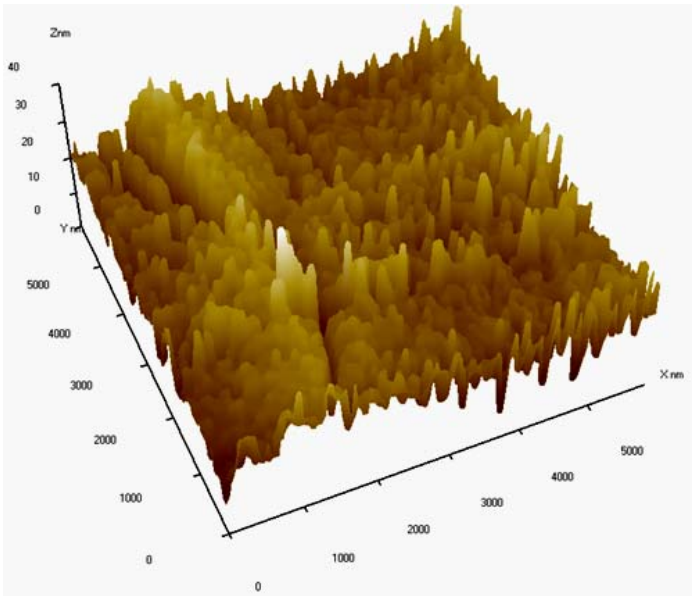

Fig.6. AFM-image of Bi_2Te_3 surface (0001) intercalated by cuprum.

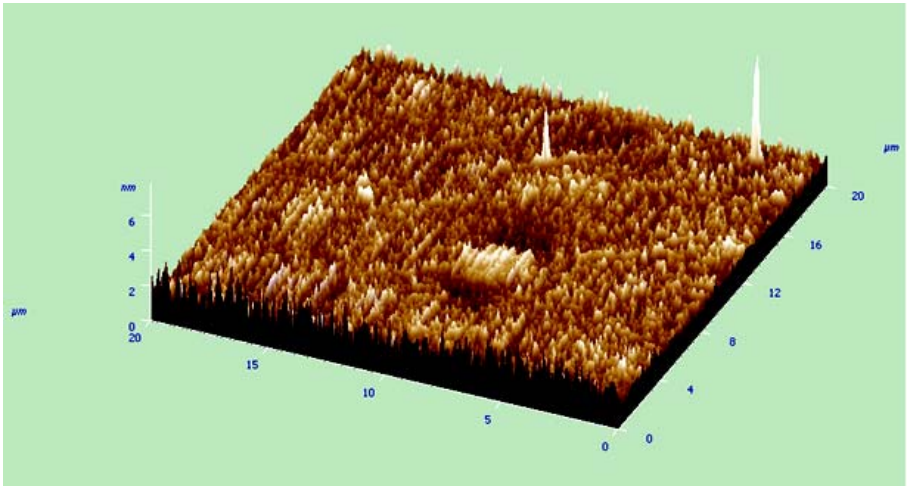

Fig.7. AFM-image of Bi_2Te_3<Cu> surface (0001) in 3D scale.

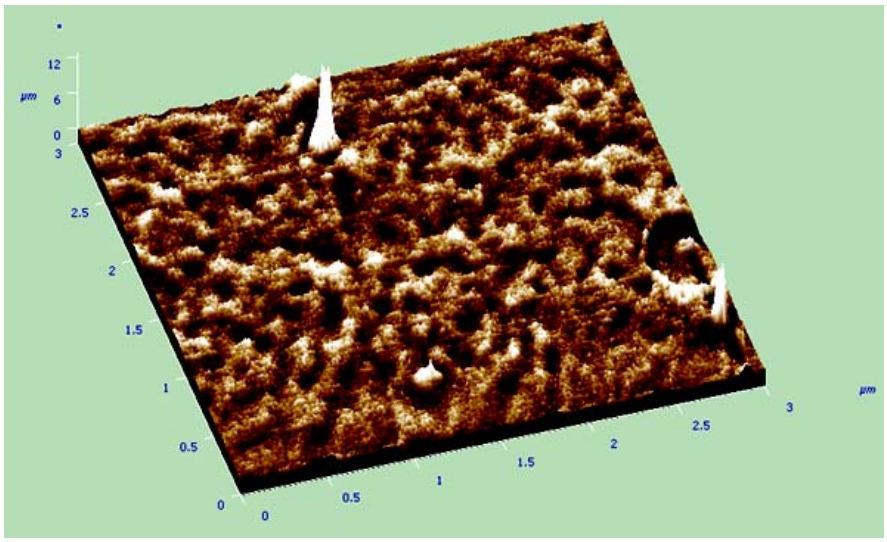

Fig.8. AFM-image of surface of alloyed Bi_2Te_3 in 3D scale.

The comparison of revealed fractal formations shows both the similarity and difference in their sizes and probably in formation mechanisms of NC.

The formation mechanism of fractal aggregates probably is connected with process of impurity filling by the places round dislocation pits, grids and vacancies from under Te on the surface (0001) Bi_2Te_3. The beginning of formation of fractal cells takes place in the process of impurity diffusion along basal surface (0001) with formation of their base on telluride quintets, including the vacancy places, being on the quintets.

The gradually growing FC, the layer filling of which between quintets is led to the formation of fractal surfaces on basal plane (0001) form in the result of growth of nano-fragment sizes, that is visually reflected on topography, which is given on the fig.6-7.

Almost all filling stages of Van der Waals bond are connected with process of rapid introduction of easily-diffused impurities (Ag, Cu, Ni) in Bi_2Te_3 in the direction of basal plane in the result of diffusion direction. Simultaneously all vacancies under from Te are filled by impurities; their aggregation and formation of nano-fragments, which we reveal by AFM method, take place. On the final stage the nano-islands are grown like "forest" perpendicular to plane (0001). The coagulation process achieves its peak, at which the hills-fractals, contacting with each other, join into unique fractal surface. This mechanism is more probable at the crystal growth with impurities (Ni and Cu) and at the next precipitation of them into interlayers.

The obtained fractals have the nano-sizes on all three directions on geometric sign: their height doesn't exceed 20 nm, width and length vary from 100 up to 300 nm; this is proved by data of figures 6-7.

From electron-microscopic images (fig.8) it is distinctly the inhomogeneous distribution both rare fractal perpendicular hills (light nano-formations in the middle) and hardly notable defect "fields" (right low part of figure 8). Such character defects exist in both stoichiometric (fig.9) and Bi_2Te_3<Ni> crystals, alloyed by nickel (fig.8). It is difficult to avoid the appearance of unnecessary blocks, growing mainly from the one crystal side, and also defect formation during the growing process. The investigations of AFM-images of stoichiometric (unalloyed) crystal show different nano-phases (see fig.9). The visible nano-formations on whole surface (0001) Bi_2Te_3 are very similar with dislocations and vacancy rings in bismuth telluride, presented on the fig.1. Moreover, the differences are observed. Thus, the island-hill in the surrounding of fractal (light) ring is notable in right low part on the fig.9 by big scale. Such islands in the surroundings of nano-rings are seen in the low part of middle of fig.9. These

AFM-images are evidence of the interaction role of different defects (including impurity ones) in the formation of nano-fractal formations on the surface (0001) Bi_2Te_3.

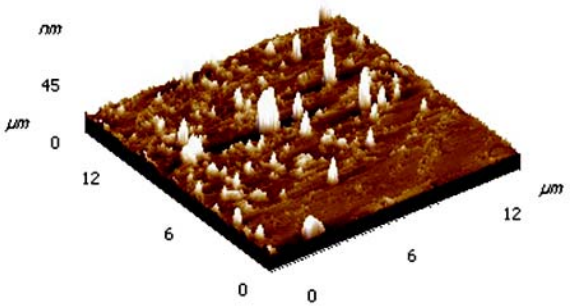

Fig.9. AFM-image of surface of unalloyed Bi_2Te_3 in 3D scale.

Let's pay attention on one more factor, connected with spontaneous transition-diffusion of main part of *Cu* atoms from penetration centers in quintets in Van der Waals spaces in the beginning period after crystallization (these are samples of second type, intercalated samples are related to the first ones). This spontaneous atom diffusion from the layers into interlayers are often named as self-intercalation.

The studied morphology of interlayer surface of bismuth telluride in alloyed (*Cu*) and further in self-intercalated space $T_e^{(1)}$-$T_e^{(1)}$ shows that:

- the cuprum layers are set in the form of nano-fractals on basal surface;
- the cuprum precipitation from quintets in interlayer $T_e^{(1)}$-$T_e^{(1)}$ takes place in grown up *n*-Bi_2Te_3<Cu> crystals during first ten days at room temperature and it leads to the change of main structure parameter (*d*) on $\Delta d = 3 \cdot 10^{-3}\ ^0A$.

The given effect of cuprum self-intercalation, leading to self-formation of nano-objects, is also accompanied by strong change of coefficient of conductivity, efficiency, decrease of thermal conduction and concentration of current carriers.

Conclusion

The analysis of surface (0001) Bi_2Te_3 morphology shows that nano-particles (in the form of nano-fractal formations) can form between layers $T_e^{(1)}$-$T_e^{(1)}$ with participation of impurities, dislocations and stacking faults. Two methods of atom introduction with small ion radiuses (Ni and Cu) in interlayer spaces are revealed: in the synthesis process with further crystal growing up, intercalation of impurity (Cu) on basal plane from telluride quintets, in the result of which the nano-fractal formations form.

It is very difficult to see the separate impurity and defect fractal structures in the connection with their interaction on AFM-images.

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BİSMUT TELLURUN QEYRİ-BİRCİNSLİ SƏTHİNDƏ (0001) NANOLAYLI FRAQMENTLƏRİN FORMALAŞMASI

İşdə göstərilmişdir ki, və (0001) səthində legirə olunmamış Bi_2Te_3 və Bi_2Te_3<Cu,Ni> fraktal aqreqatların formalaşmasında aşqarlardan başqa kristallik defektlərin də rolu vardır. Analiz dislokasiyaların və aşqarların yığma komplekslərinin qarşılıqlı təsirinu aşkar etmisdir ki, bu təsir nəticəsində də dislokasion fraktal halqaları möhkəmlənir.

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ФОРМИРОВАНИЕ НАНОСЛОЕВЫХ ФРАГМЕНТОВ НА НЕОДНОРОДНОСТЯХ ПОВЕРХНОСТИ (0001) В ТЕЛЛУРИДЕ ВИСМУТА

В работе показано, что в формировании фрактальных агрегатов на поверхности (0001) в нелегированных Bi_2Te_3 и Bi_2Te_3<Cu,Ni> участвуют, кроме примесей, и дефекты кристаллической структуры. Анализ выявил взаимодействие между дислокациями и скоплениями примесных комплексов, приводящее к закреплению дислокационных фрактальных колец.

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