Chapter

Formation of Nanostructures on the Solid Surface

Alexander V. Vakhrushev

Abstract

Forming nanostructures on the solids surface is one of the promising nanotechnological processes. It has been established that changes in the atomic structure of the solid surface due to the nanostructures formation result both in a significant change in various physical properties of the surface, and in an increase in its durability, strength, hardness, wear resistance. There are many different methods for forming nanostructures on solid surfaces: surface modification with nano-elements (nanoparticles, fullerenes and fullerites, graphene and nanotubes), formation of a nanocomposite layer on the surface, forming quantum dots and whiskers on the surface, implanting ions into the solid surface, laser surface treatment and other processes. The above processes are very complex and for their optimization require detailed research both by experimental and theoretical methods of mathematical modeling. The aim of this chapter was to provide a comparative review of different methods of forming nanostructures on the solids surface and mathematical modeling of these processes various aspects.

Keywords: solid surface, nanostructures, formation, physical processes, modeling

1. Introduction

Solids surface modification with the aim of forming nanostructures is widely used now. This is due to the fact that the creation of a nanostructure on the surface of a solid significantly changes its physical properties, which makes it possible to form various functional nanostructures, and increases the durability and strength of both the surface and the solid as a whole. Let us list the various technological methods of nanomodification of a solid surface.

1. Formation of a nanocomposite layer
2. Formation of quantum dots on the surface of a solid.
3. Formation of whiskers on the surface of a solid.
4. Formation of nanostructures on a porous surface
5. Surface modification by fullerenes and fullerites
6. Implantation of ions or atoms into the surface

7. Laser surface treatment

8. Formation of nanostructured coatings for spintronics

9. Healing of defects on the surface

10. Applying graphene to the surface

The list of technological processes for the modification of a solid body can be continued. The emergence of new processes at the moment is very intense.

The above technological processes can be divided into the following three main methods of nano-structural surface modification.

1. Application of a special coating having a nanostructure or including nano-structured elements in its composition.

2. Formation of nanostructured elements on the surface.

3. Changes in the atomic structure of the surface of a solid.

There are also complex methods that combine the above methods for modifying the surface of a solid.

The above processes are very complex and for their optimization require detailed research both by experimental and theoretical methods of mathematical modeling.

Experimental data show that the parameters of nanomodification processes of solids surface depend largely on the chemical, physical, and structural properties of the elements in their composition. It should also be emphasized that nanotechnological processes are complex and diverse, and their implementation typical scale is small, less than 100 nanometers. This requires a deep understanding of physical and chemical processes at nanoscale, but the nanometer scale of processes makes it difficult to study them by experimental methods only and brings about the need to use mathematical modeling. Mathematical modeling is a powerful tool, especially in new, "pioneer" fields of science and technology, in which operational experience has not yet been accumulated. Therefore, developing nanotechnology of solid surface modifications has required significant improvement and creating new methods of mathematical modeling and mathematical physics and their extension to the study of multilevel systems.

To model the class of problems considered in this review, a wide range of methods used in the simulation of meso- and nanoscale systems are used: quantum chemistry, molecular dynamics, mesodynamics and continuum mechanics. Each of these methods has its own challenges, capabilities, and limitations.

In the review, it is difficult to give in detail all the mathematical equations describing these complex processes. Therefore, the interested reader can study the exact mathematical formulation of problems in specific works given in the review or in the author's book summarizing methods for modeling nanosystems [1].

The aim of this chapter was to provide a comparative review of different methods of forming nanostructures on the solids surface and mathematical modeling of these processes various aspects.

The review presents works on three processes of solid surface modification: the electrocodeposition of nanoparticles in a metallic coating; magnetron deposition of nanofilms and the formation of nanolayers on a solid surface by epitaxy in which the author and his colleagues were directly involved.

2. The electrocodeposition of nanoparticles in a metallic coating

2.1 Technology of electrocodeposition of nanoparticles in a metallic coating

The electrocodeposition of nanoparticles in a metallic coating (EPD) process is the advanced method for using in practice the nanotechnology [2–5]. The composite coating with improved and unique operational characteristics, such as wear resistance, cracking resistance, antifriction properties, corrosion resistance, radiation resistance, and high adhesion to the substrate can be produced by this technology. Metal matrix composite electrochemical coatings (MMEC) are prepared from the suspensions, representing electrolyte solutions with additives of certain quantity of a superfine powder (**Figure 1**). The particles are adsorbed onto cathode surface in combination with metal ions during electrocodeposition (ECD) process and the metal matrix composite coating is formed. MMEC consists of galvanic metal (dispersion phase) and particles (dispersed phase).

There are the following steps of the ECD process:

1. The particles in suspension obtain a surface charge.

2. The charged particles and metal ions are transported through the liquid by the application of an electric field (electrophoresis), convection, and diffusion.

3. The particles and metal ions are adsorbed onto the electrode surface.

4. The particles adhere to the electrode surface through van der Waals forces, chemical bonding, or other forces and, simultaneously, adsorbed metal ions are reduced to metal atoms. Metal matrix is encompassed the adsorbed particles and thus the MMEC is formed.

Depending on the parameters of the co-electrochemical deposition process, strength, wear resistance, corrosion resistance, microhardness can be significantly improved. The EPD process and, consequently, the structure, morphology and properties of the composite coating are influenced by such electrochemical parameters as electrolysis conditions (chemical composition and method of stirring the electrochemical bath, presence of inclusions, temperature, pH), parameters of the applied voltage (current density, constant, pulse current), properties of inclusions (chemical composition, size, shape, surface charge, surface functionalization, concentration and dispersion of particles in an electrochemical bath), interaction between particles and electrolyte ions, nature and speed of fluid movement.

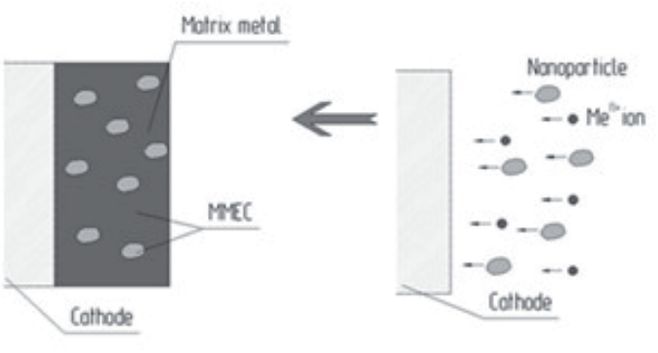

Figure 1.
The ECD process.

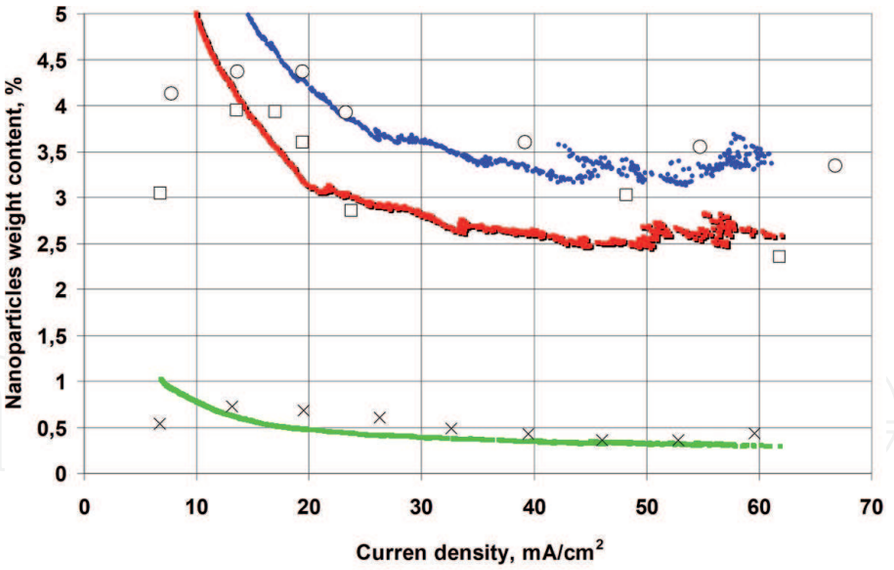

Figure 2.
Dependencies of weight content on applied current density.

The surface charge of the particles is a very important factor in the process. It should be noted that negatively charged particles are deposited more intensively, this is explained by the presence of an electric double layer around the nanoparticles. The intensity of electrolyte stirring during SEA is an important factor that affects the uniformity of the nanoparticle's distribution in the electrolyte volume due to convective flows and the delivery of particles to the cathode surface.

A large number of factors affecting the quality of the nanocomposite layer requires the use of mathematical modeling to determine the optimal parameters of the technological process of their formation.

2.2 Modeling results of nanoparticles electrocodeposition in a metallic coating

As an example, the results of mathematical modeling of copper and alumina particles ECD on RCE with consideration of electrolyte turbulent flow are depicted in **Figure 2**. A good correlation with the published experimental date [2] has been found. For the first time ever, it is found that near the RCE surface the unsteady diffusion layer is formed due electrolyte turbulent flow.

The process of nanoparticles electrocodeposition in a metallic coating can be studied in detail in [3–6].

3. Magnetron deposition of nanofilms on the surface of a solid

3.1 Technology of magnetron sputtering

In the 1970s, D. Chapin patented a planar magnetron system. This design increased the lifetime of the target and made it possible to spray on rather large areas, for example, architectural glass. Subsequently, the popularity of spray deposition grew rapidly because of the need to produce thin films with a uniform composition and good adhesion to the substrate surface, the demand is due to microelectronics [7–10].

The diagram of the magnetron chamber shown in **Figure 3** illustrates the process of magnetron sputtering.

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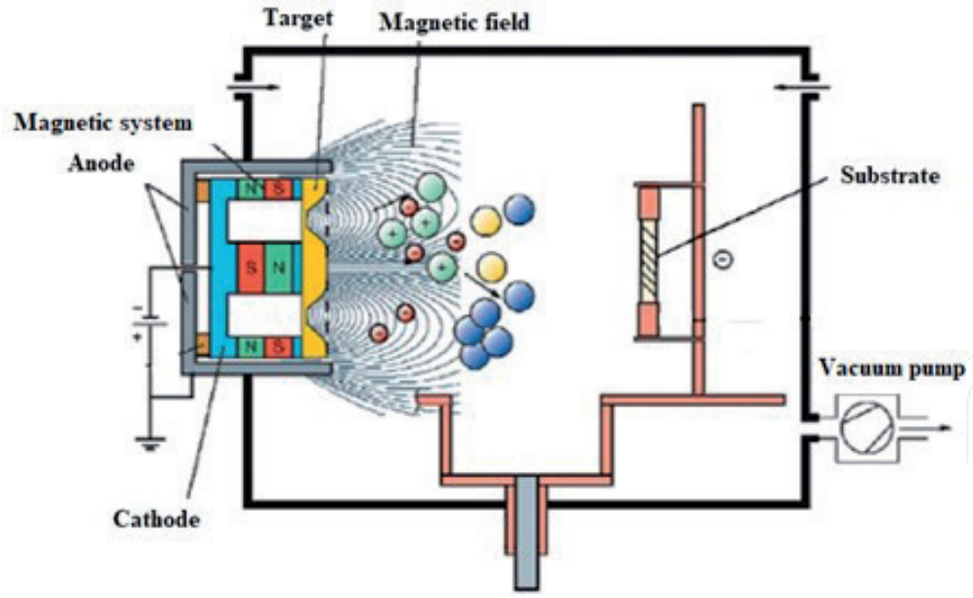

Figure 3.
Diagram of the chamber of the installation of magnetron sputtering [7].

In the above scheme, a planar target is used, colored yellow. An inert gas is required to create a plasma above the target. The black lines show the magnetic field holding the plasma; in this area, the atoms of the working gas are ionized. Then, under the influence of an electric field, the ions knock the atoms out of the target. The active gas serves to form oxide and nitride films. A bias potential is applied to the substrate, the value of which affects the structure of the formed coatings. When a negative bias potential is applied to the substrate with respect to the magnetron plasma, the ions are accelerated in the electric field of the substrate and carry out a low-energy bombardment of the substrate surface.

Magnetron sputtering is widely used for forming of new electronic devices based on new functional nanosystems, which requires a thorough study of their properties at the atomic and molecular level. Their functional characteristics depend on the structure and nanosystems morphology: optical absorption, electromagnetic parameters, etc. Recently, considerable attention has been paid to such nanosystems as superconductors, magnetics, heterostructures for spintronics. These systems are layered or nano-dispersed composites with local inhomogeneities zones. The local inhomogeneities presence results in forming stable vortex-like regions of reverse magnetization, called magnetic skyrmions and anti-skyrmions, which are very promising tools for use in the spintronics field.

3.2 Results of modeling magnetron sputtering of multilayer nanosystems for spintronics

A particularly important effect on the spintronic objects and other nanoscale elements properties is exerted by the structure of layers, domains, regions, films arising during their manufacture [11–13]. The structure generates at the atomic level. Therefore, the main mechanisms of regulation, activation, and interaction in spin nanosystems must be monitored at this scale. Atomistic modeling makes it possible to identify the modes and technological processes parameters when the functional nanostructure's structure is the closest to the required characteristics. There is an acute problem of forming multilayer nanosystem with clear boundaries of various nanolayers sections.

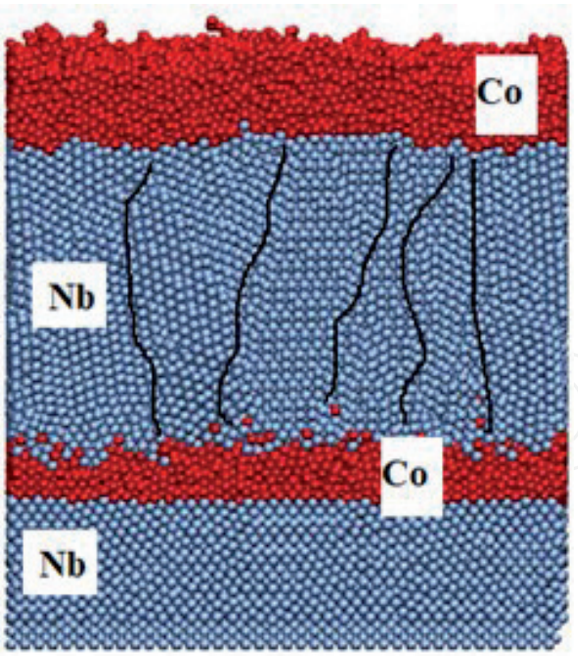

Figure 4.
Nb-Co multilayer quantum valve.

As an example illustrating the simulation of the real structure of a material, let us consider the structure of a multilayer nanosystem of an Nb-Co spin valve.

Figure 4 well characterize the qualitative picture of a spin valve forming from niobium and cobalt layers and the structure of the layers. The structure of the layers formed by niobium atoms is close to crystalline. In this case, groups of atoms are combined into nanocrystallites with vertical spatial orientation. In **Figure 4**, solid lines mark the boundaries of these nanocrystals. Cobalt nanofilms have an amorphous structure. The results obtained are in good agreement with experimental studies of the structure of various multilayer nanosystems [14].

4. Formation of nanolayers on a solid surface using epitaxy

4.1 Technology for the formation of nanolayers on a solid surface by epitaxy

At present, epitaxy is widely used to modify the surface of solids. Epitaxy is the process of building up layers on the surface of a solid [15]. **Figure 5** shows a simplified diagram of the process.

The structure of the formed epitaxial layers, as a rule, reproduces the structure of the solid's surface, and the chemical composition of the epitaxial layer and the substrate may differ. In the process of epitaxy, the chemical composition of the grown layers can be controlled both gradually and discretely. This technology makes it possible to grow multilayer nanosystems with a thickness up to atomic dimensions. The structures grown in this way are nanostructures: nanolayers, quantum dots, whiskers, etc. give the surface of a solid body unique physical properties that are absent in the base material. There are different types of epitaxies. If the materials of the resulting layer and the substrate are the same, then the process is called auto epitaxial or homoepitaxial. If the materials of the layer and the substrate are different, then the process is called heteroepitaxial.

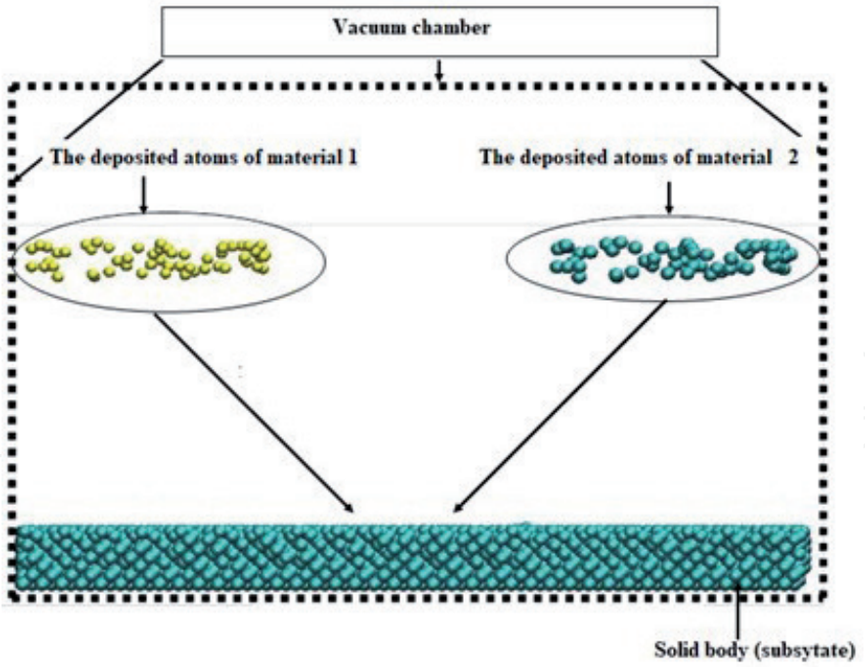

Figure 5.
Epitaxy scheme.

4.2 Results of modeling the formation of nanostructures on a solid surface by epitaxy

4.2.1 Simulation of the formation of quantum dots

As examples of modeling process for the formation of quantum dots on the a solid surface, let us consider the formation of gold nanoparticles on the silicon surface and the formation of a complex system consisting of gallium and antimony atoms. The simulation results are presented in **Figures 6** and 7, respectively.

For the simulation, a silicon substrate with orientation (100) was used, which is indicated in green in **Figures 6** and 7. Gold atoms, indicated in yellow in the figure, were deposited on the substrate. Then, silicon atoms were deposited on the resulting system. The temperature of the simulated system was kept constant and equal to 800 K.

As can be seen from **Figure 6**, gold nanoparticles of various diameters are formed on the substrate. The physical process of forming the gold-silicon nanosystem is interesting. First, gold atoms are deposited on a silicon substrate, and then they are collected in nanoparticles (quantum dots) of various sizes, spherical.

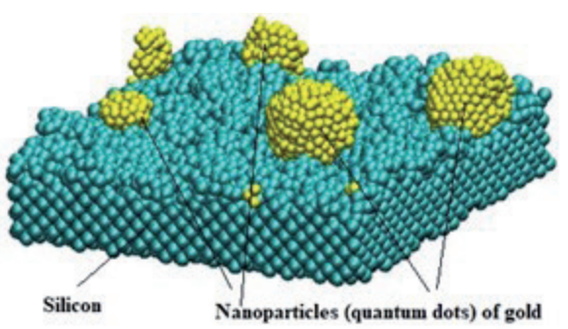

Figure 6.
Picture of a nanosystem on a solid surface obtained by simulating the deposition of gold atoms on a silicon substrate with the orientation (100).

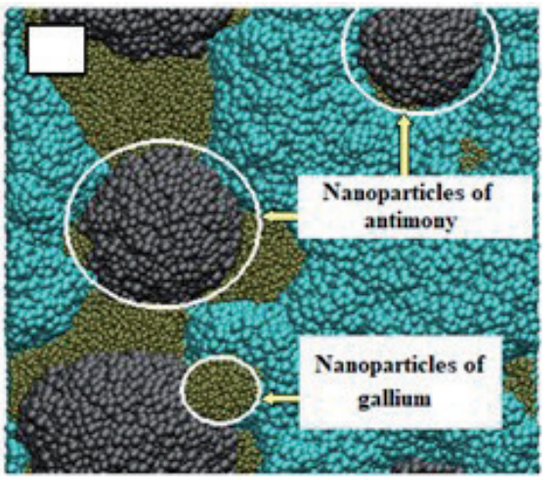

Figure 7.
Pictures of a nanosystem on a solid surface obtained by simulating the deposition of gallium and antimony atoms on a silicon substrate with the orientation (100).

As a result of modeling the formation of a complex system consisting of gallium (dark green) and antimony (lilac) atoms, gallium, and antimony atoms form conglomerates of various shapes) (**Figure 7**). Diffusion of gallium and antimony atoms into the substrate is not observed. It can be seen from the presented figures that the atoms of the substances under consideration tend to form nanoparticles on the silicon surface of various shapes. Silicon atoms fill the entire space between the formed agglomerates of gallium and antimony nanoparticles.

4.2.2 Modeling the formation of nanoelements on a porous solid surface

Let us consider the results of modeling the processes of forming ZnS nanolayers on the surface of porous aluminum oxide on matrices. Such nanostructures are actively used in optical systems in the infrared range [16].

The process of nanostructure formation in zinc sulfide nanofilms is illustrated in **Figure 8**.

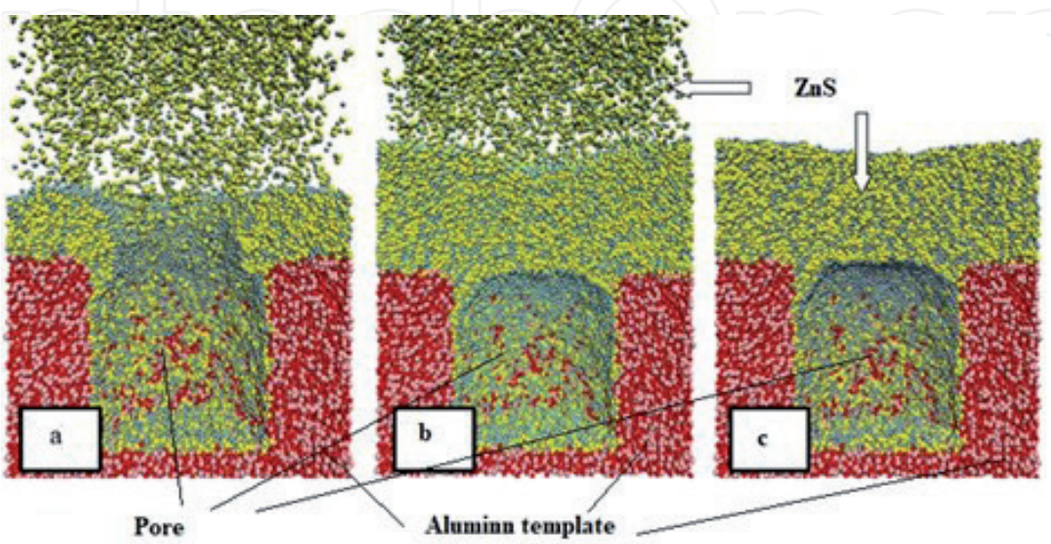

Figure 8.
Pictures of the sequential formation of a ZnS nanolayer on a porous alumina substrate for the deposition time: (a) 0.2 ns, (b) 0.4 ns, and (c) 0.6 ns.

Analysis of the nanostructure shows that the overgrowth of pores on the surface of a solid with the indicated atoms occurs gradually. First, a ZnS nanolayer begins to form near the pore (**Figure 8a**), which subsequently gradually closes the entire pore. Zinc sulfide molecules partially enter the pore, but its complete dense filling does not occur (**Figure 8b** and **c**). Nevertheless, by the end of deposition, almost the entire inner surface of the pore is covered with ZnS molecules. The gradual filling of the pore leads to the appearance of round growths over the pore.

In general, the surface of the ZnS nanolayer forms even, with a slight decrease in the thickness of the nanolayer above the pore area. The formation of molecular agglomerates in the space above the substrate during epitaxy is not observed; therefore, the nanolayer is even and there are no significant differences in the surface relief. The growth rate of the nanofilm during the deposition process was uniform. The thickness of the formed nanolayer was 6.6–6.8 nm.

Analysis of the materials structure based on zinc sulfide indicates a predominantly amorphous structure of templates and formed nanofilms with insignificant crystallization areas with different spatial orientations.

5. Conclusions

The chapter provides methods for modifying the surface of a solid and gives examples of modeling three modification processes. It is shown that mathematical modeling makes it possible to predict the structure of the modified surface and determine the parameters of technological processes of modification. To obtain more complete information on modeling methods, the reader can obtain additional information from the literature on modification methods [17–19] and modeling methods [20–24].

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