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ORIGINAL RESEARCH ARTICLE

Subnanophase coatings as new type low-dimensional nanomaterials: Ultra-high-vacuum synthesis, properties and application

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ABSTRACT

In this paper, a classification of low-dimensional nanomaterials is given, and new type of these nanomaterials — subnanophase coatings are proposed. Experimental results on the formation of a wetting layer of a transition metal on a silicon substrate by physical deposition in vacuum and results of this layer identification by the EELS method are given. Based on these results, a new approach to the formation of subnanophase coatings has been proposed by creation of an interface stresses structuring WL. The possible properties and application prospects of subnanophase coatings are considered.

Keywords: Low-dimensional Nanomaterials; Subnanophase Coatings; Wetting Layer; Ultrahigh-vacuum; Formation; Properties; Application

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1. Introduction

In the world there are many major scientific, educational and technological centers that are engaged in researches and various applications of nanotechnology and nanomaterials. In particular, there are a number of manufacturers of nanophase materials. The most famous among them is the company “Nanophase Technologies”, which produces nanodispersed powders “Nanogard” and “Nanotech” based on zinc and aluminum oxides, respectively[1].

Usually, nanophase materials are obtained by compacting bulk materials from nanodispersed particles with a diameter of 2 to 50 nm. As a result, after compacting, they consist of grains 4-30 nm in size. In their atomic structure, nanophase materials are neither amorphous, nor crystalline, nor even quasicrystalline. It is believed that they are in a low-dimensional-nanophase state. This production technology of nanophase materials is still relevant today.

Considering the main role of effects underlying their basis, low-dimensional nanomaterials can be classified as follows:

1) Low-dimensional heterocrystalline ones with the effect of intercrystalline proximity.

2) Low-dimensional heterophase amorphous ones with the effect of interphase proximity.

3) Low-dimensional ones with the quantum effect in their constituent particles.

4) Two-dimensional ones with the effect of interaction with the

substrate.

5) Two-dimensional ones with the effect of interaction with the vacuum.

6) Two-dimensional ones with a transboundary quantum size effect.

Besides, various types of low-dimensional nanomaterials are possible, including thin-film, dispersed and composite nanomaterials, which are combination of these types of nanomaterials.

Here, we will focus on subnanophase coatings (SNP) consisted of low-dimensional clusters with a decisive influence on these coatings of interaction effects with the substrate and vacuum. Due to the influence of the strained interface on their structure and properties, these coatings can have a set of unique properties that are absent in bulk coatings, as well as in massive nanophase materials.

It is assumed that SNP coatings will be used in areas of the nano industry where the use of massive (with a thickness of more than 1 nanometer) and high-stable coatings is not required. Namely, when the coating can be non-equilibrium and metastable and have a nanometer thickness.

The problem of creating SNP coatings is associated with the methods of their synthesis, as well as with the methods of structural-phase diagnosis of their state and diagnosis of their properties, both in the process of obtaining these coatings and at its completion. The combination of the synthesis and growth control of SNP coatings in an ultrahigh vacuum environment allows reducing the number of control cycles and, thus, more effectively finding nanomaterials with the required properties.

Ultra-high vacuum (UHV) is the most convenient and cleanest medium for controlling the atomic and electronic structure and various properties of coatings. UHV allows you to synthesize coatings from atomic or molecular beams[2] and use electron, ion, and photon beams to diagnose coatings[3]. In addition, UHV-vacuum provides the ability to control the surface state of the coatings during their synthesis and allows cyclically controlling the formation of ultrathin layers and their interfaces, creating the necessary composition and structure in them. In addition, UHV technology (UHVT) similar to nanotechnology (NT) is high-tech technology and use controlled manipulations with individual atoms and molecules.

In a vacuum, particle beams and fields can interact on a solid surface without interference. This property gives UHVT a unique advantage over NT in other environments. First of all, it is the controllability of the synthesis of coatings. Another important advantage of UHVT is the pure conditions for the synthesis and control of coatings. As for the lower level of practical application of UHVT due to the high cost, this is offset either by the high cost of the product (for example, in nanomedicine) or by the ability to produce a product in the form of a coating on large substrates (for example, in the field of solar energy, microelectronics and nanoelectronics).

Currently, methods and devices for the synthesis and control of coatings in vacuum have evolved significantly and reached a high level of perfection[4]. This allows, in the main, focusing not on creating these methods, but on their use. However, the specificity of SNP coatings, their non-equilibrium, subnanostructural state, requires more precise regulation and a wider range of growth parameters. For this, it is necessary to develop methods for producing directed atomic beams, which will have a higher density and simultaneously lower temperature or kinetic energy.

In addition, the structure-phase specificity of SNP coatings, which differs in their atomic density and interatomic bonding configuration from bulk phases, requires the further development of more adequate methods of structural-phase analysis directly during synthesis. Therefore, it is necessary to increase the sensitivity of these methods or adapt them to the subnanometric sample thickness and to work in real time. The solution of these problems will allow creating new types of nanomaterials in a subnanophase state.

The purpose of this work is to develop an approach to the self-organizing synthesis of subnanophase coatings using physical deposition of vapor phase in ultrahigh vacuum.

2. Creating subnanophase coatings in vacuum

For the synthesis of SNP coatings in vacuum, both new methods of obtaining atomic vapor beams with low thermal energy of vapor are needed. Also methods of electron spectroscopy, microscopy and probe measurements adapted to SNP coatings are needed. In addition, it is necessary to solve the following list of main tasks for obtaining SNP coatings:

(1) To develop design principles for their electronic and atomic structure.

(2) To develop the principles of management of their growth and self-organization by regulating the density and temperature of the atomic vapor stream, as well as the temperature of the substrate.

(3) To develop principles of subnanoscale diagnostics in real time of their structural-physical and other properties.

For this, it is necessary to conduct both theoretical studies (including computer simulation) and experimental studies.

Deposition from the vapor phase in vacuum at a low substrate temperature usually provides a non-equilibrium and, in particular, nanophase state of the coating[5]. However, to obtain a thinner coating in a sub-nanophase state, this is not enough. High kinetic energy of vapor and latent heat of phase transitions in coating lead to mixing at the interface and the formation of alloys or compounds and additionally cause cluster fusion into larger islands and, thus, coarsening of the grains and transition to the bulk phase[6].

The obvious way to solve this problem is to evaporate the material at a source with a low vapor temperature[6,7], as well as decreasing the diffusion and chemical interaction of the coating with the substrate using a sub- or single-molecular intermediate layer[8]. Also, it is necessary to modify the methods for monitoring the structural state of the coating and the interface layer thickness during the growth of coatings[7,9,10].

The possibility of realizing the self-organization of SNP coatings from the vapor phase or atomic beam was first shown by the example of metal growth on the surface of a single-crystal silicon substrate. Such a coating was first called by a surface multilayer phase[11,12], and then, a two-dimensional nanophase[13,14]. The first of these names reflected the view on the stabilizing role of the substrate, and the second on the two-dimensional nature of the SNP coating. Subsequently, the SNP coating got the short name “ν-phase”. In this name, the uncertainty and low dimension structure of the SNP coating and, accordingly, the difficulty of its identification from experimental data were reflected.

Indeed, the existing variety of experimental research methods (X-ray, electron, ion, probe microscopy and spectroscopy) is well developed for the study of single-crystal, amorphous and even quasicrystalline homogeneous structural state. But, in the case of low-dimensional, disordered and, in general, non-uniform coating, most of these methods do not allow identifying this coating and separating them from bulk homogeneous phases. As a result, the SNP coating is often interpreted as a mixture of some bulk phases.

Nevertheless, the method of electron spectroscopy of characteristic electron energy loss (EELS) allowed us to identify the integral structure of the ν-phase, namely the structure of its electron density and, indirectly, of its atomic density.

Indeed, the energy position of the loss peak in the EELS spectrum connected with the excitation of a volume plasmon gives information about the oscillation frequency of the plasma of valence electrons in the local region in which the electron loses its energy. And the oscillation frequency, in turn, gives information about the density of valence electrons and, indirectly, about the density of atoms that donate their electrons to a valence bond of one or another type.

For a solid, an approximation of solid balls is usually used. In this model, atoms are very tightly packed like solid balls. With this, the densest packing is realized in an ordered lattice — in a crystal. But, in the crystal, one can break the dense structure of the packing by means of subjecting this body to stretching, inserting vacancies and rotating interatomic bonds, forming clusters and intercluster (intergranular) defective interfaces, as well as rotating the clusters themselves relative to each other.

Something similar seems to be realized in the ν-phase under the action of tensile stresses caused by the substrate and under the action of its conjugation with this phase. It leads to the fact that the atoms in the phase at the interface are not closely connected to each other and their packaging is not compact. Due to this, in the EELS spectrum of the ν-phase, shifted bulk plasma loss (BPL) peak is formed. But if the ν-phase has an inhomogeneous structure, there will form a whole group of peaks. Each peak in this group corresponds to a local collective interaction with electrons of the same type of configuration of interatomic bonds and with the same electron density. The adaptation of the atomic and electron density in the phase to the density of the substrate, as well as the non-uniform nature of this density, cause the BPL peak to shift, expand, and decrease in intensity. Thus, it is possible to distinguish the ν-phase from the bulk coating and determine the range of thickness on which the ν-phase is formed by use the shift, the degree of expansion of the BPL peak, and a decrease in its intensity.

3. Experimental observation of metal SNP on silicon

A series of experiments was carried out to study the initial stage of growth of transition metals on silicon using the methods of AES, LEED, EELS, AFM, as well as measurements of conductivity, optical reflection and magnetization. Namely EELS data showed the formation of an SNP coating. Based on EELS data, we previously called these coatings by the ν-phase, and then we called them by the wetting layer (WL). The latter name reflects the adaptation of the atomic density of the SNP coating to the atomic density of the substrate.

Figure 1 and **2** present the EELS spectra families, showing changes of electron density in Fe and Cr layers and at the metal-substrate interface, during growth of Fe and Cr on Si (001) and Si (111), respectively. In **Figure 1a** and **1b**, electron density changes are shown in the case of mixing Fe with the Si substrate and in the case of the growth of pure Fe at elevated and lowered temperatures of metal's vapor, respectively. **Figure 1c** shows the EELS spectra of the Fe–Si phases obtained after annealing the samples of **Figure 1b**.

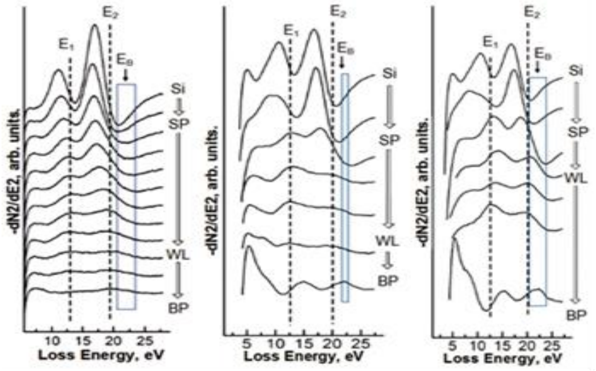

Figure 1. EELS Fe on Si (001) in the case of Fe growth at elevated **(a)** and lowered **(b)** vapor temperature, respectively; **(c)** EELS of Fe–Si phases on Si (001) after moderate annealing of the Fe coating in Figure (b)[15].

In each case, we see transitions of: 1) a pure silicon surface (Si) into the surface phase (SP); 2) SP into the wetting layer (WL); and 3) WL of maximum thickness into the bulk phase (BP) of the metal or metal-silicon compound (silicide). These transitions show a change in the position of the peaks of the surface (E_1) and bulk (E_2) losses. The transition into SP ends when the surface loss shift ceases. And the transition into WL is completed when the energy position of the peak of bulk losses stabilizes without reaching the position of the peak of bulk losses in BP (EB).

Figure 1a and **1b** also show a non-monotonic increase in the energy of the peak of bulk plasmon losses, corresponding to transitions from SP to WL and from WL to BP. The formation of WL in non-equilibrium conditions is a general phenomenon of the formation of the metal/silicon interface. With this, in the case of solid-phase epitaxy, even ordering WL occurs, as is shown in **Figure 2.** And that evokes compacting WL. Therefore atomic density of WL becomes closer to the density of bulk silicide.

However, as can be seen from **Figure 1b** and **Figure 1c**, the amplitude of the peak of volume plasmon losses at the stage of WL formation is much smaller, and the peak width is greater than in BP. This can be explained only by the formation of SNP coverage. Moreover, in the case of SNP coverage of pure Fe on Si (001) (**Figure 1b**), these differences are more pronounced, since this coating is in a more non-equilibrium state and has a more pronounced gradient of the atomic density.

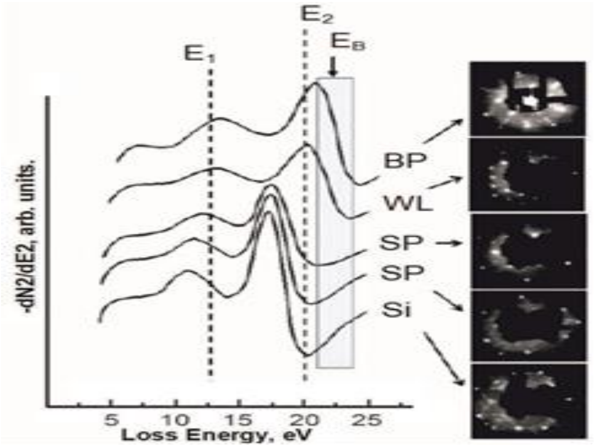

Figure 2. EELS and LEED of Cr-Si phases on Si (111) obtained by the deposition of Cr with an elevated vapor temperature and annealing[15].

Indirect evidence of the formation of the Fe SNP on Si (001) at the WL formation stage was obtained on the basis of AES and AFM data. At this stage, for samples in **Figure 1c**, the stability of the coating in composition decreased according to AES, and the height of the surface relief was significantly less than at the stage of BP formation[14].

At the same time, on the AFM images, the WL relief was not seen due to the diameter of the AFM needle near 1 nm. Invisible relief at this thickness can be explained only by a subnanophase structure of the coating. Additional confirmation of such structure of the metal WLs is also provided by data of on their electrical, optical and magnetic properties[16]. These data show a resistive type of conductivity (independence of resistance on the temperature) of Cr WL, a high UV absorption (low UV reflection) in WL of Fe on Si (001). Moreover, the dependence of polarized light reflection on the magnitude of the magnetic field perpendicular to Fe WL corresponds to the superparamagnetism of this WL. And as it is known, resistive type of conductivity, high UV absorption and superparamagnetism are most pronounced in coatings and films of metals with a nanophase or finely dispersed structure.

4. Properties and application of SNP coatings

Cluster or subnanoscale structure, uneven along the plane and subnanoscale gradient of structural properties in the transverse direction, determine the specific properties of coatings. Examples of specific properties of SNP coatings can also be increased wetting ability, increased surface area, increased surface curvature and latent energy of stresses. Due to the reduced atomic density, the presence of clusters, near amorphous type structure, a large number of vacancies, they will also have their modified electronic structure and modified optical, magnetic and electrical properties. And, as a result, there will be coatings with high UV absorption, magnetic-soft coatings and coatings with resistive conductivity type[16]. In addition, in SNP coatings, by analogy with multilayer coatings, a chemical potential gradient is possible and, as a consequence, the presence of an embedded electric field.

Due to the low thickness of SNP coatings and due to the vacuum environment during physical vapor deposition, the scope of applications of SNP coatings will be limited to the element base of electronics, optoelectronics, and telecommunications. In addition, they can be used for various specialized applications where there is no mechanical damage and the influence of the corrosive environment and the atmosphere (for example, in biosensors).

It is assumed that the main application of SNP coatings will focus in the range of nanoelectronics, nanospintronics, nanooptics, nanoplasmonics, and analytical instrumentation for ecology, biology and medicine. Another application of SNP is the use of a tension energy hidden in them for solid-phase reactions, crystallization and other processes of formation of ultra-thin coatings.

5. Conclusion

The subnanophase coatings as a class of new materials have been proposed based on the classification of low-dimensional nanomaterials. Synthesize these coatings using physical deposition from low-temperature vapor with control them in ultrahigh vacuum, and use the EELS method to identify their subnanophase structure have been proposed. The experimental observations of subnanophase coatings in the form of a metal wetting layer on silicon substrate and also the indirect evidences of their subnanophase structure on data of AFM, optical, electrical and magnetic measurements have been presented. The properties and possible applications of subnanophase coatings are considered.

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