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From Atomic-scale Interfaces - To New Nanomaterials
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ABSTRACT

The problem of the synthesis of new type nanomaterials in the form of nanocoatings with subnanometric heterogeneity has been formulated. It has been presented an analysis of influences of physical vapor deposition in ultrahigh vacuum on the process of intermixing a film with a substrate, including the results, which has been obtained under the formation of transition metal – silicon interface. The generalization of the obtained experimental results allowed to develop an approach to the development of new nanocoatings with low-dimensional heterogeneity. The principles of constructing such low-dimensional nanocoatings, their properties and their possible applications are considered.

Keywords: Low-dimensional Nanocoating; Structure; Forming; Properties; Application

1. Introduction

In the world there are many large scientific-educational and technical centers that are engaged in research and various applications of nanotechnology. In addition, there are a number of manufacturers of nanophase materials. The most famous among them is the company "Nanophase Technologies", which produces nanodispersed powders based on zinc oxide "NanoGard" and aluminum oxide "NanoTech"[1].

Usually, nanophase materials that consist of nanodispersed particles are produced from particles or atomic clusters with a diameter of 2 to 50 nm by packing them in bulk materials with a grain size of 4 to 30 nm. In terms of their atomic structure, these materials are neither amorphous nor crystalline, nor even quasi-crystalline. They are in some intermediate low-dimensional state - the so-called nanophase state. The technology for the production of nanophase materials, which use compacting nanodispersed powders, is relevant to the present day.

Nevertheless, nanophase materials in the form of nanocoatings are needed to create promising systems of nanoindustry in electronics, optoelectronics, telecommunication, healthcare, biotechnology, metallurgy, metalworking, power engineering, machine and instrument engineering, construction and industrial materials, chemistry and petrochemistry, as well as in analytical instrumentation, in nanoelectronics, in nanophotovoltaics, in nanomedicine and in a number of other devices.

These nanocoatings can have a set of unique properties that are absent in bulk or massive nanocoatings. In particular, they can be realized in the low-dimensional nanometrical (LDNM) state of matter with characteristic sizes of inhomogeneities from atomic (0.1 nm) to 1 nm. Reducing the size of the inhomogeneities to such limits will lead to a significant increase in the low-dimensional effects.

The low-dimensional nature of the electronic and atomic structure and properties of LDNM coatings will be supplied due to the heterogeneous or heterophase (with low-dimensional inclusions) structure of nanocoatings, the close-acting boundary effects, surface effects, and also due to of quantum-size effect (QSE).

The problem of creating LDNM coatings is associated with the methods of synthesis of these coatings and also with the methods of diagnostics of their structural-phase state and properties, both in the process of obtaining these nanocoatings and at its completion. Combining the synthesis and control of LDNM coatings in ultrahigh vacuum environment allows targetly and effectively search for new nanocoatings by reducing the cycles of controlling their structure and properties. Ultrahigh vacuum (UHV) is the most convenient medium for controlling the atomic and electronic
structure and various properties of coatings. UHV allows to synthesize coatings from atomic beams (molecular-beam growth)\textsuperscript{[2]} and to use focused electron, ion and photon beams for the diagnostics of coatings \textsuperscript{[3]}. Therefore, combining the synthesis and control of coatings in a vacuum is very important. In addition, UHV vacuum provides the ability to control the surface state of coatings during their synthesis and makes it possible to do this cyclically to control the formation of hyperfine layers and their interfaces, creating the necessary composition and structure in them.

At present, methods and apparatus for the synthesis and control of coatings in vacuum have developed significantly and reached a high level of perfection\textsuperscript{[4]}. This allows, basically, focusing not on the creation of these methods, but on their use.

Nevertheless, the specificity of LDNM coatings, their nonequilibrium, subnanostructured state, requires more precise regulation of growth parameters and over a wider range of their values than modern methods allow. In particular, it is necessary to develop methods for producing directed atomic beams, which will possess not only a low but also a high density and, simultaneously, not only a high but also a low temperature or kinetic energy.

In addition, the structural-phase specificity of LDNM coatings, which differ on their atomic density and atomic configuration from bulk phases, requires the further development of more adequate methods for monitoring their structural-phase state during the synthesis, including electron spectroscopy and diffraction.

Therefore, it is necessary to improve these methods and adapt them to growth control at the subnanometric spatial scale and real time. Solving all these problems will allow creating new types of nanocoatings in the form of a low-dimensional single-layered or multilayer LDNM coating in the nanophase state.

\textbf{2. Formation, structure, properties and applications of low-dimensional nanocoatings}

\textbf{2.1 Vacuum low-thermal vapor deposition}

In the methods of thermal vapor-phase physical deposition in vacuum, a decrease in the thickness of films and a decrease in the width of the their interface with a substrate (due to decrease of mixing with the substrate) is achieved in the vast majority of cases by a decrease in substrate temperature \textsuperscript{[5]}. However, for the case of LDNM coatings, this is not enough, because of the high vapor kinetic energy and latent heat of the phase transitions on the surface of the film, which leads to mixing on interface and formation of compounds\textsuperscript{[6]}.

New methods that have solved this problem are evaporation with a lowered vapor temperature during the growth of LDNM coatings from this vapor\textsuperscript{[6,7]}, as well as modification of the interaction of the film with the substrate by a monomolecular intermediate layer (see, for example,\textsuperscript{[8]}). In addition, methods have been improved to control the growth of LDNM coatings (see, for example,\textsuperscript{[7,9,10]}).

\textbf{2.2 The approach to the formation of low-dimensional nanocoatings in a vacuum}

The specificity of this approach is connected with at the mutual compatibility of two technologies: ultrahigh-vacuum technology (UHVT) and nanotechnology (NT). Both technologies relate to the advanced field of applied science and technology and use controlled manipulation of individual particles (including atoms and molecules).

The main goal of this approach is to search for and synthesize new low-dimensional nanocoatings using thermal vapor-phase physical deposition in an ultrahigh vacuum. The nanocoatings are expected to be used in those areas of the nanotechnology, where the use of massive (with a thickness of more than 1 nanometer) coatings is not required. Namely, where the coating consists of tightly packed nanoparticles in a disordered or ordered composite structure and can be made in the form of a nonequilibrium and metastable single-layered or multilayered film of nanometric thickness.

To accomplish this goal, it is necessary to modify the methods for obtaining atomic beams in vacuum and to further develop methods of electron spectroscopy, microscopy, and probe measurements.

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

The approach to low-temperature vapor-phase synthesis of nanocoatings is as follows[11]:

1. Development of the principles for designing the electronic and atomic structure of the LDNM coating based on the modification of interface of the nanocoating with the substrate and of interfaces between the particles in the nanocoating.

2. Development of principles for the use of hidden energy of LDNM coating as an additional spontaneous source of heating in solid-phase reactions and crystallization of nanocoatings.

3. Development of principles for using LDNM coating for joining nanoparticles and substrates in compositions and heterostructures in solid-phase vacuum sintering and soldering.

4. Development of the principles of controlled growth of LDNM coatings from the beam with high density and low temperature.

5. Development of the principles of atomic and nanoscale control of structural-physical and electrophysical properties of LDNM coatings.

To implement this approach, it is necessary to conduct both theoretical studies (including computer modeling) and experimental studies.

It is assumed that the main application of LDNM coatings will be concentrated on electronics and communications, as well as on nanoelectronics, nanospintronics, nanooptics, nanoplasmonics, analytical instrumentation in ecology, biology and medicine.

In the near future, it is possible to predict the creation of new LDNM coatings with record conductivity, magnetization, coercitivity, reflection coefficient, and refraction index and excitation efficiency of surface plasmons. These materials will allow creating new instruments and environmentally friendly technologies for converting, processing, transferring and storing information and energy.

2.3 Low-dimensional nanometric thickness coatings

As already mentioned, the low-dimensional nature of the electronic and atomic structure and properties of LDNM coatings is formed due to the heterogeneous or heterophase (with inclusions of low-dimensional particles) structure of nanocoatings, due to the boundary effects of close-acting of substrate and vacuum and also due to QSE.

This approach to the structure of LDNM coatings allows us to highlight principles of organization of the LDNM coatings structure, namely their types and character of influence on their properties:

1) Heterogeneous LDNM coatings with intercrystalline proximity effect.

2) Heterophasic LDNM coatings with interfacial proximity effect.

3) LDNM coatings with effects of interfaces with substrate and vacuum.

4) LDNM coatings with quantum size effect due to cross-border interaction.

5) LDNM coatings with quantum size effect, which has caused by the limitation of the internal space of particles.

Depending on the combination of these five principles of organization, different types of LDNM coatings are possible, as well as various thin-film, dispersed and composite nanomaterials based on them.

In the principle, it is possible to realize the self-organized synthesis of this kind coating from the vapor phase or the atomic beam. For example, the synthesis of metal LDNM coatings on the surface of a single-crystal silicon substrate.

Previously, we called LDNM coating of metal on silicon by multilayer non-bulk (or surface) phase[12], thin-film or 2D nanophase[13,14]. Then we gave to them the general name “ν-phases” due to their undetermined structure. Each of these titles reflects only single look at the structure of LDNM coatings. This is due to the complicated structure of the LDNM coatings and difficulty of its structure identification from experimental data.

Indeed, the existing diversity of experimental methods of investigation (X-ray, electron, ion, probe microscopies and spectroscopies) are well developed for studying a single-crystalline or amorphous state of a homogeneous massive or thin (ultrathin) film. But, in the
case of an inhomogeneous, nanophase or low-dimensional disordered or partially ordered structure of phase, most of these methods give little information about its structure. The method of electron spectroscopy of the characteristic loss of electron energy (EELS) at a low primary beam energy has made it possible to reveal the integral structure of the v-phase.

The energy position of the peak of plasmon losses in the EELS spectrum gives information on the frequency of the plasma oscillations of the valence electrons. And it, in turn, gives information on the density of atoms with a determined amount of valence electrons or the density of valence electrons of these atoms. For the solid, a approximation of hard balls works usually, in which atoms are packed very tightly one with other like hard balls. But, in general, it is possible to violate the strictly ordered and densest structure of atomic packing. It can be made by inserting vacancies, by rotating the bonds, inserting the intercluster interfaces and by rotating the clusters themselves relative to each other. In general, this leads to the fact that the atoms are not closely connected to each other and, in general, their packing will not be tight[10].

In the case of such packing faults, for example, in the case of the v-phase, not one peak of bulk plasmon losses (BPL) is formed in the EELS spectrum, but a whole group of peaks. Each peak in this group corresponds to a local collective interaction between electrons of one type of configuration of interatomic bonds with the same electron density. This leads to the fact that the BPL-peak, shifts, expands and decreases in intensity. Thus, by the shift, the degree of expansion of the BPL-peak and the decrease in its intensity, it is possible to identify the type of nanocoating (for example, to distinguish between a bulk nanocoating and a v-phase) and the thickness range at which it is formed.

Indeed, a series of experiments on studying the initial stage of growth of transition metals on silicon by EELS spectroscopy show the formation of the LDNM coatings, which are, in a sense, a nanophase wetting layers.

Figures 1 and 2 present families of EELS spectra showing changes in the formation of interfaces of Fe with Si (001) and Cr with Si (111), respectively. Figure 1a illustrates the initial stages of Fe growth on silicon with Fe-Si intermixing. Figure 1b illustrates the initial stages of growth of pure Fe. And Figure 1c illustrates the growth of Fe-Si phases after annealing films on Figure 1b. In each case, we see transitions: 1) from a substrate of pure silicon (Si) to the surface phase (SP); 2) from it to the wetting layer (WL) and 3) from WL of maximum thickness to the bulk phase (BP) of the metal or the metal-silicon compound (silicide). These transitions show position changes of the peak of surface (E1) and bulk (E2) losses and position (EB) of the peak of bulk losses in BPs.

![Example of EELS spectra showing changes in the formation of interfaces of Fe with Si (001) and Cr with Si (111), respectively.](image)

Figure 1; (a) and (b) – EELS of Fe on Si(001) at the initial stages of Fe growth with (a) and without (b) Fe-Si intermixing; (c) - the growth of Fe-Si phases on Si(001) after middle temperature (250 °C) annealing of pure Fe films[15].

It can be seen from Figures 1, that at a certain thickness, a nonmonotonic (more sharp) increase in the energy of the peak of the volume plasmon losses is observed. This increase indicates the transition from WL (v-phase) to BP of Fe or to BP of Fe silicide. And this, in turn, proves that the formation of a WL (v-phase) under non-equilibrium conditions (deposition at room temperature) in the silicon-metal-substrate system is the general pattern of the formation of the metal-silicon interface.

As shown in Figure 2, under the solid-phase epitaxy of WL, after formation of surface phases, even its ordering occurs. At the same time, the atomic density of the WL turns out to be very close to the density of the bulk silicide, unlike the atomic densities of the preceding surface phases, which are close to the density of the silicon substrate.
2.4 Properties and applications of low-dimensional nanocoatings

Due to the low thickness of the LDNM-coatings and the vacuum environment for vapor-phase physical deposition, the sphere of application of LDNM-coatings is limited by the element base of electronics, optoelectronics and telecommunications. In addition, they can be used for various specialized applications where there are no mechanical damages, the influence of the corrosive environment and the atmosphere (mainly sensors).

At the same time, a cluster or atomic/nanoscale structure, non-uniform along the plane and an atomic/nanoscale gradient of structure properties in the transverse direction, determine specific properties and limits the variety of applications of the LDNM-coatings.

The examples of them specific properties are primarily increased wetting ability, increased surface area, increased curvature of the surface. Due to the reduced density, the presence of clusters, amorphousness, large quantity of vacancies, this is also a modified electronic structure. And, as a result, this is modified optical (nanocoatings with high IR reflection and UV absorption), magnetic (magnetic-soft and magnetic-hard nanocoatings) and electrical (nanocoatings with high conductivity) properties. In addition, in LDNM-coatings, by analogy with multilayer coatings, the chemical potential gradient is possible and, as a consequence, the presence of the built-in electric field.

3. Conclusion

The low-dimensional nanocoatings (with the thickness in nanometer range), which are produced by means of thermal vapor-phase deposition technologies, have been analyzed. In particular, the results of the investigation of low-dimensional nanometric wetting layers forming at the interface between the metal film and the monocrystal silicon substrate have been presented. A new type of nanophase coatings is proposed, that is low-dimensional nanometric coatings. These coatings can be in the nanophase state, can have low-dimensional heterogeneity and can provide a number of new properties. The designing principles of the structure of proposed nanocoatings and a new approach to their building are considered. It has been proposed possible applications and properties of low-dimensional nanometric coatings.

References

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