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Optical properties of silver nanoparticles based on their structural defects

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The relation between the defects in island silver films produced by thermal spraying and their optical properties has been studied. The effect of defects in nanoparticles on the photo effect has been studied. Radiation with a wavelength of 355 nm (quantum energy 3.5 eV) causes a single-photon photo effect, while the work function of bulk silver is not lower than 4.2 eV. A hypothesis was put forward about the relation between defects in nanoparticles and their absorption spectra. In the process of deposition an absorption peak appears on the extinction spectra of a silver island film at a wavelength of 370 nm, which disappears within several tens of minutes after the end of deposition. It was also shown, that the defects in islands can be created artificially by irradiating them with ultraviolet light, that leads to an increase in the rate of self-diffusion in these islands upon heating.

Key words: nanoparticles, defects, diffusion, extinction spectra.

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Introduction

Silver nanoparticles play a big role in industry — for example, in catalysis [1], they are used in medicine due to their antibacterial properties [2–4], in other fields of technology, have been of interest for many years for fundamental science. From both applied and scientific points of view, it is interesting how and in connection with what such characteristics and parameters of nanoparticles as morphology, work function, interaction with the substrate, and others can change.

Metal nanoparticles often have the properties, which have no analogues in bulk samples. This includes, first of all, the presence of localized surface plasmon resonance in nanoparticles. These properties also include the features of the growth of island films in the process of thermal deposition, and the effect of the temperature much lower, than the melting point on the islands shape and properties [5]. The electronic properties of island films, such as photoelectron emission, also differ from the electronic properties of bulk samples [6].

Of course, most of these differences, in particular, the presence of localized plasmon resonance, are explained by the size of the islands in the island film. However, the reason for other unique properties of nanoparticles lies in the features of their formation and growth, for example, during thermal spraying. An important role in the growth of islands on a substrate is played by diffusion over the surface of this substrate, as well as by self-diffusion, i.e., diffusion of metal atoms in islands themselves, especially diffusion on their surface [7]. The diffusion rate of metal atoms in nanoparticles significantly exceeds the diffusion rate in bulk samples. Some differences are determined precisely by this fact. In its turn the diffusion rate is largely determined by the presence of certain defects in the volume or on the surface of nanoparticles [7,8]. Defects in nanoparticles, the influence of the surface, grain boundaries, substrate, one way or another manifests itself in the electronic structure of nanoparticles [9], which, in their turn, manifests itself in their optical properties.

The purpose of this study is to establish the relation between defects in nanostructures (silver island films), i.e. formed during the growth of films, as well as defects arising under the action of light, with optical phenomena inherent in these films.

Experiment

Silver films were created in a PVD 75 (Kurt Lesker) vacuum unit with cryogenic oil-free pumping at a pressure not exceeding $3 \cdot 10^{-7}$ Torr. Thermally evaporated silver was deposited on ground sapphire or polished fused quartz substrates. Prior being placed into the chamber, the substrates were cleaned in an ultrasonic bath, first in pure ethanol and then in distilled water. During deposition the substrates were at room temperature. The deposition rate, as well as the equivalent film thickness, were controlled by a quartz microbalance. The deposition rate was $0.01-0.06$ nm/s. The effective thickness of the films ranged from three to twelve nanometers. The purity of the deposited metals was 99.99%.

The experiments on the photo effect were carried out in a self-made vacuum chamber, described in [6], at a vacuum no worse than $1 \cdot 10^{-5}$ Torr Radiation from a Nd:YAG laser was directed into the chamber through a fused quartz window, generating pulses of duration 10 ns with a repetition rate of 1 to 10 Hz, or single pulses. The wavelengths of the first, second and third harmonics are 1064, 532 and 355 nm, respectively The maximum pulse energy was 200 mJ and could be reduced using neutral filters. This laser was used, for example, in the study of photoelectron emission from island films. To influence the island films with near ultraviolet radiation in the range of 4.0–3.5 eV, a mercury lamp DRSH-100 and special filters were used to separate the ultraviolet part of the spectrum [10]. The light power density in the irradiated area could vary within the range of 20–200 mW/cm^2. The decrease in power density from 200 mW/cm^2 was achieved by reducing the beam focusing. In all cases a 0.5 cm^2 film section was irradiated, that was achieved using a diaphragm installed directly in front of the film. The films were annealed in the same chamber at a temperature of 180–220°C for 20–30 min.

The extinction spectra in the course of deposition in a PVD75 chamber and immediately after deposition were recorded with a Hamamatsu spectrophotometer coupled to a vacuum chamber according to the scheme described in [5].

The morphology of the samples was studied using a Merlin scanning electron microscope (Carl Zeiss, Germany). A field emission transmission electron microscope (FE-TEM) Libra200 (CLCarl Zeiss, Germany) was used to study the structure of islands and obtain higher resolution images [11]. XPS spectra were obtained on X-ray photoelectron spectrometer ESCALAB 250Xi.

The extinction spectra after the removal from the chamber PVD75 or other effects on the films were measured on the spectrophotometer SF-56 (LOMO, Russia) or on spectrophotometer UV-3600 (Shimadzu, Japan).

Results

The electron diffraction patterns shown in the Fig. 1 indicate, that silver island films obtained by thermal deposition have a large number of defects.

The wide rings of the electron diffraction pattern in the Fig. 1 correspond to an amorphous substance. Following the annealing (Fig. 1, *d*) the rings become thinner and bright spots appear, which indicates an increased degree of crystallization.

In [5] it is shown, how in the process of film deposition, as its thickness (islands size) increases, the absorption of light by these islands, caused by localized surface plasmon resonance, increases. At the same time, a narrow peak appears and grows in the region of the wavelength of 360–370 nm (3.4–3.3 eV). After the completion of the deposition process, this peak begins to decrease rather quickly and disappears almost completely after an hour (Fig. 2).

A small heel remains at this wavelength (inset in Fig. 2). As an explanation for this peak, it was suggested in [5], that its appearance is connected with the formation of very small (2–3 nm in diameter) spherical nanoparticles, which disappear with time due to decay into atoms and diffusion over the substrate surface. However, this assumption is opposed by the fact, that at the very beginning of the nucleation of silver clusters on sapphire or fused quartz substrates, the plasmon resonance is not observed during the formation of ultrathin films at wavelengths shorter than 400 nm (Fig. 3). Besides, a small peak at a wavelength of 350–360 nm was also observed on copper island films, the plasmon resonance of which is at a wavelength of 600–650 nm (Fig. 4). A similar peak is also observed on island films of gold. The difference with silver films lies in the much slower changes in the gold and copper films: once the deposition is completed, the spectra almost do not change. Only after heating at 200°C for 30 min, the peak at a wavelength of 355 nm sharply decreases.

Another explanation seems more probable: this peak owes its presence to the absorption of light by island defects formed during deposition. In the first few minutes after the deposition, silver atoms move over the island surface, tending to occupy a more favorable energy position, the number of defects decreases, and the peak also decreases, but does not disappear completely.

Since defects formed during the growth of an island film can contribute to its electronic structure, this can manifest itself in the electronic-optical properties of such a film. An example can be the dependence of the magnitude of the photoelectron emission pulse on the energy of the laser pulse, that excites this emission [6]. In this work, the dependence of the photoemission pulse on the laser pulse energy was measured for three wavelengths: 355, 532 and 1064 nm. It is known [12], that for the two-photon photoelectric effect this dependence has a parabolic character, that was observed [6], for example, at a wavelength of 532 nm. The same character of the dependence was also observed for a massive silver sample upon excitation by light with a wavelength of 355 nm. However, for an island film at this wavelength the dependence turned out to be close to linear This indicates, that in this case a single-photon photo effect is observed (curve *2* in Fig. 5).

The photoelectronic signal for an island film is noticeably smaller, than for a bulk sample. This happens, as in the absorption spectrum of the island film the wavelength 355 nm is at a minimum. (At a wavelength of 532 nm, corresponding to the absorption maximum, the situation is reversed.) Unfortunately, a stable, well-reproducible dependence was obtained only for an unannealed film. Measurements on annealed film are difficult due to the very strong substrate (sapphire) charge. The resistance of such a film is several orders of magnitude higher, than that of an unannealed film.

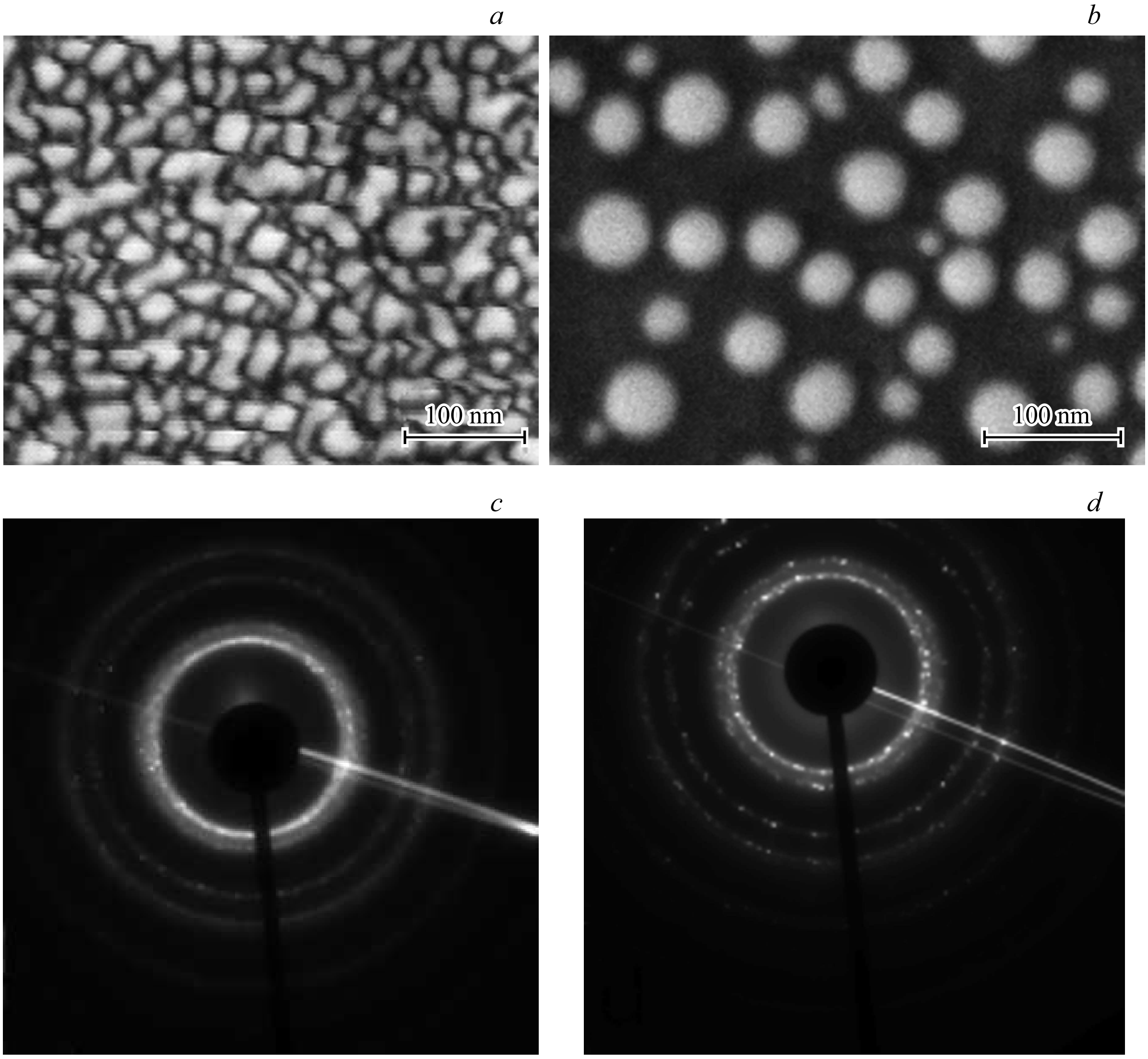

Figure 1. Microphotographs (a, b) obtained in a scanning electron microscope and electron diffraction patterns (c, d) of unannealed and annealed silver films with the thickness about 6 nm thick: a), b) - - films on sapphire. c), d) — silver films are deposited onto a carbon film.

The energy of a light quantum in a laser pulse is 3.5 eV, while the red photoemission edge of silver is equal to or exceeds 4.2 eV [13], i.e., obviously, the work function of the deposited film nanoparticles (not annealed) is significantly reduced. A significant change in the work function (both a decrease and an increase) is caused by a change in the surface state. It is possible, that such a change was the formation of a large number of defects on the nanoparticle surface.

It was noticed that the XPS spectra of deep levels of silver (Ag3d) for annealed and unannealed films differ noticeably (Fig. 6). The peaks in the spectrum of the annealed film are shifted towards lower bond energies by about 0.7 eV.

Along with the defects arisen in the course of film deposition, the defects can be formed as a result of the radiation effect on the film. The study [14] mentions the process of formation of the defects in solids during irradiation, when a large number of pores appear in a large volume of the material. In [10] the effect of irradiating a silver island film with near ultraviolet radiation on the result of subsequent annealing is demonstrated. While there is no noticeable difference in the extinction spectra of the irradiated and non-irradiated sections of the film immediately after irradiation, this difference appears after annealing at 200°C. It can be assumed, that light with a quantum energy of about 3.5–4.0 eV increases the number of defects in the unannealed island film, which, in its turn, affect the self-diffusion rate during annealing.

Discussion of results

All of the above results in the conclusion, that, firstly, an island film obtained by thermal spraying has a large number

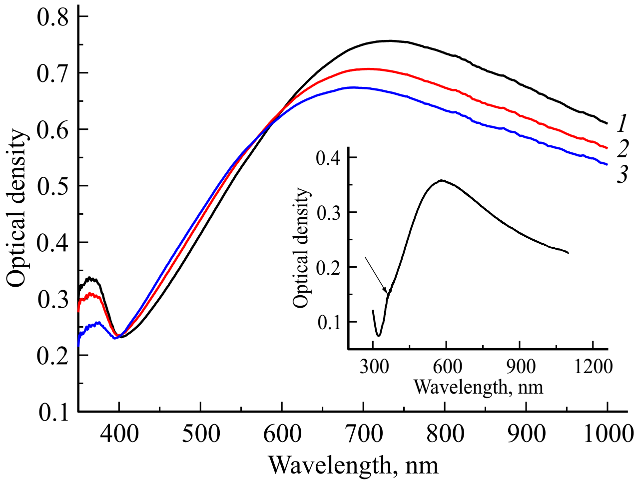

Figure 2. Time change of the extinction spectra of a 11 nm granular silver film deposited on the surface of a sapphire substrate at room temperature at a rate of 0.06 nm/s. The spectrum *1* was measured immediately after the deposition, the spectra *2* and *3* were measured after 15 and 30 min, respectively. The insert shows the extinction spectrum of a silver film taken on the spectrophotometer SF-56 three days after the film was deposited. The arrow indicates the heel region.

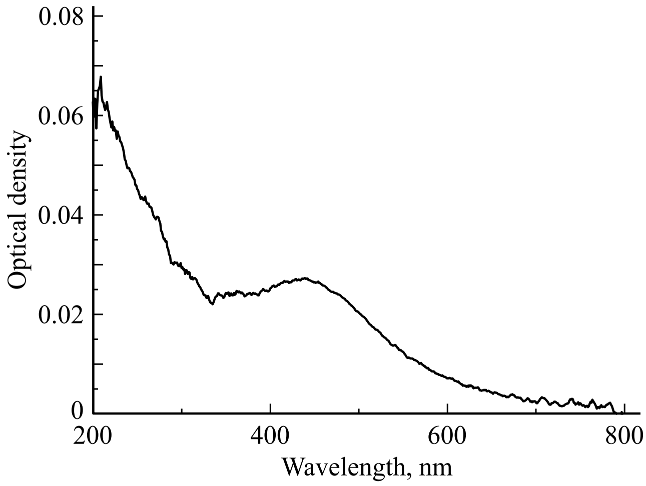

Figure 3. Extinction spectrum of an ultrathin silver film (the spectrum of the fused silica substrate is excluded).

of structural defects and, secondly, these defects considerably determine the optical and some other properties of the film.

The defects, which are formed in nanoparticles during the growth of an island film in the course of thermal deposition do not require energy costs. In fact, randomly falling atoms do not always occupy places in the crystal nodes. Diffusion can lead to the formation of a crystal, which begins immediately after the metal atom hits the substrate or an already existing island. As a rule, a polycrystal is formed at room temperature. The diffusion process goes on intensively for the first time after the completion of deposition [5].

Evidently, when metal atoms are deposited on the substrate from the vapor phase, various types of defects arise: it can be assumed, that vacancies appear most of all, since „fallen“ atoms often do not have time to occupy the position in the nodes corresponding to the minimum free energy. The vacancies play a major role in the processes of changing places, which occur in the crystal [7]. The vacancies are an equilibrium defect, when their concentration is equal to the thermodynamic equilibrium. The vacancies concentration, which appears during the deposition process, apparently, is many times higher, than the equilibrium one. The density of stocks — the places, where a vacancy can disappear, is large, since the size of the islands is small and the role of their surface is large, and the surface, as is known, is the first and main stock. Therefore, the rate of disappearance

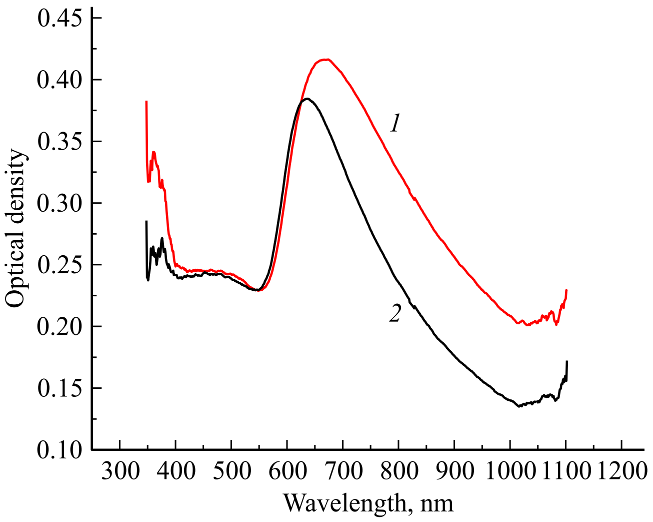

Figure 4. Extinction spectrum of a copper island film: *1* — after deposition, *2* — after annealing at 200°C.

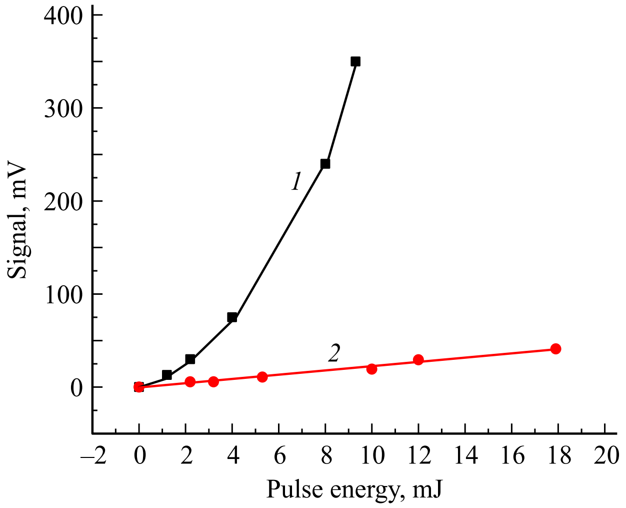

Figure 5. Dependence of the photoelectron emission on the energy of the laser pulse: *1* — massive sample. *2* — island film.

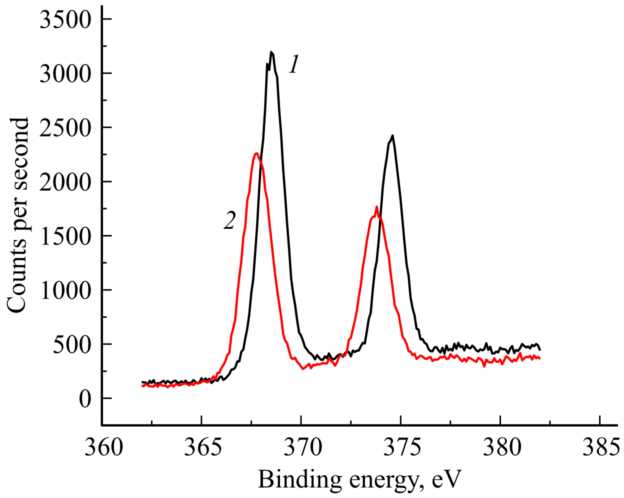

Figure 6. Peaks of Ag 3d silver in the XPS spectrum of an island silver film: *1* — film after deposition, *2* — annealed film.

of vacancies is also high. Interstitial atoms also appear, including atoms and molecules of residual gases „walled up“ in the crystal lattice of the metal. Since the distortion of the crystal lattice around an interstitial atom is greater, than near a vacancy, the activation energy of its migration is less, than the activation energy of migration of a vacancy, so interstitial atoms are more mobile, than vacancies. However, since there are much more vacancies in the metal, than there are interstitial atoms, self-diffusion occurs predominantly by the vacancy mechanism.

The appearance of a peak at a wavelength of 360−370 nm can be associated with an increase in the local density of states. One can imagine a nanoparticle (island) as a quantum well. An experimental and theoretical study of the photoemission of thin films considered as quantum wells is the subject of the review [15], where the appearance of peaks in the dependence of photoemission on the bond energy, i.e. density of states, when a thin film of another metal is deposited on the surface of a metal sample, is considered. In our case, the role of atoms of this other metal can be played by numerous defects formed during deposition on the island surface. The disappearance of the peak at a wavelength of 360−370 nm (Fig. 2) in a few tens of minutes, apparently, is determined, firstly, by a very large number of defects in the nanoparticles of the silver island film, which appeared during the deposition process (presumably vacancies), and, secondly, the relatively high rate of diffusion of silver atoms. Similar processes occur in copper and gold films, although much more slowly, than in silver films. The question may arise why the absorption maximum at 360−370 nm is approximately at the same wavelengths for silver, copper and gold. However, this is quite possible, given that these metals have a similar electronic structure, in particular, the values of the work function are close.

Of course, along with the vacancies and interstitial atoms other defects arise, which affect the rate of diffusion of metal atoms in islands. For example, such non-equilibrium defects as dislocations, grain boundaries. Diffusion processes along dislocations can proceed at a rate, which is several orders of magnitude higher than the rate of bulk diffusion [7].

The single-photon photo effect described in [6] is possible, if the work function of a silver nanoparticle is significantly les,s than the work function of a bulk sample. The defects in the bulk of a nanoparticle cannot change the position of the Fermi level. However, the work function is extremely sensitive to the surface state [16,17]. Adsorption on the surface of a metal of various atoms — both residual gases and other metals (for example, cesium atoms) can either increase or decrease the work function by several electron volts. This is due to the dipole moment of the adsorbed atom. The influence on the work function of structural defects of the metal surface during self-adsorption (adsorption of atoms of the same metal) is described in [18]. Surface inhomogeneity (spots on the cathode surface [16]) can significantly affect the work function. In our case the size of grains (and, consequently, of the faces on the surface) in a polycrystalline nanoparticle is several times smaller, than in a monocrystal [19]. This leads to a complex configuration of the electric field near its surface, that in its turn can lead to a decrease in the work function [16].

The observed shift in the core levels of silver film nanoparticles after annealing is of interest (Fig. 6). In general, the XPS method makes allows to judge the presence of chemical bonds based on the shift of core levels. For example, the oxidation of silver films leads to significant changes in the valence band, as well as a shift in the core levels [20,21]. However, in our case, this process can be excluded, since during the annealing of these films in the spectrometer chamber, the pressure was about $10^{-9}-10^{-10}$ Torr. In [21] it is shown, that the shift of the core levels relative to the positions of the peaks for a bulk crystal is characteristic of silver clusters obtained by thermal deposition on a graphite substrate. Moreover, the magnitude of the shift is inversely proportional to the size of the clusters. The authors [21] explain this effect by the cluster charging, that occurs during photoelectron emission during measurements. The charging effect is the greater, the smaller the cluster size. However, according to the calculations [22], this effect gives a noticeable shift (~ 0.1 eV) while the average cluster size is a few nanometers. In our case the size of nanoparticles is tens of nanometers (Fig. 1). In addition, the size of the nanoparticles, which make up the original and annealed films are approximately the same. Indeed, in the course of the annealing at low temperatures, when particles do not coalesce, only their shape changes. However, in this case the cross section for the interaction of nanoparticles with X-ray quanta slightly decreases (in Fig. 6, the signal for the annealed film is slightly smaller). At the same time, in our case a device for removing the charge was used to obtain the spectra.

Nanoparticles in the initial, in unannealed film are more loose„ than in the annealed one, where the particles are monocrystal. That is, the average distance between atoms is greater, the atoms are more isolated. This can lead to an increase in the bond energy of the core levels. The authors of [19] point out one more possible reason for the shift of the core levels. In this study the XPS spectra of monocrystalline and polycrystalline gold nanoparticles about 20nm in size are compared. The authors state, that in monocrystal particles the grain size is about 8 nm, while in polycrystalline particles it is about 1 nm. The gold peak $4f_{7/2}$ for polycrystalline particles is shifted by 0.2 eV towards higher bond energies relative to the same peak corresponding to monocrystal particles.

The defects in the structure of nanoparticles can appear not only during the deposition process, but can also be created artificially, for example, by irradiating an island film with light in the near ultraviolet [10]. This work describes the action of ultraviolet radiation on an island film, which results in an increase in the self-diffusion rate upon relatively low heating (during annealing), compared to the non-irradiated part of the film. The condition for increasing the rate of self-diffusion is the formation of defects. The quantum energy of the near ultraviolet light 3.5−4.0 eV is quite enough to move silver atoms both in the volume and on the island surface. Thus, the formation of a vacancy requires an energy of 1.01−1.1 eV [6]. There is also enough energy to move a silver atom from a node to an interstice (of the order of 3.4 eV) [8].

The extinction spectra of unannealed silver films taken before and after irradiation with ultraviolet light practically coincide, which indicates, that newly formed defects are not enough to significantly reduce the plasmon lifetime in a nanoparticle. At the same time, the presence of such defects can increase the diffusion rate many times over both in the nanoparticle volume and especially on its surface. An increase in the diffusion rate leads to the formation of more rounded islands (at the same temperatures and for the same time), which is demonstrated by micrographs in [10] and, accordingly, narrower plasmon resonance peaks (ibid.).

Conclusion

The defects in the metal nanoparticles obtained as a result of thermal deposition play an important role in the properties of these nanoparticles and manifest themselves, for example, in the interaction of these nanoparticles with light. These defects should be associated with the presence of an absorption peak at wavelengths of 360−370 nm, which appears during the deposition process, as well as its rapid disappearance after deposition is completed. The presence of such defects can explain the single-photon photoelectric effect in a silver island film under the action of laser radiation with a wavelength of 355 nm, i.e. with quantum energy less than the work function for bulk silver.

The creation of defects in metal nanoparticles using near ultraviolet radiation leads to an increase in the diffusion rate in their bulk and especially on the surface. This, in its turn, leads to faster and deeper changes during heating of the nanoparticles (during annealing).

Conflict of interest

The author declares that he has no conflict of interest.

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