

# Light-Induced Surface Diffusion

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## 1. Introduction

Surface diffusion of indigenous and/or foreign atoms plays a key role in a number of physical and chemical processes. To name a few, it is important in crystal growth and epitaxy, heterogeneous catalysis, nucleation and growth of supported nanoparticles, and so on. Finding a reliable tool to control the surface diffusion processes is an attractive goal for many modern technologies.

Optical photons being absorbed by the surface or by the species adsorbed onto it can alter the surface diffusion considerably. At larger intensities of illumination these alternations are mainly due to the temperature rise, while at the lower intensities non-thermal mechanisms of light-induced surface diffusion are operative. The latter are the subjects of this chapter.

The electronic excitation follows after the photon absorption and changes the forces exerted by the surface onto the adsorbed atoms. After a short period of time the energy of the photon is partitioned between the surface and the adsorbed atom. The excess energy obtained by the adsorbed atom results in the increased desorption rates from as well as diffusion rates over the surface.

An inhomogeneous illumination of the surface leads to the inhomogeneous steady state distribution of the adsorbed atoms over the surface. The situation is similar to the Soret effect but require a special theoretical consideration that is presented in this chapter. An unexpected result of the theoretical analysis is that the spatial distribution of the surface number density of the adsorbed atoms is non monotone. There is a pronounced maximum of the surface number density of the adsorbed atoms at the boundary between the illuminated and the dark regions.

The shapes of the supported metal nanoparticles obtained via Volmer-Weber growth mode are metastable. Heating is known to speed up the equilibration of the particles shapes. In our experiments with silver and sodium nanoparticles supported on dielectric surfaces we found evidences of the reversible changes of the particle shapes. Hence, the temperature of the substrate determines the equilibrium shape of the nanoparticles. In the case of sodium, illumination speeds up the particles reshaping. This process is rationalized in terms of the light-induced diffusion of the indigenous atoms over the metal nanoparticle surface, while the main step of the process is identified as the photo-induced detachment of an atom from the terraces. The latter is found to be the rate limiting step in the nanoparticle reshaping process.

## 2. Nature of the photo-induced surface diffusion process

The effect of surface photodiffusion is closely related to the well-known process of photodesorption, because both processes begin with the resonance absorption of a light quantum by an atom adsorbed on the surface of a transparent substrate. From the theoretical point of view, the existence of photostimulated diffusion is justified by analysis of the previously established mechanism of photodesorption of resonantly absorbing atoms adsorbed on a transparent substrate (Bonch-Bruevich et al., 1990). Upon the resonant optical excitation of the electronic subsystem of an adsorbed atom, the energy of the photon is converted, rapidly and virtually completely, into vibrational degrees of freedom of the adsorbed atom and its nearest environment on the surface. Only in rare cases is the portion of energy gained by the adsorbed atom sufficient for it to overcome the adsorption potential and be desorbed. It is much more likely that this energy is insufficient for the atom to be desorbed. On the other hand, if we take into account that the activation energy of the surface diffusion is several times smaller than the adsorption energy, it becomes evident that photoexcitation should substantially affect the frequency of hopping of adsorbed atoms between neighboring minima of the adsorption potential even at low intensities of illumination, when the photodesorption rate is still not sufficient to significantly change the surface density of adsorbed atoms. Under nonuniform illumination, this gives rise to a surface flow of particles, which, in the first order in the light intensity, is proportional to the irradiance gradient. Note that photodiffusion does not remove the adsorbed atoms from the surface but rather redistributes them, so that a decrease in the surface density in some places is accompanied by an increase in the density of adsorbed atoms in other locations.

## 3. Case study: Cesium on sapphire

As the object of study, a system of cesium atoms adsorbed on the surface of a single-crystal sapphire was used. This system has been thoroughly studied previously (Bonch-Bruevich et al., 1985, 1990, 1997). The advantages of this system are the chemical inertness of sapphire and its transparency in a wide spectral range, covering the entire visible and near-IR regions, in which the adsorbed cesium atoms exhibit strong optical absorption. This allows one, using convenient laser sources, to selectively excite cesium atoms leaving the substrate unexcited. Saturated vapors of cesium atoms were placed into a sealed glass cell with sapphire windows. The volume density of the atoms at room temperature was  $10^{10} \text{ cm}^{-3}$ . The experiments were performed under conditions of dynamic equilibrium between the volume phase and the phase adsorbed on the surface. According to (Bonch-Bruevich et al., 1985, 1997) the energy of adsorption of the atoms on the sapphire surface is 0.6 eV, which provides, at room temperature, a surface density of the adsorbed atoms  $n_0 = 10^{13} \text{ cm}^{-2}$ . Thus, the surface density of the adsorbed atoms appears to be fairly high, though still much lower than a monolayer. Variations of the surface density of the adsorbed atoms induced by high-power radiation were detected by measuring the transmission of a relatively weak probe light of a cw semiconductor laser. Using the value of the absorption cross section of the adsorbed atom (Bonch-Bruevich et al., 1985, 1997)  $\sigma = 3 \times 10^{-16} \text{ cm}^2$ , we find that the absorption in the adsorbed layer makes up  $n_0 \sigma = 3 \times 10^{-3}$  of the total intensity of the light passing through the layer. Thus, absorption of this kind can be reliably measured using low-noise high-intensity semiconductor lasers.

Among the important advantages of the chosen system is a relatively low quantum yield of the photodesorption process. According to (Bonch-Bruevich et al., 1985, 1997), it is as low as  $10^{-5}$ . This allowed us to hope that the main mechanism for light-induced changes in the surface density of the atoms would be the photoinduced diffusion rather than photodesorption. As shown below, these expectations were fulfilled. Since the excitation of an adsorption system by high-power optical radiation induces both the photodesorption of atoms from the surface and their photodiffusion over the surface and, in addition, is accompanied by dark desorption and diffusion, we performed experiments of two types.

In the experiments of the first type, we studied the processes of photodesorption and dark desorption. For this purpose, the cesium atoms adsorbed on the sapphire surface were desorbed by single pulses of a ruby laser generating at a wavelength of 694 nm. The diameter of the irradiated spot varied from 1 to 4 mm. After the end of the strong desorbing pulse, the surface density of the adsorbed atoms gradually recovered. The kinetics of the recovery of the surface density was detected by measuring the intensity of a semiconductor laser beam transmitted through the irradiated area of the sapphire window of the cell. The intensity of the transmitted light at the wavelength 840 nm was measured by an FD-7K photodiode and was monitored by an S8-17 storage oscilloscope. At room temperature, the characteristic time of recovery of the surface density was 25 s. It was verified that this time did not depend on the radius of the irradiated spot within the limits indicated above. This allowed us to assign it exclusively to the process of deposition of atoms from the gas phase, rather than to their surface diffusion from dark regions, because in the latter case the recovery time would be dependent on the radius of the irradiated spot. From these experimental data, we determined the rate of thermal desorption to be  $\tau=0.04 \text{ s}^{-1}$ .

The photostimulated diffusion was studied by irradiating the surface with a cw beam of an argon laser at the wavelength 514.5 nm and a power of 1 W. The focused probe beam of a semiconductor laser ( $20 \times 30 \mu\text{m}^2$  in size) was scanned in such a way that it could repeatedly pass both regions of the surface subjected and regions not subjected to the optical treatment. The scanning was implemented using a lightweight mirror glued to the diaphragm of a high-power loudspeaker. The loudspeaker was fed by a sine voltage from a low frequency oscillator. The scanning range of the probe beam exceeded by approximately an order of magnitude the diameter of the exciting beam, which varied within the range 30–130  $\mu\text{m}$ . After passing through the cell, the probe beam was detected by a photodiode. The signal thus obtained was amplified by a selective amplifier at a scanning frequency of 30 Hz and was detected by a lock-in amplifier with an XY recorder at the output. The time resolution of the setup was 0.5 s.

Because of different absorption in regions with higher and lower surface densities of adsorbed atoms, the intensity of the transmitted beam was modulated at the beam scanning frequency. Under the conditions described above, when the changes in the transmittance are concentrated within a region that is small compared to the whole scanning length, the amplitude of the first modulation harmonic in the transmitted beam, detected in the experiment, is proportional to the integral of variation of the surface density of the adsorbed atoms along the beam scanning path. In the experiment, we measured the kinetics of changes in the surface density of atoms after the argon laser beam was rapidly switched on and off. It was found that, as in the first experiments, for large spots of the exciting beam ( $\sim 0.5 \text{ mm}$ ), this kinetics was exponential, with a rise and decay time of 25 s, and did not depend on the exciting beam power. It was verified that the amplitudes of the observed

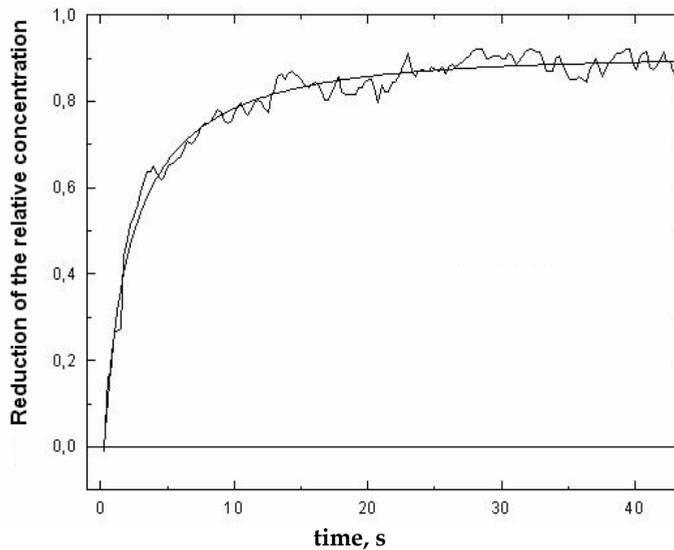


Fig. 1. Decrease of the surface concentration under illumination

signals varied linearly with the exciting beam power, while the changes in the surface density of the atoms did not exceed 20% of the equilibrium value. Upon a decrease in the diameter of the pump beam to  $110\ \mu\text{m}$ , the kinetics of the variation of the surface density of atoms changed sharply (Fig. 1). It is seen that, for such a small size of the irradiated area, the steady-state surface density of the particles is established during times substantially shorter

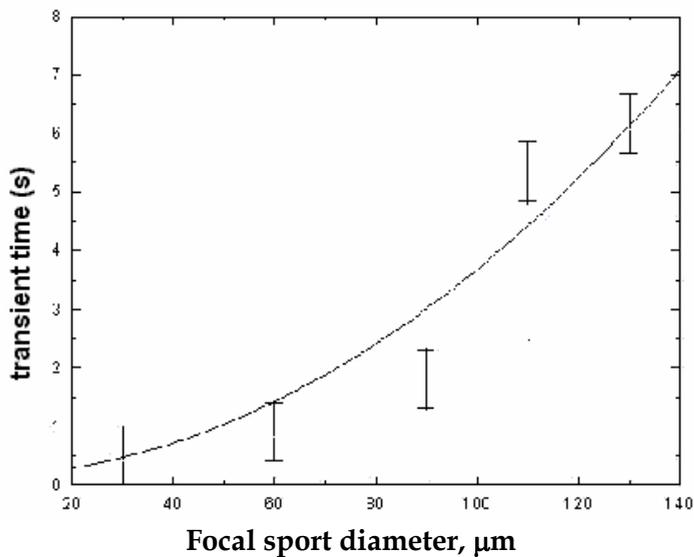


Fig. 2. Dependence of the transient time on the focal spot diameter

than the characteristic time for establishment of equilibrium with the volume phase, measured in the previous experiment. Since this time, as before, did not depend on the beam power but decreased quadratically with a decrease in the diameter of the pump beam from 130 to 30  $\mu\text{m}$  (Fig. 2), we concluded that the time of transition to the steady state was governed by the rate of dark diffusion of the atoms over the surface. In addition, it can be concluded that the main contribution to the decrease in the surface density of atoms is made by photodiffusion rather than by photodesorption. Indeed, if the decrease in the surface density were related to the photodesorption, such a decrease of the density would occur until the surface was totally depleted. Moreover, recovery of the steady-state value of the surface density after the exciting radiation has been turned off could occur only from the gas phase with a characteristic time of 25 s.

From the fact that the times of transition to the steady-state value of the surface density of atoms when the pump beam was turned on and off were approximately the same, while the signal amplitudes varied linearly with the pump beam intensity, we concluded that the photodiffusion process is substantially slower than the dark diffusion and can be described in the linear approximation..

#### 4. Theoretical description of the photo-induced surface transport

To derive the equation describing photodiffusion, we will use the standard scheme of the diffusion approximation (Lifshitz & Pitaevskii 1981). Let  $n(r)$  be the surface density of particles at the point  $r = (x, y)$  and  $v(r, a)$  be the probability of hopping of an atom from the point  $r$  to the point  $r - a$ . Then the change in the surface density of the particles at the point  $r$  is determined by the difference between the numbers of particles arriving at this point from neighboring positions and leaving this point

$$\partial n(t, \mathbf{r}) / \partial t = \int \{v(\mathbf{r} + \mathbf{a}, \mathbf{a})n(t, \mathbf{r} + \mathbf{a}) - v(\mathbf{r}, \mathbf{a})n(t, \mathbf{r})\} d^2 a \quad (1)$$

Because the photoinduced inhomogeneities of the surface density and the photoinduced changes in the hopping frequency are characterized by a spatial scale of the order of the light wavelength, while the length of the hops of the adsorbed atoms is much smaller than this value, the integrand can be represented as a series expansion, using the hop length as a small parameter. By retaining the first two terms in the expansion, we may rewrite (1) in the form

$$\partial n / \partial t = \partial_j (A_j n) + \partial_j \partial_l (B_{jl} n), \quad (2)$$

where

$$A_j(\mathbf{r}) = \int a_j v(\mathbf{r}, \mathbf{a}) d^2 a, \quad B_{jl}(\mathbf{r}) = \frac{1}{2} \int a_j a_l v(\mathbf{r}, \mathbf{a}) d^2 a \quad (3)$$

and the sum over  $j$  and  $l$  that attain the values of  $x$  and  $y$  is assumed.

Since the surface is, by itself, homogeneous and isotropic and its irradiation affects only the hopping rate and does not break this isotropy, among all the quantities presented above, only the  $B_{xx}$  and  $B_{yy}$ , equal to each other, are nonzero. Their common value may be naturally denoted by  $D(r)$ ,

$$B_{xx}(\mathbf{r}) = B_{yy}(\mathbf{r}) = D(\mathbf{r}) = \frac{1}{2} \int a_j a_l v(\mathbf{r}, \mathbf{a}) d^2 \mathbf{a} \quad (4)$$

since, in the absence of irradiation,  $D(\mathbf{r})$  is reduced to  $D_0$ , i.e., to the coefficient of the dark surface diffusion, which does not depend on the surface coordinates.

According to Eq. (4), the diffusion coefficient can be interpreted as a product of the hop frequency and the mean square of the displacement per hop. In the absence of irradiation, the frequency of hops can be estimated as a product of the vibration frequency of an adsorbed atom and the Boltzmann factor, which controls the probability of the atom overcoming the diffusion barrier at a given temperature of the surface. In this case, the displacement per hop coincides, in order of magnitude, with the distance between neighboring minima of the adsorption potential. In the case of photostimulated diffusion, the frequency of hops is determined by the probability of a photon being absorbed by an adsorbed atom. The displacement per hop may be, generally speaking, larger than in conventional diffusion, because the energy received by an adsorbed atom upon absorption of a photon substantially exceeds the mean thermal energy and, probably, the height of the diffusion barrier. Note that, in the approximation linear with respect to the pump power, the frequency of the photoinduced hops is directly proportional to the intensity, while their length is intensity-independent.

By separating, in Eq. (4), the contributions of thermal and photostimulated hops, we may represent  $D(\mathbf{r})$  in the form

$$D(\mathbf{r}) = D_0 + D_*(\mathbf{r}) \quad (5)$$

where  $D_*(\mathbf{r})$  is the photodiffusion coefficient, proportional to the intensity of irradiation at point  $\mathbf{r}$ . With these notations, Eq. (2) becomes

$$\partial n / \partial t = \Delta [D(\mathbf{r})n(\mathbf{r})] \quad (6)$$

where  $\Delta$  is the two-dimensional Laplace operator. Equation (6) allows us to describe the photodiffusion effect completely. In the next section, we will complement its right-hand side with the terms necessary to describe a number of concomitant processes important under our experimental conditions. The right-hand side of Eq. (6) differs from the conventional form of the diffusion equation with the coordinate-dependent diffusion coefficient  $\text{div}[D(\mathbf{r})\text{grad}n(\mathbf{r})]$  by the additional term  $\text{div}[n(\mathbf{r})\text{grad}D(\mathbf{r})]$ . This important distinction results from the fact that the conventional diffusion equation describes the transition to equilibrium, whereas Eq. (6) describes the transition to an established but not completely equilibrium state, caused by the nonuniform irradiation of the surface. Under these conditions, the diffusion flow is a sum of two terms, namely, the conventional contribution, proportional to the density gradient, and the photoinduced contribution, proportional to the illuminance gradient.

Various forms of the diffusion equation were discussed in (van Kampen, 1992; Zangwill 1988). An expression for the right-hand side of the diffusion equation having a similar structure is obtained for the case of thermodiffusion (Lifshitz & Pitaevskii, 1981), where the incompleteness of the equilibrium results from a specified inhomogeneity in the temperature distribution of the gas mixture.

Equation (6) fully describes the photodiffusion effect. However, to experimentally prove its existence, the theoretical model should be extended to include photodesorption, which

inevitably accompanies photodiffusion, as well as the usual thermal desorption and deposition of atoms from the gas phase onto the surface. These processes will be taken into account in the next section. This will allow us to unambiguously separate out the contribution of photodiffusion to the experimentally observed phenomena.

#### 4.1 Influence of the surface - Gas phase exchange

Under conditions of direct contact between the surface and the gas phase, Eq. (6) should include terms describing the deposition of atoms onto the surface from the gas phase and their thermal desorption from the surface. In addition, the right-hand side of Eq. (6) should be complemented with terms describing the photodesorption, whose rate, along with the photodiffusion coefficient, is proportional to the illuminance. The most complete equation may be written in the form

$$\partial n / \partial t = \Delta [D(r)n(r)] - \Gamma(r)n + J - n\tau, \quad (7)$$

where  $J$  is the flow of atoms to the surface from the gas phase,  $\tau$  is the thermal desorption rate, and  $\Gamma(r)$  is the rate of photodesorption. In the absence of light, the surface density is the same at any point and is equal to

$$n_0 = J/\tau \quad (8)$$

Let us separate out the relative change in the surface density  $p$  due to illumination according to the formula

$$n = n_0(1 + p) \quad (9)$$

Assuming  $p$  to be small compared with unity, we may neglect the terms containing the product of  $p$  and the rates of the photoinduced processes. Then Eq. (7) will acquire the form

$$\partial p / \partial t - D_0 \Delta p + p\tau = \Delta D_* - \Gamma(r)n \quad (10)$$

The entire subsequent theoretical analysis is based on Eq. (10).

#### 4.2 Surface density wells and humps due to photodiffusion

By introducing the new sought-for function

$$q(t, r) = [p(t, r) + D_*(r)/D_0] \exp(\tau t) \quad (11)$$

we transform Eq. (10) into a standard form of the inhomogeneous diffusion equation

$$\partial q / \partial t - D_0 \Delta q = f(t, r) \quad (12)$$

where

$$f(t, r) = [\tau D_*(r)/D_0 - \Gamma(r)] \exp(\tau t) \quad (13)$$

Equation (12) may be solved using conventional methods (Vladimirov, 1971) for arbitrary initial conditions and an arbitrary form of the right-hand side, which is determined by the distribution of the illumination intensity.

Turning back to the function  $p(t, r)$ , let us write out the solution of Eq. (10) corresponding to instantaneous switching on, at  $t=0$ , of a normally incident axisymmetric Gaussian beam. By denoting the effective radius of the beam by  $a$ , the intensity-dependent photodesorption rate and photodiffusion coefficient may be represented in the form

$$\Gamma(r) = \gamma \exp(-r^2/a^2), \quad D_*(r) = D_*(0) \exp(-r^2/a^2). \tag{14}$$

Assume that the surface density of the adsorbed atoms at  $t=0$  was equilibrium  $p(t=0, r)=0$ . Then, for  $t > 0$ , we have

$$p(t, r) = \frac{D_*(0)}{D_0} \left[ \exp\left(-\frac{r^2}{a^2}\right) - \frac{a^2}{a^2 + 4D_0t} \exp\left(-\frac{r^2}{a^2 + 4D_0t} - tr\right) \right] - \frac{a^2}{D_0} \left[ \gamma - \tau \frac{D_*(0)}{D_0} \right] \int_0^{D_0t/a^2} (1 + 4u)^{-1} \exp\left[-\frac{r^2}{a^2(1 + 4u)} - \frac{a^2\tau}{D_0}u\right] du \tag{15}$$

Consider, first, the photostimulated diffusion effect in its pure form, when one may neglect not only the photodesorption, but also the processes of adsorption of atoms from the gas phase and their thermal desorption. For this purpose, we suppose that, in Eq. (15),  $\gamma = \tau = 0$ .

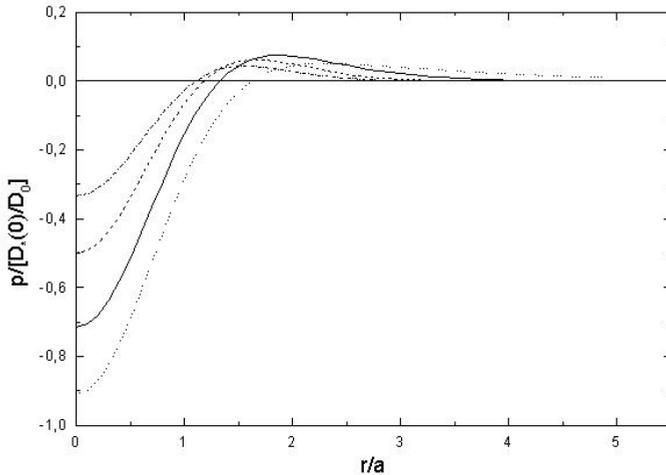


Fig. 3. A well and a hump in the surface number density due to the photodiffusion out of the illuminated region

The dependence of the surface density of the adsorbed atoms on the distance from the center of the light beam at different time moments is shown in Fig. 3. It is seen that, as a result of the photodiffusion, the surface density at the beam center decreases while increasing at the periphery. The boundary between the regions of increasing and decreasing density,  $r_1$ , shifts in time according to the equation

$$r_1 = a[(1 + a^2 / 4D_0t) \ln(1 + 4D_0t / a^2)] \tag{16}$$

and the greatest increase in the density is located at the distance  $r_2 = r_1\sqrt{2}$ . At  $t$  much smaller than  $a^2/4D_0$ , the value  $r_1$  is close to  $a$  at  $t$  much larger than  $a^2/4D_0$ , the value of  $r_1$  slowly increases.

The density minimum, attained at large times at the beam center, corresponds to  $p(t=\infty, r=0)=-D_*(0)/D_0$ , while the maximum increase in the relative density, attained at  $t=2.513a^2/D_0$  at the distance  $r=1.87a$ , equals 7.5% of  $D_*(0)/D_0$ .

When all processes except for the photostimulated diffusion are neglected, the number of adsorbed particles does not change, so that, for any moment of time, the integral of  $p(t, r)$  over the whole surface is zero.

The results obtained above should be compared with those that would have been obtained in the absence of the photostimulated diffusion, when the effect of light is reduced only to photodesorption. By setting  $D_*(0)=0$  in Eq. (15), we have

$$p(t,r) = \frac{a^2}{D_0} \int_0^{D_0 t/a^2} (1+4u)^{-1} \exp\left[-\frac{r^2}{a^2(1+4u)} - \frac{a^2\tau}{D_0}u\right] du \tag{17}$$

It is evident from the form of the integrand that the relative role of the processes of thermal desorption and thermal diffusion depends on the radius of the light beam  $a$ . If  $a^2$  is much larger than  $D_0/\tau$ , the main contribution to the integral is made by the region  $u \ll 1$ , and we may approximately write

$$p(t,r) = \frac{\gamma}{\tau} [1 - \exp(-t\tau)] \exp(-r^2/a^2) \tag{18}$$

In this case, the surface density of the adsorbed atoms decreases in exact correspondence with the local illuminance, and the kinetics of this decrease is controlled only by the rate of thermal desorption. If  $a^2 \gg D_0/\tau$ , the change in the density at the center of the illuminated region, for times  $t < 1/\tau$ , is described by the function

$$p(t,r) = -(a^2\gamma/4D_0) \ln(1+4D_0t/a^2) \tag{19}$$

This equation shows that thermal diffusion cannot stabilize a surface density perturbed by the photodesorption process. The surface density, in this case, decreases infinitely until the process of deposition from the gas phase becomes noticeable or until the conditions for applicability of the linear approximation in the pump beam intensity are violated. When Eq. (17) is valid, the radial dependence of the surface density is monotonic. No increase in the surface density is possible in the absence of photodiffusion.

In the experimental study of the photostimulated diffusion, a Gaussian beam with the effective radius  $b$  was scanned through the center of a region with the modified surface density. As shown in the next section, at  $b \ll a$ , the experimentally measured quantity can be represented in the form of an integral  $S(t)$  of the surface density variation over the straight line passing through the center of the illuminated region,

$$S(t) = n_0 b \sqrt{\pi} \int_{-\infty}^{\infty} p(x=0,y,t) dy \tag{20}$$

When  $b$  is comparable with  $a$ , then Eq. (20) should be replaced by an integral of variation of the surface density over the whole surface with a weight proportional to the probe beam intensity along the scanning path. In this case, Eq. (20) should be replaced by

$$S(t) = n_0 \iint p(t, x, y) e^{-x^2 / a^2} dx dy \quad (21)$$

By substituting the solution (15) found above into Eq. (21), we have

$$S(t) = -n_0 ab \sqrt{\pi} \left\{ \begin{aligned} & \frac{a^2 \gamma}{D_0} \int_0^{D_0 t / a^2} \frac{\exp(-a^2 \tau u / D_0) du}{(1 + 4u + b^2 / a^2)^{1/2}} \\ & + 2(D_*(0) / D_0) \int_0^{D_0 t / a^2} \frac{\exp(-a^2 \tau u / D_0) du}{(1 + 4u + b^2 / a^2)^{3/2}} \end{aligned} \right\} \quad (22)$$

Equation (22) describes the process that occurs after the pump beam is turned on. After the pump beam is turned off, the surface density recovers to its equilibrium value. In the approximations adopted here, the kinetics of recovery of the equilibrium concentration does not differ from that of its perturbation, because the rates of the photoinduced processes are assumed to be low compared with those of the processes leading to recovery of the equilibrium. This condition is well satisfied in the experiment.

## 5. Theory of the photo-induced surface diffusion versus experimental findings

Let us compare the kinetics of the surface density of adsorbed atoms measured in the experiments (Fig. 2) with the results of theoretical analysis. If the process of adsorption from the gas phase, whose rate is equal to that of the thermal desorption  $\tau$ , is neglected, then the first integral in Eq. (22), corresponding to the photodesorption process, is reduced to the simple square-root dependence

$$(1 + 4t/T)^{-1/2} - 1 \quad (23)$$

infinitely growing with time, which contradicts the experimental data. Here,

$$T = (a^2 + b^2) / D_0 \quad (24)$$

is the characteristic time of the signal variation, related only to the diffusion processes. Under these conditions, the second integral in Eq. (22), corresponding to the photodiffusion process, is also simplified and yields a time dependence gradually approaching the steady-state value,

$$1 - [1 + 4t/T] \quad (25)$$

Equation (25) adequately describes the experimental nonexponential kinetics of variation of the surface density of the adsorbed particles, excluding long times, when the effect of adsorption from the gas phase becomes noticeable. In Fig. 1, the results of the measurements for the laser beam diameter of 110  $\mu\text{m}$  are compared with the theoretical curve constructed by using the exact formula (22). By comparing the theoretical and experimental dependences, we can find the characteristic diffusion time  $T$ . Fig. 2 shows the dependence of  $T$  on the pump beam diameter, which, according to (23), should be quadratic. The best agreement with the experimental data is obtained for  $D_0 = 7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . If we assume that

the diffusion is of activation nature, with the length of an elementary hop being equal to a few tenths of a nanometer and with attempts to overcome the barrier occurring at the frequency of vibrational motion of the adsorbed atom, i.e., every several tenths of a picosecond, then the activation barrier for the diffusion can be estimated to be about 0.1 eV. This value agrees with the empirical "one sixth" rule (George et al., 1985) for the ratio of diffusion barrier height to adsorption energy. Since the photodiffusion coefficient  $D_*(0)$  is proportional to the pump intensity  $I(0)$ , it may be naturally written in the form  $D_*(0) = \kappa I(0)$ , where the value of  $\kappa$  equals, according to the results of the measurements,  $2 \times 10^{-10} \text{ cm}^2 \text{ J}^{-1}$ . If we compare this value with the absorption cross section for the adsorbed atoms, which controls the frequency of the photoinduced hops, we come to the conclusion that the mean square of displacement of an adsorbed atom per absorbed photon is of the order of  $100 \text{ nm}^2$ . The above findings mean, first, that the photoinduced diffusion does not require overcoming any energy barrier and, second, that the rate of relaxation of the excess atomic energy is rather low (of the order of  $10^{10}$ – $10^{11} \text{ s}^{-1}$ ). The first assertion agrees fairly well with the mechanism of the photoinduced diffusion discussed above, because the effective temperature of an adsorbed atom that has absorbed a photon is comparable with the value of the diffusion barrier. The low rate of the energy relaxation of an adsorbed atom upon its interaction with the surface of sapphire was already noted by us previously, both in measuring the accommodation coefficients of atoms upon their impact on the surface (Bonch-Bruevich et al., 1990) and in studying the quasi-thermal regime of photodesorption of sodium atoms from the sapphire surface (Bonch-Bruevich et al., 1999), where the energy relaxation rate was also estimated to be of the order of  $10^{10} \text{ s}^{-1}$ . The role of long free paths in surface diffusion, for other mechanisms of transfer of excess energy to an adsorbed atom, has been discussed in the literature (Brune et al., 1992; Tully et al., 1979).

## 6. Novel aspects of the photoinduced surface transport

As a result of these studies, we have found a new light-induced effect in the processes of transfer on a solid surface—the effect of surface photodiffusion. The physical basis of the effect is the conversion of the energy of radiation into the energy of motion of an adsorbed atom over a surface. At the first stage, the system of the atom passes into an excited state. Then, the electronic excitation is quenched and its energy is distributed over the vibrational degrees of freedom of the substrate and the adsorbed atom. A fraction of adsorbed atoms acquire an energy sufficient to overcome the diffusion barrier and gain the probability to shift to another adsorption site. The frequency of the light-induced hops is proportional to the surface illuminance, while the length of the hops measures tens of the substrate lattice constants. Photoinduced desorption insignificantly affects the photoinduced diffusion, because the desorption is associated with overcoming of a much higher energy barrier, equal to the surface adsorption energy of the atom, and thus its probability is much lower.

It is shown that, under nonuniform illumination of a surface, the adsorbed atoms move away from the illuminated area and, on the boundary between the light and the shadow, the density of the adsorbed atoms exceeds the equilibrium density. Thus, we have discovered and studied a new phenomenon, which makes it possible to efficiently control, by light, the diffusion processes on a surface. Unlike the known process of photoinduced desorption, which removes adsorbed particles from the surface, in the process of photoinduced diffusion, the total number of adsorbed particles on the surface does not change. An important feature of photodiffusion is the possibility to control, by means of light, the

density of adsorbed particles on a surface (i.e., both to increase and to decrease it). Since the processes of origination of a new phase on a surface essentially depend on diffusion processes the use of photodiffusion is promising for controlling processes of nucleation and growth of surface nanostructures.

## 7. Self-diffusion of atoms over the surfaces of metal nanoparticles

The diffusion of atoms over the surfaces of small metal particles is of great scientific and practical interest. This interest is related to searching for ways to create nanostructures with the necessary properties controlled by the dimensions and shape of the structure's elements. Studies of self-diffusion of atoms over the surfaces of metal nanoparticles, which form island films, have already been started. These studies have shown, however, that the long-standing previous investigations of atomic diffusion over the surfaces of macroscopic bodies have proven to be inappropriate for the explanation of the mass transfer over the surfaces of nanoparticles. The same proved to be true with regard to standard methods of studying the surface diffusion based on electron and autoionization microscopy.

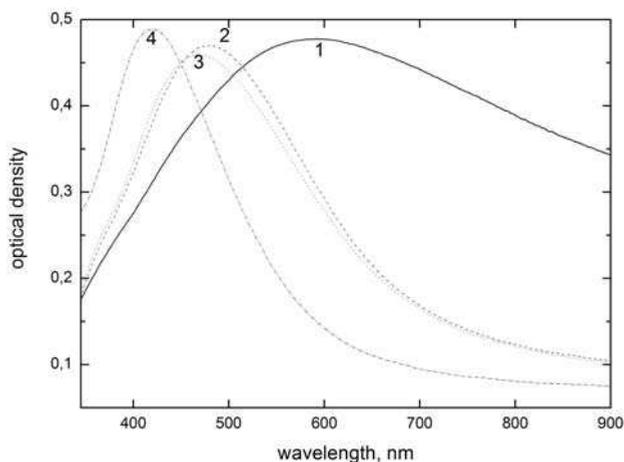
In recent years, optical methods for studying the reshaping of metal nanoparticles have entered into practice. In these methods, the optical characteristics of islands of films and, in particular, the extinction spectra, were connected with the morphology of film-forming particles. In (Warmack & Humphrey, 1986) it was found that changes in the extinction spectrum of a heated thin golden film whose nanoparticles were 5–100 nm in size are directly related to changes in the nanoparticle shape. Similar studies were performed with a silver film (Wenzel et al., 1999). In what follows the results obtained by the application of the optical technique for monitoring the processes that redistribute positions of atoms in solid silver particles ~10 nm in size are presented. The idea of the method is based on the relation between positions of plasma resonances of islands and the island shapes. The changes in the shapes of islands were induced by heating of a film and were revealed as a result of the modification of the extinction spectrum of the film. These changes were attributed to self-diffusion of atoms over the surfaces of nanoparticles. Spontaneous reshaping of isolated islands is related to the method of their creation in a non-equilibrium state when the metal is deposited onto the substrate. Transition from non-equilibrium shapes to equilibrium ones, referred to as the shape relaxation, is of thermal nature. It was found that the duration of the observed shape relaxation was determined not by the rate of the surface self-diffusion, but rather by the time of restructuring of the nanoparticles' facets.

### 7.1 Optical monitoring of silver nanoparticle annealing and aging

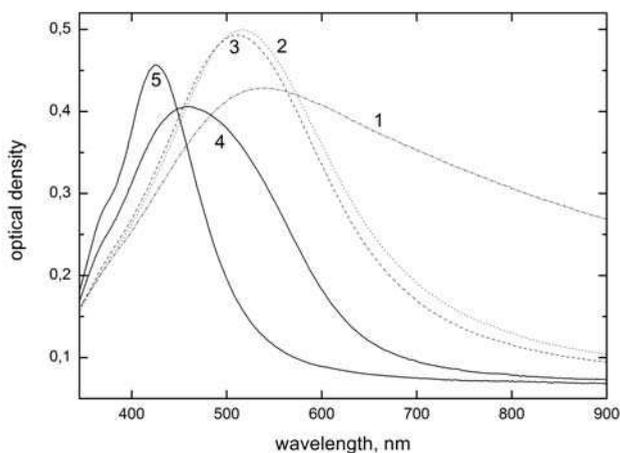
Granular silver films were obtained in a deep vacuum by deposition of silver atoms onto a quartz or sapphire substrate. Immediately after the deposition the extinction spectrum of the as-grown film was recorded in air. Then, the film was placed into the vacuum chamber and heated for a certain time. After that the spectrum was recorded again. This cycle of actions was repeated several times.

Fig. 4 shows extinction spectra of silver films after their heating at two fixed temperatures  $T = 473$  and  $553$  K during different time intervals. The spectra are seen, first, to exhibit substantial changes for a short time; then, the rate of changes decreased. It should be emphasized that the detected changes in the extinction spectrum are not connected with the evaporation of the silver heated in a vacuum. The estimates have shown that no more than  $10^{-3}$  of the total amount of the substance of the island film can be evaporated during this

time at  $T= 553$  K. A certain decrease in the area under the curves of the extinction spectra (this quantity characterizes the total amount of substance in the film) is connected, as shown by numerical estimates, with the type of the frequency dispersion (differing from that of Drude-Lorentz) of the silver complex permittivity in the region of 2–4 eV.



a)

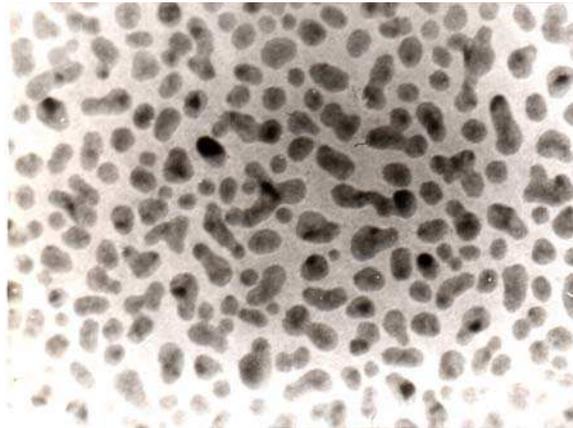


b)

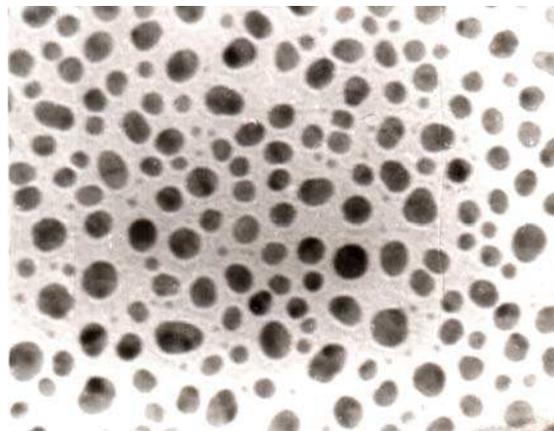
Fig. 4. Annealing kinetics of the granular silver films (a) 1 – as prepared, 2 to 4 - after annealing at 473 K for 8, 16 and 56 minutes. (b) 1 – as prepared, 2 to 5 - after annealing at 553 K for 2, 4, 8 and 20 minutes

Fig. 5 shows the transmission electron microscopy images of (a) an as-grown film and (b) of the film annealed during 30 minutes at  $T= 553$  K. One can see that agglomerates formed on the as-grown film (except for the smallest ones) are diverse in shape. As a result, the

extinction spectrum acquires a strong inhomogeneous broadening, which decreases under heating because islands are getting apart and more uniform in shape. It is likely that, at the initial stage of heating, the links between islands in agglomerates are being rapidly destroyed or separate islands are being formed due to merging of the smallest ones. Then, separate islands are being rounded (Fig. 5b). At the final stage, this transformation occurs at  $T = 553$  K only by a factor of 3.3 faster than at  $T = 473$  K.



a)



b)

Fig. 5. TEM micrographs of the granular silver films, a - as grown, b - after annealing

If the rounding of the islands at the final stage is related to the surface diffusion, then the above acceleration in the shape relaxation is provided by the activation energy  $E = 0.36$  eV. This agrees with the experimental (0.4 and 0.33 eV) and theoretical (from 0.5 to 0.25 eV) data (Brune, 1998).

In this case, according to (Mullins, 1957; Nichols & Mullins, 1965) the shape relaxation time  $\tau_T$  can be estimated by the formula

$$\tau_T = N^{4/3} \kappa T / \gamma v_T. \quad (26)$$

Here,  $N$  is the number of atoms in a granule and  $\gamma$  is the surface tension coefficient (the energy of a single bond of an atom in the crystal equal, by the order of magnitude, to the fusion heat per atom). The frequency of jumps  $v_T$  that determines the surface diffusion coefficient at the temperature  $T$  is given by the relationship

$$v_T = v_0 \exp(-E/kT), \quad (27)$$

where  $E$  is the activation energy of the surface diffusion,  $k$  is the Boltzmann constant, and  $v_0$  is the Debye frequency.

For the size of granules of about  $10 \pm 2$  nm and the cell size of 0.5 nm an estimate of  $N$ , yields  $N \approx 10^4$ . Assuming that  $E = 0.36$  eV,  $v_0 = 10^{13}$  c<sup>-1</sup>,  $\gamma = 0.1$  eV  $\mu$   $kT = 0.04$  eV we obtain from the above relationship that  $\tau \approx 10^{-3}$ , which is by six orders of magnitude smaller than the observed quantity. This, a large discrepancy cannot be substantially corrected by either taking into account the dependence of the relaxation time on the initial particle shape or by varying numerical values of the quantities entering this equation.

## 7.2 Theoretical estimates

In conformity with the commonly accepted ideas (Ehrlich, 1974; Naumovets & Zhang, 2002), atoms are heat transferred over surfaces from places with a higher chemical potential to those with a lower chemical potential. At temperatures much lower than the melting point, most atoms of the surface are located in terraces, i.e., facets with small indices. The atoms transferred over the terraces, torn away from the steps (boundaries of terraces) reach other steps and get stuck there. Thus, the sources of the transferred atoms are considered to be steps whose density characterizes facets of bulk crystals.

The shape of microcrystals (granules) also changes upon variation of temperature due to the surface selfdiffusion. In small rounded granules (smaller than 100 nm in size), the facets are rather small (smaller than the surface area of the granule by a factor of 10–20). The facets with the area of  $\sim 100$  surface cells are separated from the neighboring facets by transition regions, i.e., by rough imperfect facets [8] referred to as atomic rough. The structure of surfaces of rounded crystal nanoparticles is mosaic, i.e., each facet borders several other with different structures. As the temperature changes, the free energies of the facets change differently and, as a result, the shape of the granules noticeably changes with no changes in their volumes.

With increasing temperature, the granules are getting rounder and their surface area decreases. Indeed, the increasing temperature of the granules leads to their melting, i.e., to total elimination of their flat terraces. For this reason, it is natural to assume that the area of the terraces, in the process of rounding, decreases, and the rough regions become wider. This process is possible when the chemical potential of atoms on the terraces ( $\mu_t$ ) is greater than the potential ( $\mu_r$ ) of atoms in the roughed regions. Changes in the shape of the granule shape stop when the potentials become equal.

In the continuum model of the crystal shape relaxation (Mullins, 1957; Nichols & Mullins, 1965), the shape of granules is characterized by the curvature of the surface. The curvature in the places where the roughed facets are localized is considered to be higher than in the places with flat facets. This simplification makes it possible to describe the mass transfer as a frictional flow of atoms over the surface induced by the capillary forces of surface tension.

This model provides the relationship (26), which we used to estimate the shape relaxation time.

The continuum model is evidently too rough to describe the phenomenon under study. This is obvious from the fact that the difference between flat facets cannot be characterized by the curvature. Fundamental reason for inapplicability of the continuum model to the description of the shape relaxation of crystalline atomic clusters has been revealed in (Combe et al., 2000). Using the methods of computer simulation, it was established that, at temperatures far away from the melting point (more precisely, below the temperature of roughening), the shape relaxation rate is limited by the stage of attachment of transferred atoms to flat facets, which, in this process, are being rounded. Since the presence of steps on small flat facets is extremely unlikely, the attachment of transferred atoms to these facets is hampered. The stage of the rounding of facets starts with the appearance of critical nuclei on flat facets. At low temperatures, the appearance of critical nuclei is unlikely and, for this reason, the shape relaxation of facets is retarded.

In the same paper (Combe et al., 2000), it was established that the law  $\tau_T \sim N^{4/3}$  of the continuum model is obtained in the model under consideration at elevated temperatures, when granules practically have no flat facets. With decreasing temperature, the relation between  $\tau_T$  and  $\sim N$  changes and can be well approximated by the relationship  $\tau \sim N^m$ , where  $m(T)$  monotonically increases from  $4/3$  to  $5$  with decreasing  $T$ .

The parameters of the model considered in (Combe et al., 2000) regrettably are more appropriate for the description of aluminum, rather than silver, clusters. However, the qualitative results obtained for  $N \leq 10^4$ , in our opinion, allow one to apply them to the system under study.

For the values of  $\tau \approx 10^2$ s and  $N \approx 10^4$ , close to ours, from the data of (Combe et al., 2000), we have  $m \approx 4.2$  and, correspondingly,  $T = 450$  K. As the temperature decreases by 50 K, the shape relaxation time increases by a factor of three. These data are close to those obtained in our experiments.

The model contains a single energy parameter, 0.4 eV, which, by its meaning, is the activation energy of the surface diffusion over the [100] facet of a cubic body-centered crystal. With allowance made for a slight difference between this energy and the appropriate quantity for silver (0.33–0.34 eV) and the difference between the surfaces of the body-centered lattice of the model and face-centered lattice of silver, the proximity of the model shape relaxation time to the observed value allows us to conclude that our observations can be qualitatively explained by the model of (Combe et al., 2000). Thus, we believe that, in the above experiments, we observed a delay of the self-diffusion mass transfer over the surfaces of nanoparticles at the stage of roughening of their facets.

### 7.3 Mechanism of the shape relaxation of metal nanoparticles

The agreement between our experimental data and the model proposed in (Combe et al., 2000) is only a qualitative result. For the strong dependence of the shape relaxation time of granules on their sizes, the order-of-magnitude errors are inevitable in experimental determination of the rate of changes of the islands' morphology and other characteristics of islands. At the same time, it is evident that, in spite of the inhomogeneity in the films of nanoparticles, their surfaces, and the parameters of self-diffusion of atoms over them, the temperature dependence of the mass transfer rate is characterized by the activation energies of various processes providing shape relaxation of granules. Due to the mosaic structure of

the granule surfaces, the self-diffusion depends not only on their material, but also on their shape. This results, in particular, in the characteristic nonexponential kinetics of the shape relaxation demonstrated by long intervals of absence of any changes (Combe et al., 2000). The proposed optical method makes it possible to reveal these features.

It follows from the proposed mechanism of the shape relaxation of nanometer-sized granules that the time of relaxation to the equilibrium shape is determined not only by the temperature at which the relaxation occurs, but also by the state from which they relax. In particular, a non-equilibrium granule obtained by cooling a hot equilibrium granule to a certain temperature will relax faster than a granule obtained by heating an equilibrium cold granule to the same temperature. The difference between the two relaxation times results from the fact that, in the first case, the initial surface of the granule is disordered, and the facets on the surface will form faster than in the second case when a slow stage of formation of the critical nuclei is needed for roughening of the initial flat facets. The proposed reason for slowing down the shape relaxation of granular particles with flat facets presents new opportunities for controlling their shape by external perturbations of particles at the stage of their relaxation.

## 8. Illumination-stimulated reshaping of metal nanoparticles

At present, metal nanoparticles are used in various fields of science and engineering. Their optical properties associated with collective electronic excitations are of particular interest. In most cases, ensembles of nanoparticles obtained on dielectric surfaces by means of the self-organization of atoms adsorbed from a vapor phase are investigated and used. The shapes of the particles thus obtained are often nonequilibrium and vary with the time. The shapes vary more rapidly when the substrate is heated (Ivlev et al., 1988). These facts are well known and reported in detail in papers devoted to electron microscopy investigations, atomic force microscopy data, and the optical extinction spectra of metal island films (Warmack & Humphrey, 1986).

Although it is clear that the equilibrium shape of nanoparticles should depend on the temperature (Combe et al., 2000, as far as we know, this dependence has not yet been studied systematically. A change in the shapes of the particles is usually treated as an irreversible transition to the equilibrium state, and heating accelerates the transition process. We observed reversible changes in the optical extinction spectra of silver and sodium films on dielectric substrates under repeated cyclic variations of their temperatures. Moreover, it was found that the illumination of sodium films noticeably accelerates the transition of their spectra to a stable state corresponding to room temperature with the negligibly small heating of nanoparticles by light. The nonthermal photoevaporation of atoms from nanoparticles, i.e., photoatomic emission (Abramova et al., 1984; Bonch-Bruevich et al., 1998; Hoheisel 1988; Burchianti et al. 2009) was also insignificant owing to the choice of the wavelength of light near the threshold of this relatively low probable process. Light-induced changes in the shapes of metal nanoparticles are actively investigated at present. The most well-known works in this field are separated into two groups. In the first group (Huang et al., 2005; Stietz, 2000; Habenicht et al., 2005), the effect of light is reduced to the thermal effect, owing to which individual nanoparticles are either rounded or displaced on the substrate and coagulate when meeting each other. In the second group (Sun et al., 2003; Jin et al., 2001; Kim et al., 2009), light induces physicochemical processes in colloids of metal nanoparticles, which result first in their transformation usually from spheres to prisms and,

then, in the formation of complex aggregates of the latter. The nature of the effect of light on the formation of metal nanocrystals in liquids remains unclear. Note that in all of the mentioned works, irradiation induced significant irreversible changes in the nanoparticles, which were manifested as a substantial change in their optical spectra.

Here, we consider the observation of the effect of light on the formation of nanocrystals of absolutely different nature than that mentioned above. The observed light-induced acceleration of the relaxation process is due to the nonthermal photostimulation of the diffusion of metal atoms on the surface of metal nanoparticles. The light-induced acceleration of the relaxation of the shapes of nanoparticles is due to the same processes as photoatomic emission (Abramova et al. 1984). An attempt to observe photostimulated surface mass transport was reported in (Vartanyan et al., 2009a).

### 8.1 Observation of the illumination accelerated nanoparticle reshaping

The experiments were performed with silver and sodium films. The sodium films were obtained in sealed off evacuated cells with quartz, sapphire, or glass windows. The probing and illumination of the films were performed through the transparent windows of the cells. The silver films were obtained by thermal sputtering in a vacuum. The substrates were maintained at room temperature during the growth of the films. The optical probing of the silver films was the films from the vacuum setup.

The films formed under the indicated conditions are metastable. The kinetics of their morphology, which can be seen, e.g., in a change in the optical extinction spectra, is complex and long term. The annealing of the films accelerated the processes resulting in the stabilization of their structure. The sodium and silver films were annealed at temperatures of 50 and 200°C for 10 and 30 min in a vacuum, respectively. Annealing was followed by the fast cooling of the films. Further, variations in the temperature induced small, but regular and reversible changes in the extinction spectra.

The changes in the spectrum of the annealed sodium film were investigated at room temperature. Fig. 6 shows (1) the optical extinction spectrum of two separated regions of the film immediately after annealing. Then, the film was aged for an hour at room temperature and one of the regions was illuminated by a cw laser with a power density of 4 mW/cm<sup>2</sup> (10<sup>16</sup> photons per centimeter squared per second) and a wavelength of 810 nm ( $h\nu=1.53$  eV), whereas the other region remained unilluminated. The spectrum of the unilluminated region changed very slightly and almost coincided with initial spectrum 1. The spectrum of the illuminated region changes noticeably (spectrum 2 in Fig. 1).

Fig. 7 shows the differences between the spectra of the unilluminated and illuminated regions after and before illumination. It is seen that the integral of the difference extinction spectrum is much smaller than a change in extinction. For this reason, it can be assumed that the light-induced change in the volume of nanoparticles is insignificant and the observed effect is attributed to a change in their shape. Note that an increase in the irradiation intensity, which did not noticeably heat the particles, was accompanied by an increase in photoatomic emission and a noticeable decrease in the size of the illuminated particles. This effect is not considered below.

A reversible change in the extinction spectra upon a variation of the temperature of the substrate was also observed in annealed silver films. Changes in the spectra were detected immediately after the cooling of the film and lasted for 40–60 min; after that, the extinction spectrum was stabilized. Fig. 8 shows the extinction spectra (1) immediately after deposition, (2) after annealing and fast cooling to room temperature, and (3) after aging at room

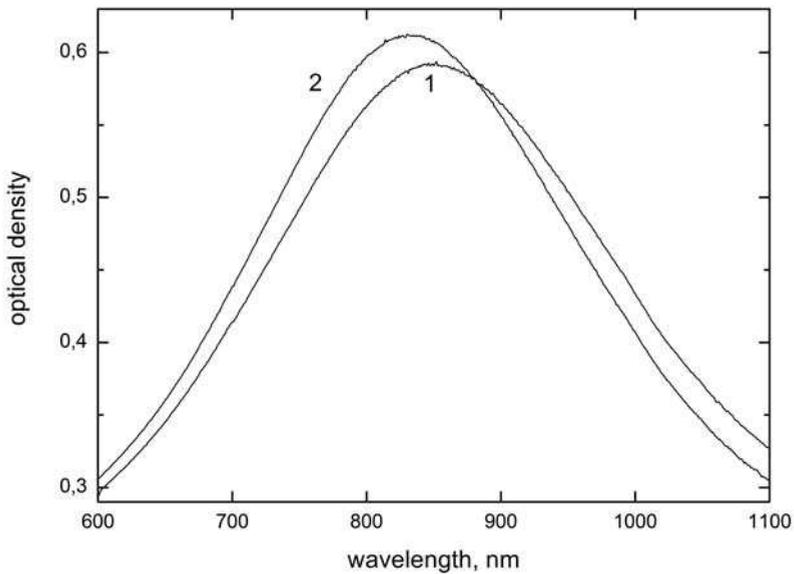


Fig. 6. Optical density of the annealed sodium film (1) and the same after an hour of illumination

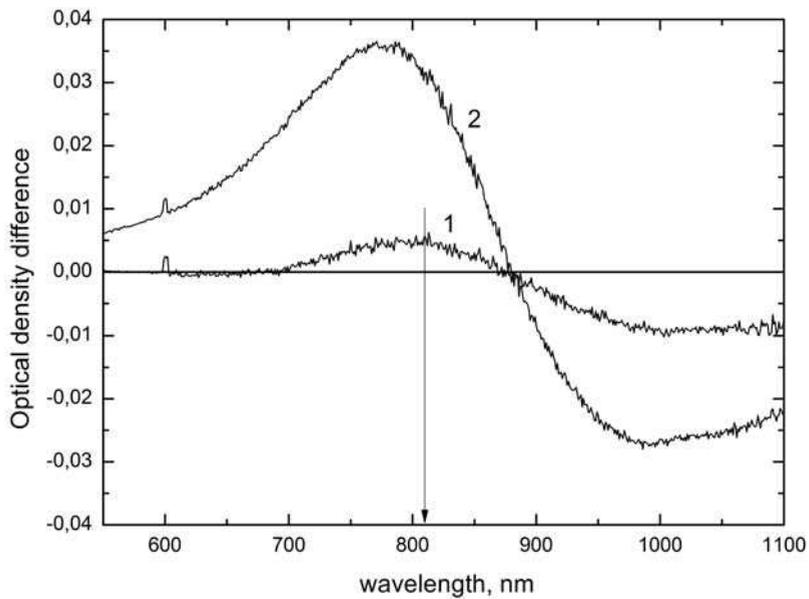


Fig. 7. Reshaping of sodium nanoparticles under laser illumination. Optical density differences in the dark region (1) and in the illuminated region (2). The laser wavelength is indicated by an arrow

temperature for an hour. Note that the extinction maximum at the last stage was shifted toward the opposite side with respect to the annealing induced shift. A change in the spectrally integrated absorption in the case under consideration is due not to the evaporation of nanoparticles, which is insignificant at the indicated heating. The change is caused by the interband transition induced difference of the dispersion of the relative permittivity of silver from that accepted in the Drude model. This is confirmed by the fact that the repeated annealing at 200°C in a vacuum for 5 min or a slightly longer time returned the extinction spectrum to the initial position (spectrum 2 in Fig. 8). The cycles of changes in the shape of the spectrum under the heating and cooling of the film were repeated many times. In this case, the almost complete reversibility of the changes in the extinction spectrum was observed, indicating a direct relation of the shapes of the islands with the temperature of the substrate. The illumination of silver films by available laser sources did not noticeably accelerate the relaxation processes.

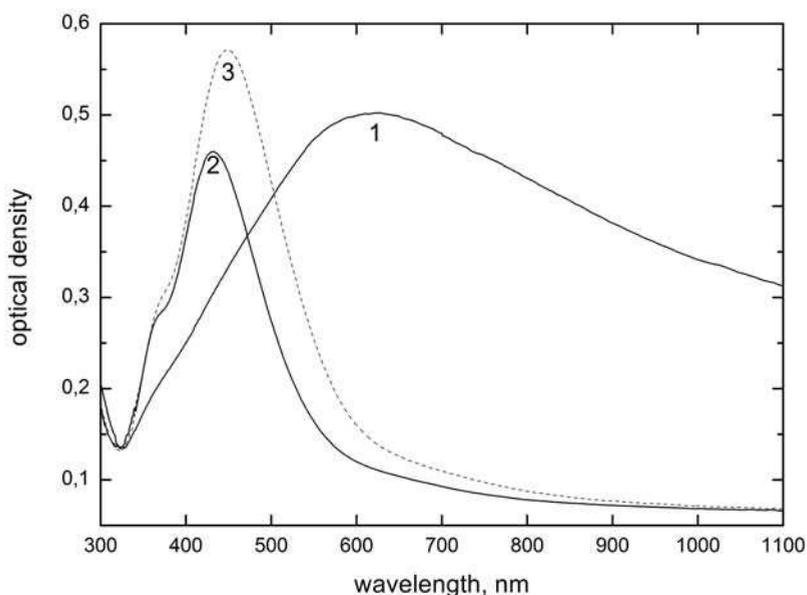


Fig. 8. Reshaping of silver nanoparticles in the dark

### 8.2 Sodium versus silver nanoparticles reshaping

The optical extinction spectra of metal nanoparticles are determined primarily by their shapes. The dependence of the shape of the spectrum on the size of the nanoparticles is not very noticeable. The extinction spectra of ensembles of particles are determined by the shape distribution of the particles. For this reason, the revealed reversible changes in the extinction spectra of silver and sodium films with the variation of their temperature can be attributed to changes in the shapes of individual islands, i.e., autocoalescence (Ivlev et al. 1988).

Other possible mechanisms of a change in the shapes of the particles, which are associated with the displacement of the material between the particles or the motion of particles themselves on the substrate, can be rejected in view of the transmission electron microscopy

data. It is seen on the microphotographs (Vartanyan et al., 2009a) of our annealed silver films that the nanoparticles with a mean diameter of 14 nm are separated at large distances. Moreover, all of the changes associated with the mass transport on the substrate should be irreversible and manifested in the deviation of the spectra from the stable shapes, which increases in time; these features were not observed in our experiments.

We do not know any consistent theoretical description of the shape of nanoparticles. The numerical simulation (Combe et al., 2000) indicates that the rate of the relaxation of the shapes of the crystal nanoparticles owing to surface mass transport is limited not by the displacement of atoms through terraces, which is a very fast process, but by the escape of atoms from relatively stable positions near the steps and the attachment of diffusing atoms at the positions corresponding to the final equilibrium shapes. The activation energy of the escape of the atoms from the positions attached to the steps to a terrace is obviously lower than the evaporation heat, but can be comparable with the latter. The activation energy of the incorporation of atoms into stable positions can be low, but the incorporation process can be very long owing to the complexity of the path of the assembly of the stable final shapes of the nanoparticles.

In the light of the above discussion, the observed light-induced acceleration of the relaxation of the shapes of sodium nanoparticles is explained by the fact that photons trigger the mechanism of surface diffusion by separating atoms from the steps and their transfer to terraces. It is assumed that light excites electrons quasilocalized near the atoms situated on the surface at irregular positions, and the energy of the excitations is converted into the energy of the displacement of atoms on the surface. A similar, but low probable process results in the separation of atoms from the surface, which is manifested as the photoatomic emission (Bonch-Bruevich et al., 1998).

In the absence of illumination, the attachment of atoms diffusing on the terraces to the steps decelerates the relaxation of the shape, and nanoparticles are "frozen" in metastable shapes, so that the mean thermal energy is much lower than the energy of the separation of an atom from a step. In the presence of the illumination of sodium nanoparticles, the energy of a photon is sufficient for initiating separation. The efficiency of the light effect can be estimated as follows. In particular, if the cross section for the absorption of photons by atoms attached to the steps is taken to be a molecular value of  $10^{-16} \text{ cm}^2$  and the quantum efficiency of the separation of the atom from the step is taken to be 0.01, the frequency of the photostimulated acts of the separation of the atom from the step for the radiation intensity corresponding to a photon flux of  $10^{16} \text{ cm}^{-2} \text{ s}^{-1}$  is  $0.01 \text{ s}^{-1}$ . This is the frequency of the thermal activation of the separation at room temperature and at an activation energy of 0.8 eV (a sodium evaporation heat of 1.14 eV) of the transfer of the attached sodium atom from the step to the terrace. According to these estimates, light can noticeably affect the rate of the relaxation of the shape of the sodium nanoparticles. The evaporation heat of silver is larger than that for sodium. For this reason, high energies of photons are required to transfer attached silver atoms from steps to terraces. This circumstance can explain why illumination did not accelerate the relaxation of the shapes of the silver nanoparticles in our experiments.

## 9. Conclusion

Photostimulated mass transport over the solid surfaces is a wide and promising area of research in which only the very first steps are already made (Leonov et al. 2010). Several directions of the future development may be identified right now. First, the electronic

excited states of the atoms adsorbed onto the surface and interacting with their neighbours are to be investigated thoroughly (Vartanyan et al. 2009b). Of prime interest here are such questions as the localization of the electronic excitation on the metal and semiconductor surfaces, their decay times, the pathways and probabilities of the transformation of the electron energy into atomic displacements. Second, photo-induced surface transport is to be studied on a wider range of objects, in particular, those with a metastable structure because in the case the one can expect more pronounced changes (Vartanyan et al. 2010). Finally, practical implementations of photo-induced surface transport may find their way into industry for non-thermal modification of the surfaces at low temperatures (Vartanyan et al., 2011).

## 10. Acknowledgment

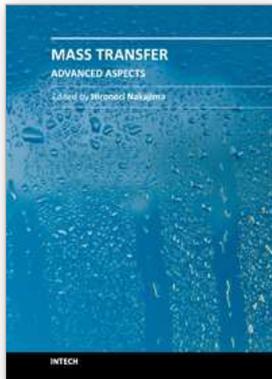
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Our knowledge of mass transfer processes has been extended and applied to various fields of science and engineering including industrial and manufacturing processes in recent years. Since mass transfer is a primordial phenomenon, it plays a key role in the scientific researches and fields of mechanical, energy, environmental, materials, bio, and chemical engineering. In this book, energetic authors provide present advances in scientific findings and technologies, and develop new theoretical models concerning mass transfer. This book brings valuable references for researchers and engineers working in the variety of mass transfer sciences and related fields. Since the constitutive topics cover the advances in broad research areas, the topics will be mutually stimulus and informative to the researchers and engineers in different areas.

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