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Collective migration of adsorbed atoms on a solid surface in the laser radiation field

V.V. Andreev, D.V. Ignat'ev, G.G. Telegin

***Abstract*. The lateral (in the substrate plane) interaction between dipoles induced in particles adsorbed on a solid surface is studied in a comparatively weak laser radiation field with a Gaussian transverse distribution. It is shown that the particles migrate over the surface in the radial direction either outside an illuminated spot with the formation of a 'crater' or inside the spot with the formation of a 'mound'.**

Keywords: *lateral interaction, induced dipole, adsorption, surface migration.*

1. Introduction

Surface phenomena induced by relatively low-power laser radiation have been studied in many theoretical and experimental papers [1 – 7]. These effects attract attention due to the outlook for their wide applications in high technologies. However, the kinetics of surface phenomena induced by optical radiation is not adequately studied so far. The mechanism of interaction of a light field with adsorbed atoms is usually explained by the nonradiative relaxation of the electron interaction of an atom with the surface, which can cause desorption of the atom [1]. At the same time, optical radiation can polarise adsorbed particles, and the interaction between these particles can be sometimes strong [4].

It is important to note that the authors of papers [1 – 7] studied mainly the influence of an external light field on the behaviour of an individual adsorbed particle. The aim of our paper is to investigate the collective behaviour of particles adsorbed on the surface of a dielectric, a semiconductor or a metal.

2. Theoretical model

The one-dimensional kinetic equation describing the establishment of a local adsorption equilibrium in the case of physical adsorption of atoms on the homogeneous surface of a dielectric, a semiconductor or a metal illuminated by light with an inhomogeneous spatial intensity distribution was obtained in Ref. [5]. In the real case of the two-dimensional distribution of the incident radiation with an axial symmetry, this equation has the form [6]

$$\frac{\partial N}{\partial t_1} = S_0 F - \frac{N}{\tau} + \mu \frac{\partial}{r\partial r}\left(rN\frac{\partial U}{\partial r}\right) + D\frac{\partial}{r\partial r}\left(r\frac{\partial N}{\partial r}\right). \qquad (1)$$

Here, t_1 is the current time; r is the radial distance; N is the surface concentration of adsorbed particles (atoms, molecules, etc.); F is the flux of particles from the gas phase to the surface; S_0 is the coefficient of particle adhesion to the surface; τ is the residence time for particles in the adsorbed state; μ is the particle mobility; D is the surface diffusion coefficient; and U is the potential of interaction between adsorbed particles. The values of μ and D are assumed constant.

We assume that the distribution of the amplitude of an external electric field on a solid surface has an axial symmetry. Taking this into account in the averaging over the period of the external electromagnetic field, we obtain the potential energy for a photoinduced dipole in a local electric field produced by the external electric field and the rest of induced dipoles [5]

$$U(r) = -\frac{\varepsilon_0 \alpha E_0^2(r)}{2(1 - A\alpha)^2}, \qquad (2)$$

where ε_0 is the electric constant; α is the polarisability of an individual adsorbed particle; $E_0(r)$ is the amplitude of the electromagnetic field with the radial symmetry directed to the surface; and the parameter A depends on the surface concentration of adsorbed atoms and the angle of incidence and polarisation of the external electromagnetic field [5].

We can write the expression for the time-averaged radiation intensity I in the approximate form

$$I(r) = \varepsilon_0 c E_0^2(r).$$

Let us assume that the time-averaged radiation intensity distribution over the laser-beam cross section is described by a Gaussian

$$I(r) = I_0 \exp(-r^2/r_0^2),$$

where r_0 is the effective radius of the incident laser beam; I_0 is the laser radiation intensity at the point $r = 0$. Taking into account the two last relations, we obtain

V.V. Andreev, D.V. Ignat'ev, G.G. Telegin I.N. Ul'yanov Chuvash State University, Moscow prosp. 15, 428015 Cheboksary, Russia; e-mail: avv@chuvsu.ru

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$$E_0^2(r) = \frac{I_0}{\varepsilon_0 c}\exp(-r^2/r_0^2). \quad (3)$$

We find from (2) and (3) the expression

$$U(r) = -\frac{\alpha I_0}{2c(1-A\alpha)^2}\exp(-r^2/r_0^2) = A_0\exp(-r^2/r_0^2) \quad (4)$$

for the effective potential energy of a particle with the coordinate r on the surface. Below, we assume that the proportionality coefficient A_0 is a constant.

Taking expression (4) into account, we represent equation (1) in the dimensionless form

$$\frac{\partial n}{\partial t} = 1 - n - \xi\frac{\partial}{R\partial R}\left[nR^2\exp(-R^2)\right] + \varphi\frac{\partial}{R\partial R}\left(R\frac{\partial n}{\partial R}\right), \quad (5)$$

where $t = t_1/\tau$; $R = r/r_0$; $n = N/\beta$; $\beta = S_0 F\tau$; $\xi = 2A_0\mu\tau/r_0^2$; and $\varphi = D\tau/r_0^2$. We supplement equation (5) with the initial condition for $t = t_0$

$$n(R, t_0) = n_0(R) \quad (6)$$

and two boundary conditions. It follows from the symmetry of the problem that the boundary condition

$$\frac{\partial n}{\partial R} = 0 \quad (7)$$

should be specified at the point $R = 0$.

This condition means that there is no diffusion flow to the point $R = 0$ or from it. In addition, it follows from equation (5) that the 'drift' part of the flow is zero at the point $R = 0$. It also follows from physical reasoning that the functions $n(R, t)$ and $\partial n/\partial R$ should be limited at $R \to \infty$. To find the asymptotic behaviour of the function $n(R, t)$ for large R, we omit the terms in (5) containing $1/R$ and $\exp(-R^2)$, which tend to zero for large R (taking into account that $\partial n/\partial R$ is limited). As a result, we obtain the equation

$$\frac{\partial n}{\partial t} = 1 - n + \varphi\frac{\partial^2 n}{\partial R^2}. \quad (8)$$

Because the influence of laser radiation can be neglected for $R \to \infty$, we can assume that $\partial n/\partial R = 0$ due to the homogeneity of the particle flux incident on the surface. Equation (8) is solved by the methods described in Ref. [8]. Its solution, satisfying the boundary conditions and the condition $\partial n/\partial R \to 0$ for $R \to \infty$, in the case when $n(R, t_0) = n_0 = \text{const}$, has the form

$$\lim_{R\to\infty} n(R, t) = 1 + (n_0 - 1)\exp(-t). \quad (9)$$

3. Discussion of the results

The coefficient of surface diffusion and the mobility are described by expressions [5]

$$D = W(\Delta r)^2, \quad \mu = \frac{D}{kT}.$$

Here, $W = v\exp[-E_{\text{dif}}/(kT)]$ is the probability of transition of an adsorbed atom to a neighbouring cell in the radial direction per unit time; k is the Boltzmann constant; E_{dif} is the diffusion activation energy; T is the absolute temperature; and Δr is the average distance between neighbouring cells to which atoms adsorbed on the solid surface can enter.

In most cases, the energy $E_{\text{dif}} \approx 0.01 - 0.1$ eV. We will determine the pre-exponential factor v in the expression for W from the condition $hv \approx kT$. Therefore, we have $v \approx 0.84 \times 10^{13}$ s^{-1} at temperature $T = 400$ K. Then, the transition probability is $W \approx (0.46 - 6.3) \times 10^{12}$ s^{-1}, and for $\Delta r \approx 0.6$ nm, the surface diffusion coefficient is $D \approx (0.017 - 0.23) \times 10^{-5}$ m^2 s^{-1}. In this case, the mobility is $\mu \approx (0.03 - 0.4) \times 10^{15}$ m^2 s^{-1} J^{-1}.

In experimental studied reported, for example, in Refs [1, 7], the blue–green radiation from an argon or a He–Cd laser with a power density of 20 or 10 W cm^{-2}, respectively, was focused into a spot of diameter $\sim$2 mm ($r_0 \approx 1$ mm). In this case, we obtain $\varphi \approx (0.17 - 2.3) \times 10^{-4}$ for $\tau \approx 10^{-4}$ s. However, the parameter τ very strongly depends on the properties of a particular solid surface and on the characteristics of a particle adsorbed on the surface. For example, for Na atoms adsorbed on glass, τ can be a few seconds [1, 7]. For $\tau = 1$ s, we obtain $\varphi \approx 0.17 - 2.3$.

We obtain from expression (4)

$$A_0 = -\frac{\alpha I_0}{2c(1-A\alpha)^2}.$$

The value of A in this expression can be estimated as [5]

$$A \approx \frac{2\pi N}{\Delta r}.$$

For the surface concentration of adsorbed atoms $N \approx 10^{20}$ m^{-2}, we have $A \approx 1.34 \times 10^{30}$ m^{-3}. The polarisability α is usually $\sim 10^{-30}$ m^3. Then, for the values of parameters specified above, we obtain $A_0 \approx -3.7 \times 10^{-33}$ J for the 20 W cm^{-2} radiation from the argon laser and $A_0 \approx -1.85 \times 10^{-33}$ J for the 10 W cm^{-2} radiation from the He–Cd laser. In this case, the parameter $\xi = -(0.2 - 2.65) \times 10^{-16}$ for the argon laser and $-(0.1 - 1.33) \times 10^{-16}$ for the He–Cd laser.

It is obvious that, when the parameter φ is more than ten orders of magnitude greater than ξ, the effect caused by the lateral interaction between induced dipoles on a solid surface will not be observed. However, the parameter A_0 can change in a very broad range due to the presence of the term $(1 - A\alpha)^2$ in the denominator and can become very great when this term tends to zero (i.e., $A\alpha \to 1$). The, the parameter ξ can be comparable with the value of φ or even exceed it by a few orders of magnitude. Thus, for $|1 - A\alpha| \approx 10^{-6}$, the parameters ξ and φ will be already of the same order of magnitude. Note that for $|1 - A\alpha| \approx 10^{-8}$, the parameter ξ is $-(0.2 - 2.65)$ for the argon laser and $-(0.1 - 1.33)$ for the He–Cd laser.

The values of $|1 - A\alpha|$ close to zero correspond to the case when a weak external electric field can induce considerable dipole moments in adsorbed particles. As a result, the local electric field produced at a given point by all adsorbed particles and the external field will exceed the latter in the absolute value by many times.

Therefore, the effect under study strongly depends on the type of adsorbed atoms and the properties of a solid surface on which adsorption occurs, as well as on the laser

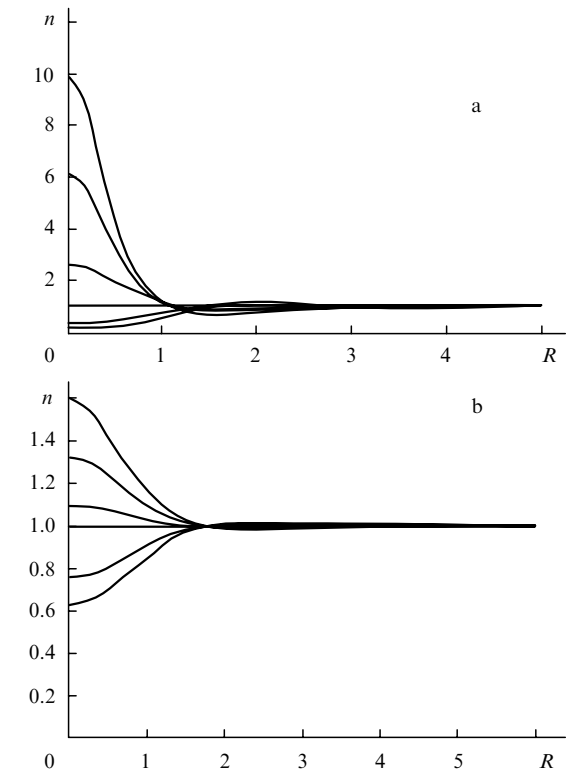

Figure 1. Dependences of the dimensionless surface concentration n on the dimensionless distance R for $\varphi = 1$, $\xi = -7, -5, -3, 0, 3, 10$ (a) and $\varphi = 10$, $\xi = -10, -6, -2, 0, 6, 10$ (b). The values of ξ increase from top to bottom at the point $R = 0$.

radiation frequency because the polarisability α is a function of the laser frequency. Note also that the sign of ξ depends on the direction of a local electric field. If the field is directed along the radius to the centre, then the sign of ξ should be positive.

Let us analyse first a steady-state process [i.e., we assume that $\partial n/\partial t = 0$ in (5)]. In this case, the boundary condition (9) takes the form

$$\lim_{R\to\infty}(R, t) = 1. \tag{10}$$

The results of numerical integration of equation (5) with boundary conditions (7) and (10) are presented in Fig. 1. One can see that, as the parameter φ increases the distribution $n(R)$ of the concentration on the surface becomes more homogeneous. If φ increases due to an increase in the surface diffusion coefficient, it is obvious that the distribution becomes more homogeneous. If the parameter φ increases due to an increase in τ, it is also clear that an increase in the residence time for particles in the adsorbed state also should facilitate the establishment of a more homogeneous distribution of their surface concentration. Finally, if the parameter φ increases due to a decrease in z_0, the surface distribution of adsorbed particles becomes more homogeneous because the region illuminated by laser radiation is smaller.

Figure 1 also shows that, as the absolute value of the parameter ξ increases, the distribution $n(R)$ becomes more inhomogeneous. The increase in $|\xi|$ corresponds to the increase in the efficiency of interaction of laser radiation with adsorbed particles, resulting in the effect observed.

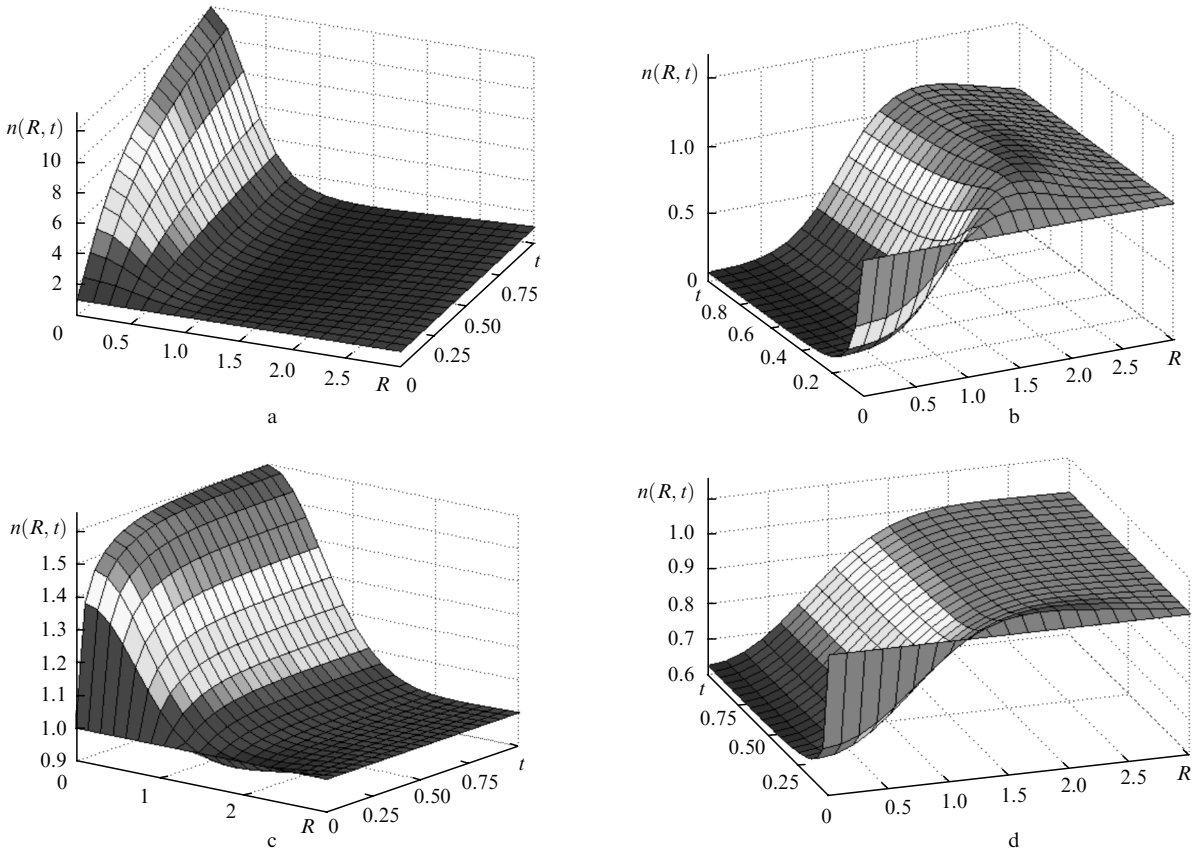

Figure 2. Time evolutions of the distribution profile for the dimensionless surface concentration n at the initial concentration $n_0 = 1$ for $\varphi = 1$, $\xi = -10$ (a); $\varphi = 1$, $\xi = -10$ (b); $\varphi = 10$, $\xi = -10$ (c); and $\varphi = 10$, $\xi = 10$ (d).

Some of the results of the numerical solution of nonstationary equation (5) with boundary conditions (7) and (9) for the case $n(R, t_0) = n_0 = \text{const}$ are presented in Figs 2a–d. These figures demonstrate the time evolution of inhomogeneous planar structures on the solid surface exposed to laser radiation for different values of the parameters φ и ξ. The dependences presented in Figs 2a–d show that, as a rule, the steady-state regime is established faster with increasing φ. This is explained either by a more intense surface diffusion of the adsorbed particles or by the fact that they remain in the adsorbed state for a longer time (when the increase in φ is caused by the increase in τ).

In addition, as mentioned above, the value of φ can be increased by decreasing the effective radius r_0 of the laser beam. In this case, the area of the illuminated adsorption layer becomes smaller, which obviously also facilitates a more rapid establishment of the stationary state. At the same time, an increase in the absolute value of the parameter ξ leads to the increase in the time t_s of establishing the stationary state.

Figure 3 shows the numerically calculated dependences of the time t_s on the initial surface concentration n_0 of adsorbed particles. One can see that the time t_s first decreases with n_0 and then increases. The minimum value of t_s is achieved for $n_0 = 1$.

The increase in the time t_s required for achieving the stationary state at high concentrations n_0 can be explained by the fact that the number of free adsorption centres is small in this case, which requires a longer time for the redistribution of particles in the external field. In the case of low concentrations n_0, the potential energy of interaction between the particles is quite low, and therefore a longer time is required for the establishment of the stationary distribution.

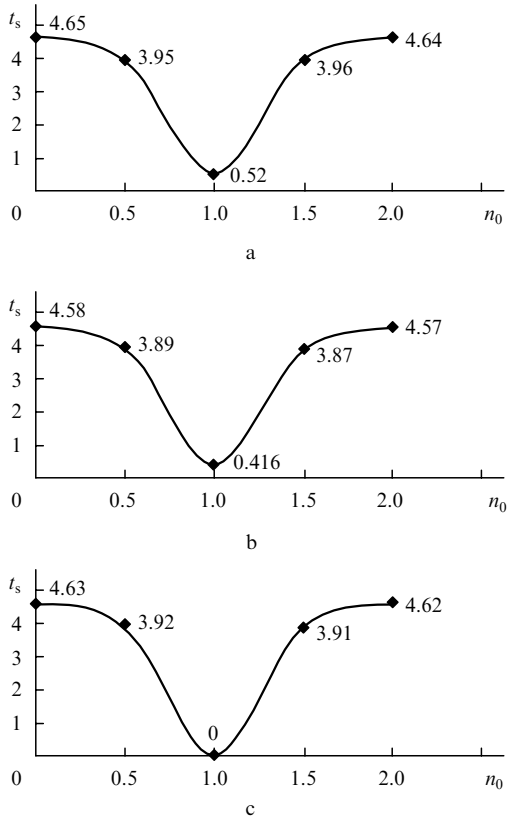

Figure 3. Dependences of the dimensionless time t_s of the establishment of the stationary regime on the initial concentration n_0 at the point $R = 0$ for $\varphi = 10$, $\xi = -10$ (a), 10 (b), and 0 (c).

The dependences presented in Figs 1 and 2 show that the lateral interaction of the induced dipoles results in the surface migration of adsorbed particles in the radial direction outside the illuminated region and in the formation of a 'crater' if $\xi > 0$ or in the migration of the particles into the illuminated region and in the formation of a 'mound' if $\xi < 0$. These results are, in particular, in qualitative agreement with the experiment described in Ref. [7].

Therefore, the analysis performed above provides a physical basis for the fabrication of planar structures of various configurations using laser radiation.

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