Photoemission of neutral atoms from the surface of a metal

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The results are given of an experimental study of photoevaporation of a sodium metal film. It is shown that optical radiation results in photolysis of the surface and photoemission of neutral metal atoms which is independent of the thermal effect of this radiation. The dependence of the photoevaporation rate on the intensity and wavelength of the exciting radiation, and on the film temperature were determined. It was found that the kinetic energy of atoms emitted by a surface considerably exceeded the thermal energy and amounted to 0.4–0.5 eV. The photolysis is explained by the photoexcitation of the metal electronics to states where they are located in lattice sites. The degree of such localization increases with the displacement of the site from the surface. It is assumed that in the case of large displacements these states degenerate into a repulsive potential describing the interaction between a neutral atom and the surface.

Nonthermal evaporation of a sodium metal film as a result of interaction with radiation from a cw He–Ne laser was reported in Ref. 1. We shall now give the results of further investigations of this phenomenon. In spite of the preliminary nature of these results, they are sufficient to draw the conclusion that the interaction of optical radiation with alkali metal films results in photolysis of the surface and photoemission of neutral metal atoms.

In a sense, the new effect is similar to electron-beam and optically stimulated desorption of molecules and ions from the surface of a metal.[2-5] Although such effects have been known for a long time, there is as yet no generally accepted theoretical model to describe them (for critical reviews see Refs. 4 and 5). This is due to the difficulties encountered in the description of surface states and also due to the small number and the contradictory nature of the experimental results. We shall consider the photodesorption of metal atoms from the surface of the same metal, which greatly simplifies the experimental situation and makes it possible to use fairly simple investigation methods.

Most of the experiments were carried out on sodium metal films evaporated on sapphire plate surfaces. These films were evaporated repeatedly in a sealed glass cell where the residual pressure was on the order of 10^{-5}–10^{-6} Torr. Such repetition of deposition-evaporation cycles made it possible to avoid formation of layers of oxides or other chemical compounds on the surface of a film (all possible chemical compounds of sodium are much less volatile than the metal itself). The film thickness was varied by altering the evaporation time and was inferred from transmission in the visible part of the spectrum. As a rule, experiments were carried out on films with optical density $\lesssim 0.3$. The structure of a film of this kind could not be resolved with the aid of an optical microscope; its thickness, deduced from the known optical characteristics of a metal[6] (on the assumption that the film was continuous), amounted to 300–500 Å. As the film thickness was increased, its structure became clearly of the island type: large drops of the metal were observed (their diameters were 1–100 μm) and the space between them was filled with smaller drops.

The main results were as follows.

1. Interaction of optical radiation of power density 10^2–10^4 W/cm^2 with a metal film of this kind resulted in the evaporation of the film in the region where the laser beam was focused. A determination of the intensity of the beam transmitted by the film made it possible to established that the thickness l (deduced from the extinction coefficient) of a film of low optical density ($\leqslant 0.3$) decreased linearly with time (Fig. 1). This dependence makes it possible to introduce readily a simple quantitative characteristic of the process: this was the film evaporation rate w, defined as the reciprocal of the time in which the film thickness was halved. It should be pointed out that the kinetic of evaporation of thicker films with a clear island structure became much more complex: it reflected the presence of large and small drops in the film (and the large ones evaporated more slowly). Therefore, the majority of our experiments were carried out on thin continuous films.

2. It was established that the rate of evaporation of a metal film was a linear function of the incident radiation power (Fig. 1), which indicated clearly that the process was nonthermal (the rate of thermal evaporation of a metal is an exponential function of the film temperature and the latter is related linearly to the power of the incident radiation). Esti-
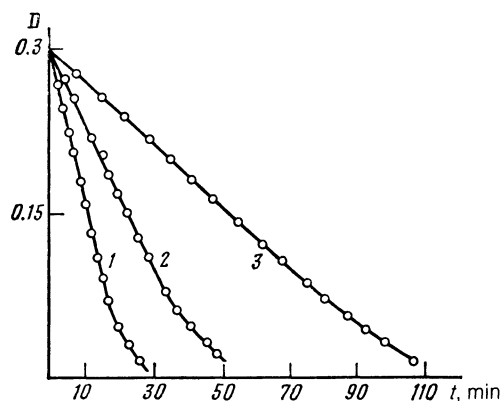

FIG. 1. Optical density ($D = kl$) of a sodium metal film as a function of the duration of its irradiation with focused He–Ne laser radiation. The intensity of the radiation for curves 2 and 3 was reduced by factors of 2.2 and 4.76, respectively, compared with that for curve 1. The laser radiation power was 10 mW and the laser beam was focused into a spot ≈ 0.1 mm in diameter.

mates of the possible temperature rise of the metal at the highest power density of the incident radiation (10^4 W/cm^2) were made allowing for the reflection coefficient and for the thermal conductivities of the metal and the sapphire substrate. They indicated that the temperature rise did not exceed 10 K. Measurements of the radiation power density and of the film evaporation time, and estimates of the film thickness (from the initial absorption) enabled us to find roughly the quantum efficiency of the evaporation process, which was 10^{-6}–10^{-7} relative to the incident He-Ne laser radiation.

3. The influence of the film structure on the process of photoevaporation was determined in several experiments in which a similar effect was studied in the case of a bulk piece of metallic sodium. With this in mind, we focused radiation from an argon laser to form a spot 40–50 μm in diameter on a mirror-smooth surface of a solidified metal drop of sodium which was 4–5 mm in diameter. After 1-h irradiation it was found that a recess 40–50 μm in diameter and 10–20 μm deep formed on the surface of the drop. A recess of the same dimensions was observed also when the laser power was reduced by a fctor of 2–5, provided that the irradiation time was suitably increased, which was once again proof of the nonthermal nature of the metal evaporation process.

4. Figure 2 shows the spectral dependence of the film evaporation rate determined using focused radiation from a mercury lamp (when the necessary spectral interval was selected by a set of optical filters) and also using argon and He-Cd laser radiations. This dependence was obtained by determining the initial absorption in the film, the kinetics of its evaporation, the energy of the incident radiation, and the sized of the evaporated spot in the film. In these experiments we used the same film. We have represented the dispersion of the extinction coefficient in Fig. 2 by a dashed curve. The horizontal segments in Fig. 2 represent the transmission bands of the optical filters used and the vertical segments give the error in the determination of the evaporation rate. Some of the energy characteristics of metallic sodium are identified on the abscissa in Fig. 2: $E_a = 1.13$ eV is the binding energy of a sodium atom to the metal; $E_{iph} = 2$ eV is the threshold of the internal photoelectric effect; $E_w = 2.25$ eV is the work function of the electron emitted from the metal; $E_F = 3.25$ eV is the Fermi energy.[7]
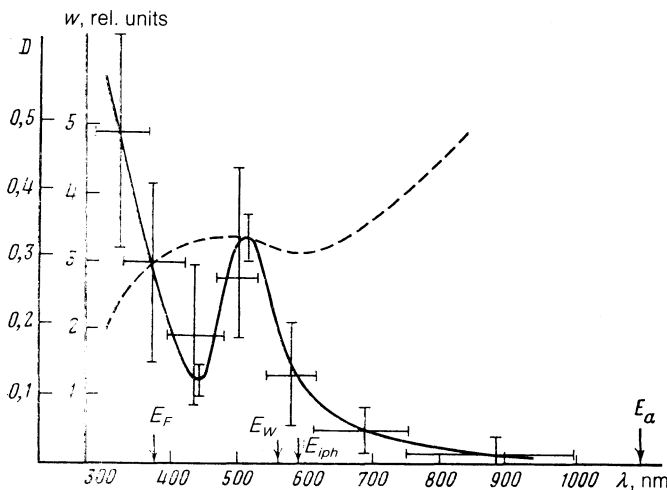
5. The distribution of the evaporated sodium atoms with respect of their kinetic energy was determined using the "time-of-flight" method. The deposited metal was evaporated by an unfocused pulse at the second harmonic of neodymium laser radiation ($\lambda = 5300$ Å, $\Delta t = 10^{-8}$ sec, $I \sim 10^4$–10^5 W/cm^2) and the atoms emitted from the surface were detected by recording their luminescence excited with resonance radiation from a cw single-mode dye laser ($\lambda = 5890$ Å, $I = 50$ mW), which was in the form of a beam 0.1 mm in diameter traveling parallel to the film surface at a distance of 60 mm from it. A luminescence pulse due to the atoms which left the surface as a result of evaporation was detected with a photomultiplier and the signal was recorded using a storage oscilloscope. The same oscilloscope stored also the exciting pulse of the second harmonic of neodymium laser radiation (this pulse triggered the recording system). A typical luminescence signal obtained in this way is shown in Fig. 3. Here the short pulse at the beginning of the sweep represents the second harmonic of neodymium laser radiation and the second much longer pulse is the luminescence signal due to the evaporated sodium atoms.

We checked that the recorded signal disappeared completely when the dye laser frequency was detuned away from the frequency of the $3S_{1/2}$–$3P_{3/2}$ transition in the sodium atom; it was established that the amplitude of the luminescence signal due to the sodium atoms depended linearly on the power of the pulse which evaporated the film (right up to power densities of 10^4–10^5 W/cm^2), whereas the profile of the signal and the position of its maximum were independent of the power of the evaporating pulse.

The actual profile of the luminescence pulse due to the sodium atoms did not represent quite accurately the distribution of the velocities of the atoms, because the trailing part of the luminescence pulse probably included contributions from atoms reflected repeatedly by the cell walls until they reached the region of resonantly exciting radiation; this was due to the small diameter (30 mm) of the cell containing metallic sodium. Therefore, the results of this experiment could be used only to find the most probable energy of the evaporated atoms (corresponding to the maximum of a pulse). It was 0.4–0.5 eV. It should be recalled that the enegy of a photon in the radiation exciting the film was 2.34 eV and the energy required to detach an atom from the surface was 1.13 eV.

The same apparatus was used, for the sake of comparison, to study also the process of ordinary thermal evaporation of a metal film. In this case a film was irradiated with neodymium laser pulses ($\lambda = 10\,600$ Å, $\Delta t = 10^{-8}$ sec, $I \sim 10^6$ W/cm^2) because in this case there was no photoevaporation effect (Fig. 2). The luminescence signal due to thermally evaporated atoms was also determined (dashed

FIG. 2. Dependence of the rate of evaporation w of a sodium film on the wavelength of the interacting radiation.
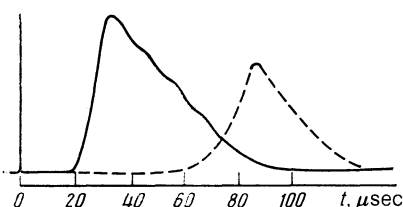

FIG. 3. Oscillogram of a fluorescence pulse produced by atoms flying away from the surface of metal film (see text).
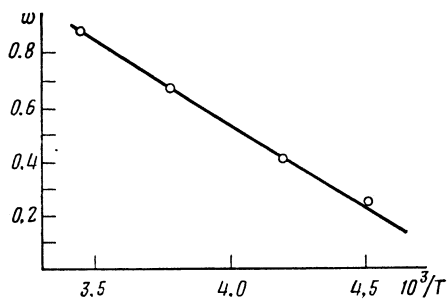
FIG. 4. Temperature dependence of the film evaporation rate w.

curve in Fig. 3). Clearly, this signal corresponded to much lower (by about an order of magnitude) kinetic energies of the atoms (0.04 eV); the amplitude of the signal depended so strongly on the power of the exciting pulses that this dependence could not be established because of the narrow dynamic range of the recording system.

6. It was found that the rate of photoevaporation of a film depended exponentially on its temperature (Fig. 4). This dependence was investigated by evaporating a film with argon laser radiation and cooling the substrate carrying the film by a jet of evaporating nitrogen. It was found that the evaporation rate obeyed

$$w \propto a \exp(-\Delta E/kT),$$

where $\Delta E = 1000 \pm 200$ cm^{-1}, i.e., the photoevaporation process had a fairly large activation threshold.

7. Our attempts to detect the photoevaporation effect in the case of several other metal films showed that it occurred in the case of cesium films. However, there was no such effect at all in the case of zinc, thallium, and cadmium films (in all these experiments we used argon laser radiation). The set of the investigated substances was governed by the natural requirement that the binding energy of an atom to the metal should be less than the photon energy of the interacting radiation.

In the case of cadmium we found that at the highest power densities of the incident radiation ($\sim 10^3$–10^4 W/cm^2) the film evaporated rapidly (in a matter of a few seconds), but the effect disappeared completely when the laser power density was halved (there was no significant increase in the transparency of the film after irradiation lasting several hours). Such a strong dependence of the rate of evaporation of the cadmium films on the intensity of the incident radiation demonstrated that the evaporation process was thermal in nature.

All these experimental results led us to the conclusion that the interaction of optical radiation with some alkali metal films results in photolysis of the surface layers. In our opinion, this effect is different from the familiar photodesorption of atoms and molecules from substrates representing metals, insulators, or semiconductors not identical with the absorbed atoms or molecules.[2-5] In fact, an atom adsorbed on the surface of, for example, an insulator is assumed to retain its specific properties in the sense that the electron state of this atom may be strongly modified by the interaction with the surface, but it is still localized near the ion core. The surface of a metal cannot obviously be regarded as a layer of adsorbed atoms. If we leave aside the complex problem of the surface structure, then in an idealized representation the main difference between adsorbed atoms and the surface atoms of a metal is the sharing the delocalization of electrons in the latter case and the associated considerable restrictions on the ability to describe them in terms of the interatomic potentials. There is as yet no sound and self-consistent theory of the photoexcitation of atoms on the surface of a metal and the development of such a theory would be a difficult task.

The strong temperature dependence of the efficiency of the new effect suggests that vibrations of the ion lattice of the metal play an important role is the photoevaporation process. We recall that the majority of our experiments were carried out at room temperature, i.e., near the melting points of the metals for which the effect was observed (the melting points of sodium and cesium are 97.5° C and 36°C).

It is qualitatively clear that a displacement of the surface site in the metal lattice may result in partial localization of an electron at a given site. In the band description such a quasilocalized state should exhibit a number of singularities in their density due to displacement of a surface site of a semiinfinite regular lattice. These singularities (resonances) should become sharper as the site moves away from the lattice (which corresponds to more complete localization of an electron) and the energy positions of the singularities should tend to the limit representing the energies of the ground (and excited) states of an atom which has left the surface. The widths of these resonances determine the electron localization time in the one-particle approximation. These resonances with energies above and below the limiting value may be compared with two interaction potentials, repulsive and attractive, which are used to describe the adiabatically slow removal of an atom from the surface.

In this qualitative description the action of optical radiation reduces either to direct excitation of such quasilocalized states or to electron filling of those states above the Fermi level, which at large distances from the surface go over into a repulsive potential between the atom and the surface. The smaller the width of such quasilocalized states, the longer their lifetime and the further that the distance of a site can move away from the surface, which sharpens the resonance and this may result in complete detachment of an atom. Similar processes occur in an excited energy band if the photon energy is sufficient for the excitation.

A similar qualitative description of the process accounts for two experimental observations. The first is the inelasticity of the process of photodetachment of an atom: the energy of an absorbed photon $\hbar\omega = 2.34$ eV exceeds the sum of the energy of an atom flowing away from the surface and the energy of its binding to the metal (0.4 + 1.13 eV). The excess energy is transferred to that subsystem which ensures the energy relaxation of electrons at the surface. The second observation is an increase in the efficiency of photodetachment as the temperature increases: it may be explained by the fact that an increase in temperature increases the amplitude of the vibrations on the surface atom and, therefore, the localization time of electrons, which is needed to allow an atom to move away from the surface until an electron is no longer in the repulsive resonance region.

Obviously, this qualitative description does not deal with the important topics of nonadiabatic coupling of electron transitions to the motion of a site or the problems of the electron-electron correlation. Moreover, one could describe

the main photodetachment process in a different way, for example, by invoking localization due to modification (planar or normal) of the surface. Further experimental and theoretical investigations of these topics are needed.

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