Photostimulated desorption of metal atoms from surfaces of transparent insulators

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It has been found that illumination of the surface of a transparent insulator affects the adsorption of metal atoms there. It has also been found that there is a photoevaporation of the atoms making up a metal film on such a surface. The mechanism for the effect of the light is nonthermal in all cases.

The overwhelming majority of the many recent studies[1-3] of the photosorption and desorption of particles at solid surfaces have dealt with the sorption and desorption of molecules at surfaces that absorb radiation. In this letter we report observing clear evidence of the photodesorption and sorption of metal atoms on the surface of a transparent insulator illuminated by a beam from a low-power cw laser. Together, the observations demonstrate that the events that occur are not of a thermal nature and that the interaction of the light with adsorbed atoms is linear.

1. Most of the present experiments dealt with adsorption of sodium atoms on the surface of a sapphire plate. A beam of sodium atoms was deposited on the plate at room temperature; the plate was illuminated with a laser beam at the same time. The power density of the laser beam was adjusted by focusing. The thickness of the resulting film reached 100–2000 Å; the deposition rate was varied over the range 0.1–5 Å/s. The residual gas pressure in the chamber was no greater than 10^{-6} torr. No special measures beyond baking in a vacuum were taken to clean the adsorbing surface.

The first set of experiments was carried out with light that was resonant with the $3S$–$3P$ transition of the sodium atoms (5890 Å; this wavelength was chosen because the original purpose of the study was to learn about the accommodation of excited atoms by the surface). We found that a metal film would not form on the illuminated part of the surface. We quickly learned that the effect persisted when the frequency of the laser was tuned 100 Å away from the resonance and also when we switched to the wavelength 6328 Å (from a He-Ne laser). The effect was totally absent when we used the wavelength 1.15 μm from the He-Ne laser, although the output power in this line was three times that in the 6328-Å line in the same spot.

There is a threshold for the effect in the sense that, at a given beam power density, the situation does not change as the deposition rate is varied up to a certain level, but above this level the effect disappears, and a metal film forms in the illuminated region. This threshold deposition rate increases with increasing laser power density.

The same effect was observed during the deposition of zinc and tin on sapphire; it was not observed in the case of silver or aluminum. During the deposition of aluminum on fused quartz we observed an effect of the opposite sign: The film thickness in the aluminum zone was greater than that in the nonilluminated zone. Only an argon laser was used in the experiments with these metals.

2. The observed effect—an optical control of the sorption of the metal— is of a nonthermal nature. The primary evidence for this assertion comes from estimates of a possible heating of the surface by the laser beam. At the power densities used (1–100 mW over an area of 10^{-1}–10 mm^2) and at the low absorption level, the heating could not exceed some tens of degrees. The effect did not change when the substrate was cooled to $-30\,°$C. Further evidence that the process is not of a thermal nature comes from the high spatial resolution: When the substrate is illuminated by a light focused with a cylindrical lens, slit-shaped apertures 20 μm wide are formed in the film. The duration of the deposition is much longer than the thermal relaxation time. The last piece of evidence is the "red limit" on the effect.

We do not have enough experimental data to go into a detailed discussion of the mechanism for the observed effects. However, the fact that they occur at genuinely moderate light intensities and the fact that they are not of a thermal nature suggest that they are related to an electronic excitation of quasimolecular systems which are formed in the interaction of an atom with the surface. A radiationless relaxation of such an excitation can lead to a dissociation of the system, i.e., to the desorption of the atom. Mechanisms of this type have been discussed[1,4] in connection with the desorption of electronically and vibrationally excited molecules. Pursuing this possibility, we see why there would be a threshold in the deposition rate: At a given photodesorption probability (determined by the cross section for the process and the light intensity), the

competition between deposition and desorption would lead to a steady-state concentration of adsorbed atoms. As long as the deposition rate is small, the adsorbed atoms would not form a solid film. When the deposition rate reaches the threshold value, the atoms form a monolayer on the surface, and at this point the photodesorption from the surface of the insulator gives way to a photodetachment of atoms from the surface of the monolayer. The cross section for this process is much smaller (or zero; see Section 3 below), so that the film thickness would begin to grow without hindrance. The threshold deposition condition yields a rough estimate of 10^{-18} cm^2 for the effective cross section for the photodesorption of sodium from sapphire.

The effect of the opposite sign which occurs during the deposition of aluminum on quartz also fits into the model of the photoexcitation of adsorbed atoms. The excitation would change the interaction potential between the adsorbed atom and the surface,[1,5] raising the additional possibility of a relaxation of the translational (or vibrational) energy of the atom, so that the probability for the accommodation of the atom on the surface would increase.

3. In addition to this effect of light on the deposition of a metal film, we have observed a "photoevaporation" of an existing metal film. The light causes the film thickness to decrease linearly over time. This process is observed only for the sodium films. The probability for the photodetachment of an atom from a metal film is much lower than that for the desorption of an atom from the surface of sapphire. While a few minutes are sufficient for the deposition of a film with a hole in the laser beam, tens of minutes are required to burn a hole through an existing film under the same conditions. The quantum yield of the process is estimated to be 10^{-7}–10^{-8}.

The photoevaporation of sodium is also of a nonthermal nature. This assertion is supported by the same arguments as for the photodesorption from the surface. In addition, there is the fact that the photoevaporation of a film of a given thickness depends on only the bombardment dose; i.e., the evaporation rate increases linearly with the intensity. This result is in sharp contradiction of a model of thermal evaporation, because of the exponential temperature dependence of the vapor pressure above the metal.

We note in conclusion that a study of the photostimulated growth and evaporation of metal films, which are easily monitored by optical methods, has significant advantages over the conventional methods for studying photosorption and photodesorption.

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