

Photodesorption of metal ions in a semiconductor-water system

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The effect of a low-intensity laser beam on the desorption of metal ions from the surface of a semiconductor has been studied. The results reveal an increase in the desorption of potassium ions from a silicon surface during illumination by an argon laser at an intensity of 100 mW/cm^2 .

Particles adsorbed on a solid surface strongly influence processes which occur in the solid and in the medium in contact with it. For example, an induced change in adsorption properties of one component of a gas mixture or solution may disrupt a phase equilibrium,^{1,2} and metal molecules or ions on the surface of a solid may alter its electrical properties.³ There is accordingly the interesting problem in surface physics of seeking new possibilities for altering the composition and number of adsorbed particles. Some promising methods here are contactless methods, e.g., a method involving the photodesorption which occurs during exposure of an interface to laser light. Resonant excited molecules on the surface either are ionized and carried off by the external electric field or, while remaining in the molecular state, acquire an energy sufficient to overcome the adsorption potential.^{4,5}

It is possible, however, to change the number of molecules on a surface by acting on the solid, rather than by acting directly on these molecules. For example, the laser illumination of a semiconductor in an electrolytic solution can make it possible to deposit metals on the surface or to etch it.^{6,7} These processes occur at a light intensity $I \approx 10^3 \text{ W/cm}^2$, which is required for producing a significant thermoelastic stress in a surface layer of the semiconductor. A nonuniform heating of this sort usually results in a change in the number and distribution of crystal lattice defects, and such changes are often undesirable. For this reason, methods for changing the quantity of a surface

impurity which do not alter interior inhomogeneity of a sample are of interest for imparting desired surface properties to semiconductors.

In this letter we are reporting the results of a study of the effect of low-intensity laser illumination on the desorption of metal ions from the surface of a semiconductor. In the experiments, a system consisting of a semiconductor and deionized water ($\rho_{\text{H}_2\text{O}} \approx 20 \text{ M}\Omega \cdot \text{cm}$ at $T = 293 \text{ K}$) was exposed to the beam from argon laser. The light intensity was $I \approx 10^2 \text{ mW/cm}^2$, and the wavelength $\lambda = 514 \text{ nm}$. After several *n*-type silicon substrates (type KÉF-4.5, with a [100] surface orientation) were washed in detergents, they were contaminated with potassium ions (K^+) in a 1% KCl solution. The semiconductor substrate was illuminated in a quartz cell filled with deionized water. The exposure time ranged from a few minutes to a few tens of minutes. We note at the outset that over this time we observed no effect of the illumination time on the photodesorption process.

To determine the surface concentration of K^+ ions on the plates, we used a thermal method to form the oxide (SiO_2), and we deposited aluminum contact surfaces; i.e., we formed a metal-insulator-semiconductor structure. The surface state and the state of the Si-SiO₂ interface were evaluated qualitatively by a contact-potential-difference method, through measurements of the breakdown field of the insulator (E_b), which depends on the K^+ concentration. We compared regions of the semiconductor surface which were exposed to laser light and those that were not exposed to it. The breakdown electric field for the insulator in the metal-insulator-semiconductor structure was measured by applying an enriching potential to the metal electrode. Figure 1 shows E_b as a function of the discrete coordinate along the surface of the plate. We see a gradual increase in E_b ; i.e., the decrease in the number of K^+ ions in the insulator is a reflection of a Gaussian intensity profile of the laser light. After a certain illumination intensity is exceeded, the growth of E_b comes to a halt, and the behavior is approximately that predicted theoretically. At the boundary of the "shadow" the field E_b decreases sharply, because of impurity centers in the insulator. Consequently, when the surface of the semiconductor is illuminated, changes occur in its adsorption properties, and the number of adsorbed potassium ions decreases. These conclusions are confirmed by the changes in the relaxation time of the inversion capacitance in "darkness," τ , at $T = 293 \text{ K}$ as a function of the extent of the illumination. The relaxation time was found through measurements of the voltage-capacitance characteristics of the metal-insulator-semiconductor structures. The results of these

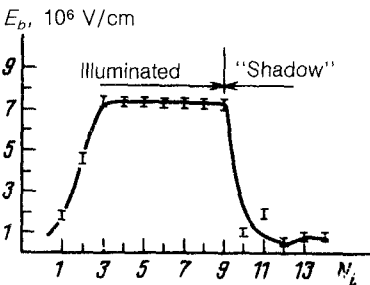


FIG. 1. Distribution of the breakdown field E_b along the surface of the sample (N_i is the index of the contact surface). The exposure time was 10 min.

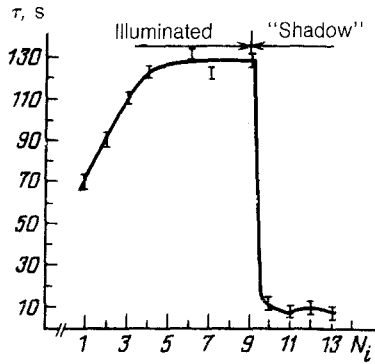


FIG. 2. Profile of the relaxation time τ along the coordinate along the surface of the sample (N_i is the index of the contact surface). The illumination time was 10 min.

measurements are shown in Fig. 2. The profile of τ along the coordinate is similar to that of E_b . The increase in τ in the region of strong illumination can be attributed to a decrease in the surface concentration of K^+ .

The clearest confirmation of a photodesorption of K^+ ions comes from measurements of the depth distribution of K^+ in the Si-SiO₂ system, carried out by a method of secondary-ion mass spectrometry. We measured the behavior of the current of secondary ions of silicon ($^{28}Si^{++}$) and the isotope ions $^{18}O^{--}$, $^{39}K^+$, and $^{35}Cl^-$ in illuminated and control regions of a plate. Figure 3 shows depth distributions of the ion concentration in the semiconductor. We see that there are essentially no K^+ ions in the surface region of the semiconductor which has been illuminated, while in a region of the semiconductor which has not been illuminated these ions are present, as a result of a diffusion from the surface during the thermal oxidation of the silicon. This effect can be attributed to a sharp increase in the desorption of K^+ ions from the silicon surface during the exposure to laser light.

In summary, this multifaceted study including electrical measurements of the Si-SiO₂ structure and measurements by secondary-ion mass spectrometry leads to the

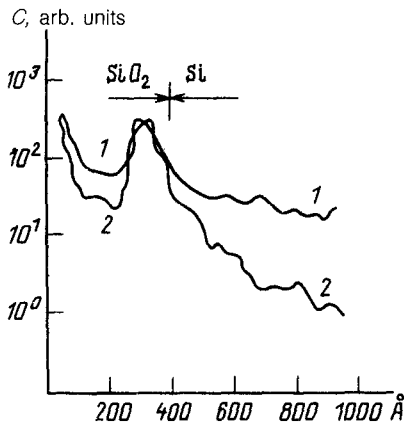


FIG. 3. Depth distribution of K^+ ions in the Si-SiO₂ sample. 1—Control sample; 2—after exposure to laser light for 10 min.

conclusion that laser light can be used to control the desorption of positively charged ions from the surface of a semiconductor. The sharp changes in the adsorption properties of the system cannot be explained on the basis of thermal effects, because the intensity of the light was clearly too low to heat the surface. Further evidence for this conclusion comes from the presence of a sharp boundary between the breakdown voltages in the illuminated and shadowed regions. A direct effect on the adsorbed ions can also be ruled out, because the frequencies of the light are not the same as the resonant frequencies of the ions or of their bonds with the semiconductor. It might be suggested that photoexcitation of the semiconductor is playing a major role here. The internal photoelectric effect (with a photon energy of 2.4 eV and a band gap of 1.12 eV) would generate excited electrons into the conduction band. The adsorbed K^+ and Cl^- ions might be thought of as impurity centers in a surface layer of the semiconductor (the surface density of the K^+ ions is $\approx 10^{14} \text{ cm}^{-2}$). We know that potassium has an energy level in the band gap of silicon, lying $\Delta E = 0.04 \text{ eV}$ below the conduction band.⁸ Since the time scale of the relaxation of injected electrons at charged impurities is considerably shorter than the time scale of the interband relaxation, the electrons recombine more rapidly at K^+ ions. The adsorption energy of the potassium atoms is substantially lower than that of the ions, so their number on the surface decreases. The semiconductor accordingly becomes positively charged. This process also promotes a desorption of K^+ ions and a stronger binding of the negative Cl^- ions. The energy balance can be maintained through the participation of phonon excitations in the process.

Similar experiments on the photodesorption from a silicon surface have been carried out with ions of sodium, copper, and iron. The nature of the desorption of these ions is similar to that of potassium ions. It may be that this effect is of a general nature and will be seen in a longer list of metals and semiconductors.

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