

Selective laser control of electrochemical processes

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(Submitted 5 April 1984)

Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 10, 464–466 (25 May 1984)

Electrochemical processes can be selectively controlled by laser beams. In particular, the deposition of ions of a particular species on an electrode can be accelerated or retarded.

Kozlova *et al.*¹ have shown experimentally that laser bombardment of a metal-electrolyte interface can increase the rates of several electrochemical processes to levels 20–30 times the rates of the same reactions under equivalent local thermal conditions. Kozlova *et al.*¹ suggested that the increases in the reaction rates were caused by a convection of nonuniformly heated electrolyte near the electrode. An alternative explanation is that the acceleration of the reactions in Ref. 1 was caused by thermodiffusion processes during the selective absorption of the laser beam by electrolyte ions. In the present letter we report an effort to determine the role played by this alternative mechanism.

The present experiments were carried out with a 50-W YAG:Nd laser ($\lambda = 1.06 \mu\text{m}$). Two steel electrodes (an annular one and a solid one) lie inside a glass cell holding an aqueous solution of FeCl_3 , which absorbs this laser beam. The electrodes are oriented perpendicular to the laser beam and are separated from each other by a distance on the order of the absorption length. Convection in the electrolyte is studied by a transmission shadow method. The results show that when the laser beam is applied the masses of both electrodes decrease, but not identically: The mass of the “cold” electrode (the remote one) decreases twice as fast. No significant dependence of the rate of

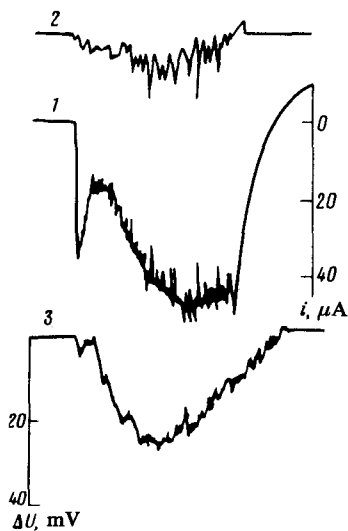


FIG. 1. 1—Time evolution of the current in the circuit of the electrodes, $i(t)$; 2—time evolution of the solenoid current, $i_s(t)$; 3—voltage across the electrodes. Curves 1 and 2 were measured simultaneously.

the electrochemical reaction on the convection intensity in the liquid was found. Since the process occurred in the absence of external electric fields, we have two possibilities for explaining the observed results: Either the dissolution of the electrodes is accelerated by some autocatalytic reactions, similar to the reduction of nickel from special solutions,¹ or electric fields and currents are generated in the electrolyte by the laser beam. In particular, an estimate of this hypothetical current from the change in the mass of the cold electrode yields ≈ 0.8 A at a laser-beam power $P = 30$ W at a beam diameter of 2 mm.

The potential difference ΔU between the hot and cold electrodes was measured. When the laser beam was turned on, ΔU reached 40–50 mV (Fig. 1). Estimates from the Nernst formula show that under these laser-bombardment conditions the value of ΔU is determined primarily by effects due to a change in the ion concentration due to thermodiffusion, not a change in the electrolyte temperature. In another version of the experiments, we measured the current flowing through a galvanometer connected between the two electrodes in the electrolyte. The maximum current $i(t)$ was ≈ 40 μ A, and it decayed to zero in 3–10 s after the laser beam was turned off (Fig. 1). The values of ΔU and i depend on the laser beam power, the electrolyte concentration, and the distance between the electrodes.

We also measured the magnetic fields generated by the currents in the electrolyte in the presence and absence of the electrodes. For this purpose, we placed a solenoid in the electrolyte and passed the laser beam through it. When the beam was turned on, a current appeared in the solenoid circuit (Fig. 1). When the steel electrodes were inserted into the electrolyte, the maximum current amplitude increased severalfold. The current which arose in the electrolyte was also determined from the deflection of the needle of a compass held ≈ 3 cm from the axis of the laser beam. The same needle

deflection occurred when the compass was held an equal distance from a conductor carrying a ≈ 0.5 -A current. The total current ($\approx 40 \mu\text{A}$) over the cross section of the cell is much smaller than the current flowing through the central part of the beam (≈ 0.5 A).

In some other experiments, we applied a magnetic field of about 800 G to the currents flowing through the electrolyte. We observed a deflection of the laser beam from its original propagation axis through an angle $\sim 5^\circ$. This effect of the magnetic field on the beam propagation path implies that a change in the refractive index of the electrolyte is induced along the central current tube.

An exceedingly important circumstance is that the formation of the temperature and current gradients in the electrolyte is caused by the motion of predominantly those ions which absorb the laser beam. When we applied a laser beam to a solution of the salts of several elements we were able to achieve a selective precipitation of those elements whose ions have absorption bands at the laser wavelength. For example, the precipitation of iron on nickel from a FeCl_3 solution does not occur during ordinary electrolysis, since nickel lies to the right of iron in the voltage series. Consequently, the ordinary electrolysis of a mixture of FeCl_3 and NaCl results in the precipitation of sodium on a nickel electrode, with the further result that the pH of the medium is changed. During laser bombardment, the precipitation of iron on nickel occurs both in the pure electrolyte FeCl_3 and in a mixture of this electrolyte with a saturated NaCl solution, which does not absorb the laser beam. We find no change in the pH of the electrolyte in this case. Some analogous selective effects were observed previously by Karlova et al.²

Examining all these results, we conclude that the acceleration of electrochemical processes during laser heating of the electrolyte results from the generation of electric current through the thermodiffusion of the absorbing ions under the influence of the laser beam. As in the case of thermodiffusion in gases,³ a feedback arises between the concentration and thermal degrees of freedom of the system during the laser bombardment. Since we are dealing with the thermodiffusion of charged particles in this case, however, we should speak in terms of a feedback among the ion concentration and the distributions of the temperature, the currents, and the magnetic fields in the electrolyte. The currents simultaneously affect the electrode potential and the distribution of the electric double layer (an "induced galvanic effect").

We also obtained data on electrochemical reactions with semiconductors. During the bombardment of a plate of strongly absorbing germanium by a laser beam with $\lambda = 1.06 \mu\text{m}$, for example, we observed an effective etching of germanium in a FeCl_3 solution, independent of the nature of the doping (Fig. 2a). Iron was precipitated from the same electrolyte onto transparent silicon (Fig. 2b). Iron was precipitated on the side of a GaAs plate nearer the laser beam; the GaAs was etched on the beam exit side because of the different directions of the temperature gradient on the two sides of the GaAs plate. In a CuSO_4 solution, which also absorbs strongly at the wavelength $\lambda = 1.06 \mu\text{m}$, the etching of semiconductors and the ion drift were similar. We carried out several experiments on the use of the beam from a CO_2 laser to etch semiconductors. Since the absorption of light with $\lambda = 10.6 \mu\text{m}$ in water is very strong, we etched a semiconductor doubling as the entrance window of the cell at this wavelength. In an

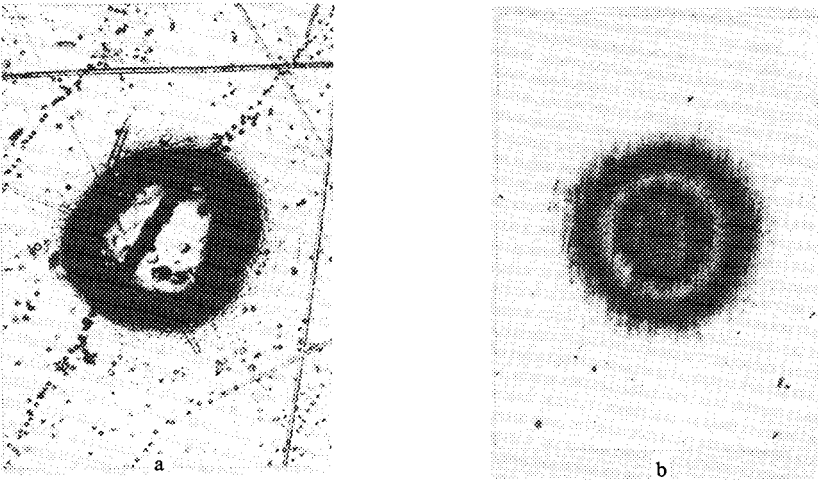


FIG. 2. a—Photograph of a germanium surface after etching in a FeCl_3 solution during laser bombardment (the etching depth is $\sim 30 \mu\text{m}$, and the diameter is 0.5 mm); b—iron precipitated on silicon from a FeCl_3 solution.

electrolyte containing FeCl_3 , we carried out an etching of germanium and a precipitation of iron on silicon.

In summary, these experimental results demonstrate that it is possible to use laser beams to selectively control electrochemical processes. The acceleration of the particular reaction of interest results from a thermodiffusion of absorbing ions in the laser beam.

¹E. K. Kozlova, A. I. Portnyagin, A. N. Romanchenko, and A. E. Filippov, Preprint No. 14, Physics Department, Moscow State University, 1983.

²E. K. Karlova, N. V. Karlov, G. P. Kuz'min, B. N. Laskorin, A. M. Prokhorov, N. P. Stupin, and L. B. Shurmel', *Pis'ma Zh. Eksp. Teor. Fiz.* **22**, 459 (1975) [*JETP Lett.* **22**, 222 (1975)].

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Translated by Dave Parsons

Edited by S. J. Amoretty