Kinetic analysis of photoelectrochemical hydrogen evolution over p-type silicon in acidic aqueous solutions of electrolytes

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The kinetics of photoelectrochemical hydrogen evolution at p-Si single crystals in acidic aqueous solutions of electrolytes under pulse photoexcitation was studied. Despite a low stability of the silicon surface under the experimental conditions, a distinct interrelation between the characteristic time of interfacial charge transfer and stationary current was found. The determination of the characteristic transfer time does not need the detailed elaboration of generation-recombination processes in the semiconductor. The steady-state current density was shown to be determined both for the dark current and photocurrent by the surface charge density.

Key words: photoelectrochemistry, hydrogen evolution, interfacial charge transfer, kinetics, silicon.

Photostimulated electrolysis of water at semiconducting electrodes is a promising way for direct solar energy conversion to chemical energy.[1,2] The efficiency of photoelectrochemical conversion depends to a great extent on the dynamics of charge transfer through the semiconductor/electrolyte interface and generation-recombination processes in the semiconductor.

The use of n- and p-type silicon crystals as photoelectrodes has been considered.[3,4] However, the behavior of silicon in aqueous solutions of electrolytes varies because of its oxidation, dissolution, and saturation with hydrogen.[5] Various modification methods are used to overcome the instability of the silicon surface and enhance its catalytic activity.[6,7] Standard steady-state measurements are insufficient to understand the processes that occur on the silicon surface and are related to interfacial charge transfer. Kinetic studies have shown that the efficiency of the silicon photocathode in aqueous solutions is affected by the high density of the charged surface states[8] and the relationship of the kinetic parameters of charge transfer to the insertion of hydrogen[9] and illumination intensity.[10]

The kinetics of hydrogen evolution on the irradiated silicon surface is based on a linear approximation,[11,12] in which the surface processes of charge transfer and recombination of charge carriers are considered as reactions of pseudo-first order. The factors indicated above and a noticeable steady-state current (*i.e.*, the conditions are far from the real conditions for the work of the photocathode of a photoelectrochemical converter) were ignored.

In this work, we obtained new experimental data, which allowed us to propose a more general approach to the description of the kinetics of hydrogen evolution over the illuminated silicon surface in acidic aqueous solutions of electrolytes.

Experimental

Experiments were carried out by a three-electrode scheme under potentiostatic conditions in an electrochemical cell with an optical window containing a semiconducting cathode, platinum counterelectrode, and saturated calomel reference electrode (SCE). All potentials were measured relative to the reference electrode. The semiconducting electrodes with a working surface of 0.03—0.15 cm^2, were made from single crystal p-silicon plates (specific resistance 0.2 Ohm m) 0.4 mm thick. The back ohmic contacts of these electrodes, prepared from indium/gallium alloy or thermally sputtered aluminum, were separated from electrolyte solution by epoxide resin. The cell was filled with 0.5 *M* H_2SO_4, through which high-purity argon was passed to remove dissolved O_2. Before measurements, the working surface of the electrodes was etched in a mixture of acids HNO_3+HF+AcOH (1 : 3 : 2 v/v/v) and washed with bidistilled water. All experiments were carried out at ~20 °C. The complex measuring system provided potentiostating, detection, accumulation, averaging of pulse signals and steady-state currents, monitoring of the radiation intensity, and primary processing of the results. The total time of increase in the transient parameter of the measuring system potentiostat—pulse amplifier of photocurrent did not exceed $3 \cdot 10^{-6}$ s. An electrically controlled light emitting diode assembly ($\lambda \approx 0.9$ μm) was used as a source of steady-state and pulse (with a front $<5 \cdot 10^{-6}$ s) radiation. The maximum intensity of the steady-

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state illumination was $L_{max} \approx 15$ W m^{-2}. The duration of rectangular pulses of the probing radiation was varied within T = 0.3—300 ms; the frequency of pulse repetition was f = 1—4 Hz. The parameters of the photocathode response to the probing light (photoresponse), *viz.*, the initial amplitude j_f and the characteristic time τ (for achievement of stationary amplitude), were determined by numerical exponential extrapolation of the signals. To increase the accuracy of measurements, the photoresponse was detected in a time interval 3—5-fold longer than the characteristic time of the photoresponse decay.

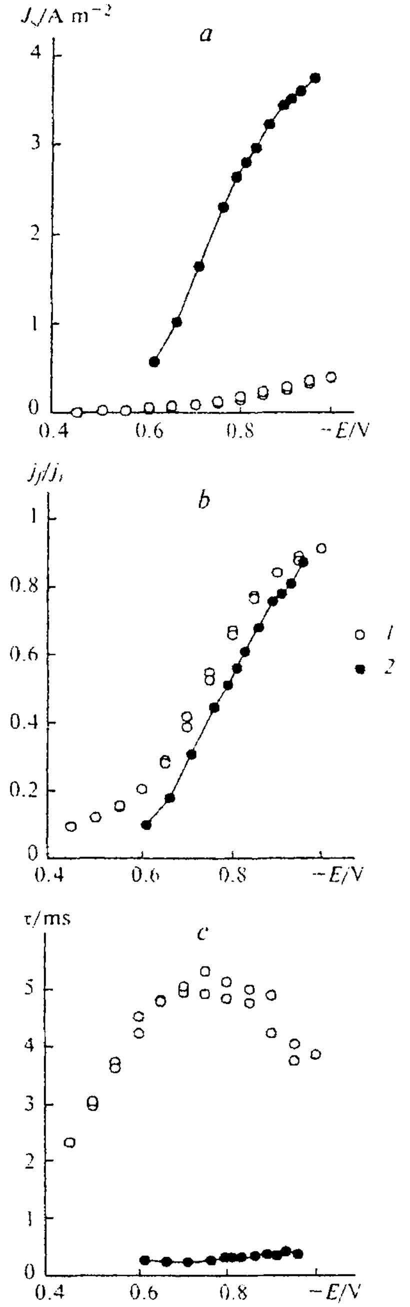

Fig. 1. The plots of SCE potential *vs*: *a*, stationary current J_s; *b*, differential efficiency of photoconversion j_f/j_i; and *c*, effective time of photoresponse decay τ. *1*, dark regime and *2*, regime of steady-state illumination with $L = 0.3 \cdot L_{max}$.

Before measurements, the working electrode was subjected to cathodic treatment with a negative charge of 10^4—10^5 C m^{-2} under steady-state illumination ($L \approx 0.5 \cdot L_{max}$, cathodic bias $E \approx 1.1$ V), which stabilized the voltammetric and kinetic parameters of the system[7,10] to ensure reproducible results.

Typical experimental plots of the stationary current J_s *vs* the cathodic bias E both in the dark regime (*i.e.*, without steady-state illumination of the photocathode) and under irradiation with an intensity of *ca.* 0.3 of the maximum intensity used in the work are presented in Fig. 1, *a*. Similar plots of the differential efficiency of photoconversion j_f/j_i and characteristic time τ for the same regimes are shown in Fig. 1, *b* and *c*.

Results and Discussion

The essence of the used experimental approach is the probing of the silicon/electrolyte interface (at different electrode potentials and steady-state illumination levels) by rectangular low-intensity photopulses under potentiostatic conditions. An important feature of the detected transient parameters of the photoresponse[11] in the system under study is the previously mentioned exponential decay of the pulse photocurrent to its stationary level. This effect is independent of the experimental conditions (*viz.*, in the dark or under steady-state illumination) when a low amplitude of the probing photopulse is maintained.[10] The obtained[12] semicircles on the complex plane of the photocurrent components with sinusoidal modulation of the illumination of the silicon electrode confirm this conclusion. This important experimental fact, indicating only one limiting step of a complicated charge transfer from the semiconductor to the electrolyte solution, allows a simple kinetic analysis of the system to be performed.

For a high density of the charged surface states of silicon in an aqueous electrolyte solution, it is reasonable to assume that it is precisely the establishment of a steady-state concentration of the surface charge which mainly determines the kinetics of charge transfer through the semiconductor—electrolyte interface.

The balance equation for the absolute value of the surface charge density Q can be written in the form

$$dQ/dt = e \cdot W - J, \qquad (1)$$

where J is the current density of charge transfer through the interfacial layer, e is the charge of an electron, and W is the density of the total generation-recombination electron current from the semiconductor onto its surface stipulated by both thermal processes of generation-recombination and photogeneration under the external IR illumination of the p-Si electrode. Thus, for the current in the external circuit (calculated per unit surface of the electrode), we obtain

$$I = J + dQ/dt = e \cdot W. \qquad (2)$$

As follows from the general physical concepts, if only one characteristic time of the transient parameter is present, the generation-recombination current (W) depends on the current density (L) of the IR radiation, the drop of the electric field potential in the semiconductor—electrolyte interfacial layer (Helmholtz layer) ΔU, and the semiconductor potential U_{sc} relative to the back side of the p-Si electrode. Since the sum $\Delta U + U_{sc}$ is equal (with a constant accuracy) to the measured potential E of the calomel electrode relative to the back side of the p-Si electrode (potentiostatic regime), and the potential drop of the interface is related to the surface charge density Q, the generation-recombination current W is determined by E, L, and Q. In addition, let us accept that the charge transfer current through the interfacial layer J is unambiguously related to the potential drop of this layer and, hence, depends only on the surface charge density Q. In this case, it is convenient to use E, L, and J as variables, Q and W can be considered as the corresponding functions of them, and the balance correlation (1) can be written in the comprehensive form

$$\mathrm{d}Q(J)/\mathrm{d}t = e \cdot W(E,\ L,\ J) - J.$$

In the stationary regime, the current in the external circuit is equal to that of the transfer through the interfacial layer J_s, which is calculated from the correlation

$$e \cdot W(E,\ L,\ J_s) = J_s, \qquad (3)$$

where $J_s \equiv J_s(E,\ L)$.

In the potentiostatic regime ($E \approx \mathrm{const}$), a weak stepwise change in the IR steady-state illumination of $\delta L < 0.01 \cdot L_{\max}$ increases the charge transfer current by $j \equiv \delta J$. In this case, linearized equation (2) has the form

$$\frac{\mathrm{d}j}{\mathrm{d}t} \cdot \frac{\mathrm{d}Q}{\mathrm{d}J}\bigg|_{J=J_s(E,L)} =$$

$$= e \cdot \left[\delta L \cdot \frac{\partial W}{\partial L}(E,L,J) + j \cdot \frac{\partial W}{\partial J}(E,L,J)\right]_{J=J_s(E,L)} - j$$

or in brief form,

$$\tau_J \cdot (\mathrm{d}j/\mathrm{d}t) = j_i \cdot (1 - j/j_f) \qquad (4)$$

with the initial condition $t = 0$, $j = 0$. Here τ_J is the effective time of charge transfer through the interfacial layer

$$\tau_J \equiv \mathrm{d}Q(J_s)/\mathrm{d}J_s,$$

and j_i and j_f are parameters of Eq. (4) that depend on E and L

$$j_i = \delta L \cdot e \cdot \frac{\partial}{\partial L} W(E,L,J)|_{J=J_s(E,L)}, \qquad (5a)$$

$$j_f = j_i \cdot \left[1 - e \cdot \frac{\partial}{\partial L} W'(E,L,J)|_{J=J_s(E,L)}\right]^{-1} \qquad (5b)$$

and represent the initial and final (stationary) photoresponse, respectively. The solution of Eq. (4) has the form

$$j = j_f \cdot [1 - \exp(-t/\tau)],$$

where the characteristic time (τ) of the establishment of equilibrium in the system is proportional to the effective time of charge transfer through the interfacial layer (τ_J)

$$\tau = (j_f/j_i) \cdot \tau_J. \qquad (6)$$

Correspondingly, for the current pulse (i) in the external circuit we have

$$i = j + j_i \cdot (1 - j/j_f).$$

It follows from this that at the initial instant $t = 0$, $j = 0$, and $i = 0$, and in equilibrium $t = 0$, $j = i = j_f$.

When the steady-state correlation (3) is differentiated with respect to L

$$e \cdot \left[\frac{\partial W}{\partial L}(E,L,J)|_{J=J_s(E,L)} + \right.$$

$$\left. + \frac{\partial W}{\partial J}(E,L,J)|_{J=J_s(E,L)} \cdot \frac{\partial J_s(E,L)}{\partial L}\right] = \frac{\partial J_s(E,L)}{\partial L}$$

and Eq. (5b) is used for the amplitude j_f, we obtain an evident relationship between j_f and the stationary current J_s

$$j_f = (\partial J_s/\partial L) \cdot \delta L$$

or

$$J_s = J_s^T + (1/\delta L) \cdot \int_0^L (j_f)_{E\approx\mathrm{const}} \cdot \mathrm{d}L \qquad (7)$$

where J_s^T is the stationary current in the dark regime at the same potential E as that for the amplitude j_f in the intergrand expression.

We performed a series of experiments in which the potential E was maintained unchanged and the density of the steady-state illumination intensity L was smoothly varied, which made it possible to calculate sufficiently exactly, using the experimental data, the integral increment of the final photoresponse amplitude in relative units

$$I_L = \int_0^L (j_f)_{E\approx\mathrm{const}} \cdot \mathrm{d}L$$

in Eq. (7). The amplitude of the probing photopulse ΔL remained unchanged in all experimental series. As can be seen in Fig. 2, the experimental data thus processed in the coordinates (I_L, $J_s - J_s^T$) lie on one straight line

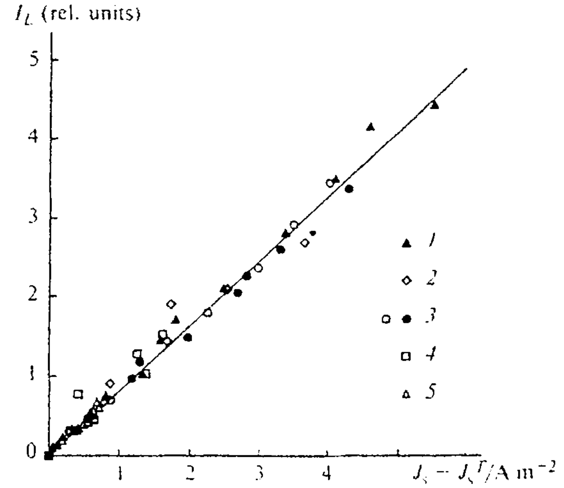

Fig. 2. The plots of the integral increment of the final photoresponse amplitude I_L *vs* the current density increment $J_s - J_s^T$ upon steady-state illumination for different SCE potentials $-E$/V: 1.0 (*1*), 0.9 (*2*), 0.8 (*3*), 0.7 (*4*), and 0.6 (*5*).

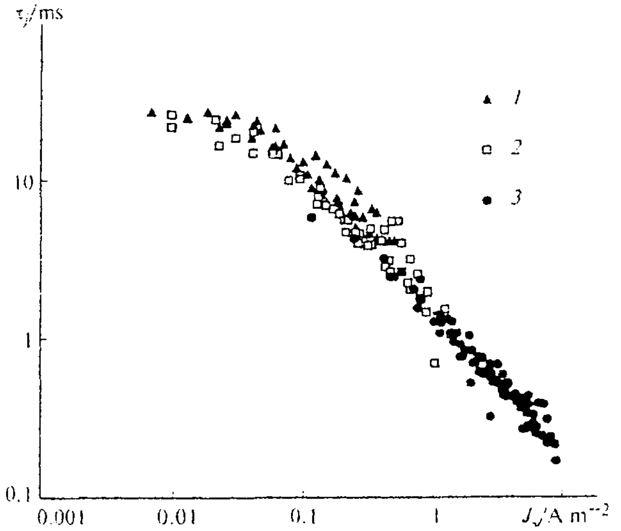

Fig. 3. The plots of the characteristic time of charge transfer τ_J *vs* the steady-state current J_s at different IR radiation levels: *1*, dark regime; *2*, illumination with $L \le 0.1 \cdot L_{max}$; and *3*, high levels of illumination.

regardless of the potential. This experimentally confirms, in particular, that the system reaches, in fact, the steady-state level within the detection time.

It follows from Eq. (6) that the effective time of charge transfer through the interfacial layer τ_J (under the assumption that τ_J is a function only of the stationary current J_s rather than of two independent parameters E and L) is calculated through the experimentally determined values. The plot of the thus calculated effective time of charge transfer through the interfacial layer *vs* the steady-state current in semilogarithmic coordinates is presented in Fig. 3. The points corresponding to the dark regime, the regime of weak IR illumination ($L \le 0.1 \cdot L_{max}$), and the regime of intense IR illumination ($0.1 < L/L_{max} \le 1$) are specially marked on this curve. Despite the pre-stabilization of the electrode, in prolonged experiments (several h) the voltammetric characteristics and the relationships of the characteristic time of the photoresponse pulse decay and ratios of its initial and final amplitudes to the cathodic bias are strongly shifted along the potential scale. Nevertheless, a distinct interrelation between τ_J and J_s is observed because, according to our concepts, to find the effective time of charge transfer through the interfacial layer from the experimental data, the generation-recombination processes, which are most likely a reason for the instability of the electrode, should not be considered in detail.

The increment of the surface charge density ΔQ (relative to the charge corresponding to zero current) as a function of the stationary current density J_s can easily be calculated from Fig. 3. We arrange all points in the plot in order of increasing current J_s and perform the summation over them, which is equivalent, with a sufficient accuracy, to integration over J_s. Because of many experimental points and their statistical scatter, we obtain a plot (points in Fig. 4) extrapolated by the expression

$$J_s = J_0 \cdot [\exp(\Delta Q/Q_0) - \exp(b \cdot \Delta Q/Q_0)],$$

where the parameter b depends on the approximation conditions (whether the points corresponding to the higher currents are priority or initial points with respect to J_s) and lies in the interval 0—0.2. The solid line in Fig. 4 corresponds to b = 0. The formal interpolation function can be considered as the result of averaging on the electrode surface of the more appropriate (in the kinetic sense) correlation

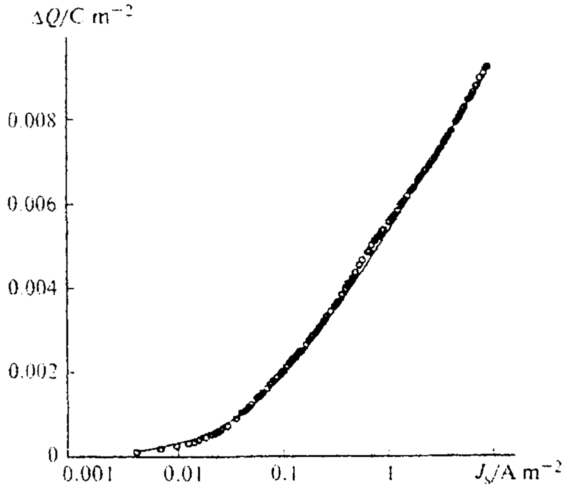

Fig. 4. The increment of the surface charge ΔQ as a function of the steady-state current J_s. The interpolation plot at b = 0 is shown by the solid curve.

$$J_s = J_0^{*} \cdot (\Delta Q/Q_0) \cdot \exp(a \cdot \Delta Q/Q_0)$$

over the dimensionless parameter a in the limits (b, 1).

Taking into account the relationship between the increment of the surface charge density and the potential drop of the interfacial layer, we may write

$$\Delta Q/Q_0 = (C \cdot \Delta U)/Q_0 = \alpha \cdot [(e \cdot \Delta U)/(kT)].$$

where α is the so-called transfer coefficient.[1,7] Hence, the ratio of the effective interfacial layer capacity to the charge transfer coefficient can be found from the presented experimental data

$$C/\alpha = (e \cdot Q_0)/(kT).$$

In our experiments, for different silicon samples and regimes of pre-treatment of the electrode surface, this value varied from 0.08 to 0.3 F m^{-2}.

Thus, we proposed and experimentally substantiated a simple kinetic model of charge transfer through an interfacial silicon layer—acidic solution of an electrolyte. This system exhibited a distinct relation between the transfer time and the steady-state current density, and the latter regardless of its nature (dark current or photocurrent) is an exponential function of the surface charge density.

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