ISSN 1063-7826, Semiconductors, 2008, Vol. 42, No. 1, pp. 59–66. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.F. Kharlamov, A.V. Kostin, M.V. Kubyshkina, F.V. Kharlamov, 2008, published in Fizika i Tekhnika Poluprovodnikov, 2008, Vol. 42, No. 1, pp. 60–67.

SEMICONDUCTOR STRUCTURES, INTERFACES, AND SURFACES

Metal-to-Semiconductor Emission of Hot Electrons Excited on Catalytic Reaction

V. F. Kharlamov^, A. V. Kostin, M. V. Kubyshkina, and F. V. Kharlamov
Orel State Technical University, Orel, 302020 Russia
^e-mail: Kharl@ostu.ru
Submitted March 12, 2007; accepted for publication May 3, 2007

Abstract—The properties necessary for the chemoemission of hot electrons through the interface between a metal film and a semiconductor are established for a metal–semiconductor structure in which hot electrons are excited during a catalytic reaction at the interface between the metal film and the gas mixture. The possibility of generating electric energy using a method based on this effect is substantiated.

PACS numbers: 73.40.Sx, 79.20.Kz, 68.47.Fg, 68.47.De, 68.48.Df, 68.60.-p, 34.50.Dy
DOI: 10.1134/S1063782608010089

1. INTRODUCTION

When an atom (or a molecule) of a gas collides with the surface of a solid, energy of about 1 eV is released as a result of the formation of a chemical bond. The processes of stabilization of the resultant chemical bonds by dissipation of the released energy play an important part in heterogeneous phenomena (growth of nanotubes, nanoparticles, and nanocrystals, formation of nanocomposites, epitaxy, catalysis, plasma-assisted treatments of materials, etc.). The excited chemical bonds are stabilized at the surface due to generation of phonons or excited electronic states in the solid. Since the released energy (~1 eV) is much higher than even the energy of the highest-frequency photons (~10^{-2} eV), the electron-assisted accommodation can successfully compete with the phonon-involving processes. In particular, at the metal surface, the just formed (excited) adsorption bond [1] and the molecules at the first vibration level [2, 3] relax mainly by generation of electron–hole pairs in the metal rather than by generation of phonons. In this case, the electronic channel of dissipation of the vibrational energy is formed due to the interaction of the electromagnetic field of the dipole (quadrupole) of the excited chemical bond with the electrons of the crystal.

On adsorption and chemical transformations at the surface of semiconductors, the electron-assisted accommodation occurs with the participation of bound electrons residing in the valence band or at the local levels of the surface electron states. In solids, the electron-excited states appear due to Landau–Zener's transitions, adiabatic transitions, tunneling of nuclei [4], and dipole interactions. In this case, excitation of the electronic subsystem of the surface manifests itself in the nonequilibrium conductivity [4, 5] and luminescence [6, 7] of the semiconductors, as well as in the emission of electrons into the gas environment [6, 8].

The high activity of certain metal catalysts with respect to heterogeneous chemical reactions can be due to the participation of conduction electrons in stabilizing the molecules of intermediate substances or products [1–3, 7–9]. However, the role of electron-assisted accommodation in the metal-induced acceleration of heterogeneous chemical processes is poorly known, since the methods of tracking the electronic excitation of metals during heterogeneous processes have not yet been developed. For such a method, one can use the effect of passage of the flux of hot electrons, excited during the chemical reaction, through the metal–semiconductor interface [9]. In this case, the thickness of the metal film deposited onto the semiconductor surface should be no larger than the length L of the energy dissipation of hot electrons in the metal [10]. The length L is defined as $L \approx v\nu^{-1}$, where v is the velocity of an electron at the Fermi surface and ν is the frequency of electron collisions with energy exchange. In rather pure metals within a wide temperature region, the basic mechanism of equilibration is the interaction of conduction electrons with phonons (the electron–electron collisions can become the dominant mechanism of equilibration only at very low temperatures) [10]. With increasing temperature, the energy-dissipation length of hot electrons decreases because of the increase in the frequency of electron–phonon collisions. This frequency is $\nu \sim kTh^{-1}$ at high temperatures ($T \gg \theta$) and $\nu \sim kT^3h^{-1} \cdot \theta^{-2}$ at low temperatures ($T \ll \theta$), where θ is the Debye temperature of the metal and h is Planck's constant [10]. With $v = 10^6$ ms^{-1} and $T = 300$ K, we obtain the estimate $L \approx v\nu^{-1} \approx 10^{-7}$ m.

The effect of chemoemission of electrons from the surface of metals and semiconductors into the gas environment [6, 8] indicates that the energy exchange dur-

ing exothermic catalytic reactions is accompanied by generation of excited electrons in the solids, with the excess energy up to 2–4 eV, higher than the work function of certain materials. A similar effect of chemoemission of hot electrons from a metal to a semiconductor is possible [9]. In this case, the potential barrier for electrons at the interface between the metal film and semiconductor is relatively low and depends on either the difference between the work functions of the materials in contact or the charge at the semiconductor surface; this surface charge depends on the density of surface states, the type of conductivity, and the concentration of charge carriers in the semiconductor [11]. Due to the small height of the barrier at the contact, the currents of chemoemission of electrons from the metal to the semiconductor can be very large.

The purpose of this study is to analyze the conditions for emission of hot electrons, excited during the catalytic reaction in a metal, through the metal–semiconductor interface and to provide theoretical basis for the possibility of the practical use of this effect in electric current sources.

2. SUBSTANTIATION OF THE EXPERIMENTAL METHOD

Let a thin metal film be at the surface of an n-type semiconductor, in which the film forms a depletion layer. Let the thickness of the film, d, satisfy the condition $d \ll L$, where L is the energy-dissipation length of hot electrons in the metal. As the voltage U is applied, the electric current begins to pass between the metal film and semiconductor; the current density is [11]

$$j = j_s[1 - \exp(aU)]. \quad (1)$$

Here,

$$j_s = 0.25 e n_0 \vartheta \exp(-a u_c),$$

where e is the elementary charge, n_0 is the concentration of conduction electrons in the semiconductor, ϑ is the average thermal velocity of electrons in the semiconductor, u_c is the contact potential difference between the metal and semiconductor, $a = e(kT)^{-1}$, k is the Boltzmann constant, and T is the temperature.

Let electrons at the surface of the metal film be excited with the use of a catalytic reaction. Then, a diffusion flux of hot electrons is generated; the energy of these electrons in the metal layer with thickness d decreases by a factor of $\sim\exp(-d\nu v^{-1}) \approx 1$, i.e., only slightly. Let the energy of the hot electrons be sufficiently high to overcome the potential barrier at the interface. In this case, when having reached the plane of the contact, the hot electrons pass into the semiconductor, and the electric field of the contact pushes them out into the semiconductor bulk due to the upward band bending at the semiconductor surface (the upward band bending is caused by the appropriate choice of the particular metal–semiconductor system). If $eu_c \gg kT$, the Debye screening length L_D is shorter than the momentum relaxation length of hot electrons in the semiconductor, L_i, and the above-barrier reflection of the hot electrons can be disregarded, a considerable portion of the hot electron transfers from the metal into the semiconductor. As a result, the current density j changes by the quantity j_r and becomes equal to

$$j^* = j_r + j = e\eta J + j_s[1 - \exp(aU)]. \quad (2)$$

Here, $j_r = e\eta J$, J is the rate of the heterogeneous reaction, $\eta = \beta_1\beta_2$, β_1 is the probability of the formation of the electron-excited state in the metal on the formation of the product molecule, and β_2 is the probability of propagation of a hot electron through the metal film and interface.

If the electric circuit involving the semiconductor with the metal film at its surface is open, the electron excitation of the surface of the film induces a potential difference V between the film and semiconductor. In the steady-state conditions, the quantity V is defined by the condition of equality between the current of hot electrons transferred from the metal to the semiconductor, j_r, and the current of electrons transferred from the semiconductor to the metal, j_n. The current j_n consists of the current of hot electrons, scattering experienced in the semiconductor after passing through the contact, and the current of equilibrium electrons. Since the scattered electrons are thermalized, the contribution of hot electrons to the quantity j_n can be disregarded. Using the equality $j_r = j_n$ and the expression [11]

$$j_n = j_s[\exp(aV) - 1],$$

we find

$$V = \frac{kT}{e}\ln\left(1 + \frac{e\eta J}{j_s}\right). \quad (3)$$

If the electric circuit is closed, the voltage at the contact, V_1, is smaller than V, and the currents j_r and j_n now do not compensate each other. Therefore, the circuit experiences a current flow, the density of which is

$$j_0 = e\eta J - j_s[\exp(aV_1) - 1]. \quad (4)$$

Thus, the emission of hot electrons from the metal into the semiconductor involves the effects described by expressions (2)–(4).

There are no principal prohibitions upon the condition $\eta \approx 1$, where $\eta = \beta_1\beta_2$, $\beta_1 \le 1$ [1–4], and $\beta_2 \approx \exp(-d\nu v^{-1}) \le 1$. Therefore, according to expressions (3) and (4), it is possible to create a current source that operates on the energy of heterogeneous chemical reactions at the interface between a metal catalyst and a gas. (In galvanic current sources, the electrochemical processes occur at the surface of electrodes placed into an

electrolyte.) The power released in the external circuit of such a source is

$$P = j_0 V_1 S = \frac{kT}{e} j_0 S \ln\left(1 + \frac{e\eta J}{j_s} - \frac{j_0}{j_s}\right), \quad (5)$$

where S is the surface area of the metal film. In order to increase the power of the current source by decreasing j_s (see expressions (1), (3)–(5)), for the substrate, one can use a planar p–n junction (or a heterojunction), whose internal electric field draws the hot electrons deep into the crystal. At a certain takeoff current $j_0 = j_m$, the power is maximal: $P = P_m$. To determine the quantities j_m and P_m, numerical calculations are needed. According to the results of the numerical calculations, the maximal load power P_m steadily increases with increasing J. Assuming that the pressure of the gas mixture takes different values in the range 10^{-1}–10^5 Pa and the parameters are $T = 300$ K, $S = 1$ cm^2, $j_s = 10^{-6}$ A cm^{-2}, and $\eta = 1$, we use expressions (3)–(5) to obtain the following results: at the rate of the chemical reaction $J = 10^{17}$, 10^{19}, 10^{21}, and 10^{23} cm^{-2} s^{-1}, the quantities P_m and j_m are equal to 2.8×10^{-3}, 0.4, 62, and 8×10^3 W and 1.4×10^{-2}, 1.5, 150, and 1.5×10^4 A cm^{-2}, respectively. The power of the current source can be several orders of magnitude larger than the power of electrochemical sources, in which the power is limited by the diffusion of chemical reagents in the electrolyte. As an example of catalytic reactions that can probably be used in the current source, we can refer to the exothermic heterogeneous processes $2H_2 + O_2 \longrightarrow 2H_2O$, $C_2H_2 + H_2 \longrightarrow C_2H_4$, and $C_2H_4 + H_2 \longrightarrow C_2H_6$ that occur at the surface of platinum and palladium at the temperature $T = 300$–350 K. (The last two reactions are of considerable practical importance.)

We now estimate the momentum relaxation length of hot electrons in the semiconductor, L_i, and the Debye screening length L_D in the case of experimentally studied n-type silicon (see below) with the resistivity $\rho = 100$ Ω cm. Taking the electron mobility in the slightly doped Si crystals at $T = 300$ K to be $\mu = 1.3 \times 10^3$ cm^2 V^{-1} s^{-1} [11], we obtain $n_0 = (e\mu\rho)^{-1} = 5 \times 10^{13}$ cm^{-3}. It is worth noting that, at the concentration of dopant atoms $N_t \approx n_0 = 5 \times 10^{13}$ cm^{-3}, the scattering of electrons at impurities does not virtually influence the electron mobility [11]. We use the expression $\mu = e\tau_i m^{-1}$ [11], where τ_i and m are the momentum relaxation time and the effective mass of an electron in the semiconductor, respectively. Then we have $L_i = \bar{p}_i \tau_i m^{-1} = \bar{p}_i \mu e^{-1}$, where $\bar{p}_i$ is the electron momentum in the semiconductor. If $L_D < L_i$, we have $\bar{p}_i \approx p_i$, where p_i is the momentum of a hot electron in the metal (this electron then transfers into the semiconductor). In this case, we obtain the estimate $L_i \approx p_i \mu e^{-1} = (10^{-7}$–$10^{-6})$ m (at the temperature $T = 300$ K). In this case, we also have $L_D = (\varepsilon kT)^{1/2}(4\pi e^2 n_0)^{-1/2} = 2 \times 10^{-7}$ m. For p-type silicon with $\rho = 100$ Ω cm and $\mu_p = 500$ cm^2 V^{-1} s^{-1} [11], we can similarly find $L_D = 1 \times 10^{-7}$ m. Thus, at $T = 300$ K and $N_t \approx 10^{14}$ cm^{-3}, the condition $L_D \leq L_i$ is satisfied at the metal–silicon interface.

3. EXPERIMENTAL

In the experiments, we used p-type Si crystals (doped with Ga) with resistivity 100 Ω cm and n-type Si crystals (doped with As) with resistivity 100 Ω cm. The thickness of the crystals was 0.4 mm, and the area of the larger face (further referred to as the b face) was $S = 2$–100 mm^2. A layer of gold or nickel was deposited onto the b face of the crystal by thermal evaporation in vacuum. The layer thickness was $d = 10^{-8}$, 3×10^{-8}, and 10^{-7} m. (The films with the thickness 3×10^{-8}, and 10^{-7} m do not satisfy the condition $d \ll L$, where $L \approx 10^{-7}$ m at $T = 300$ K.) Simultaneously, the metal was deposited onto the surface of the quartz sensor of a piezoelectric balance placed near the Si samples. The thickness d was determined from the decrease in the frequency of characteristic vibrations of the piezoelectric balance, f, measured with a ChZ-54 frequency counter: $d \propto \Delta f$, where $\Delta f = f_0 - f$ and f_0 is the initial characteristic frequency of the piezoelectric balance. (It is known that a change in the thickness of the quartz plate of the piezoelectric sensor by Δx yields a change in the characteristic frequency of the quartz oscillator, $\Delta f = f^2 k_f^{-1} \Delta x$, where k_f is the frequency coefficient.) In determining the quantity d, the relative error was 20%.

The surface of the Si crystals was coated with an oxide film formed due to the interaction of silicon with atmospheric oxygen [11]. Before depositing the metal, this oxide film was removed from the surface with the use of the HNO_3–HF acid mixture. In the experiments, we used also crystals with no deposited metal films ($d = 0$). A contact of area S was soldered or pressed to the opposite b face of the crystal. A spring "point" contact was attached to the deposited metal layer. For crystals with the b faces of area $S = 2$ mm^2, all faces except b were coated with a protective epoxy layer. The resulting metal–semiconductor–metal (MSM) structures exhibited photovoltage and thermopower, suggesting that there exists a potential barrier for electrons or holes at the interface between the semiconductor and the metal film. The parameters of the barrier are controlled by the charge at the Si surface [11]. In this study, the height of the barrier was not measured.

The MSM structure was connected with the metering circuit and placed into a flow reactor. For electronic excitation of the surface of the metal film, we used the reaction of heterogeneous recombination of hydrogen atoms, $H + H \longrightarrow H_2$. Spectrally pure hydrogen was steadily pumped through the reactor at the pressure 50 Pa. To produce the gas, we used a GVCh-6 hydrogen

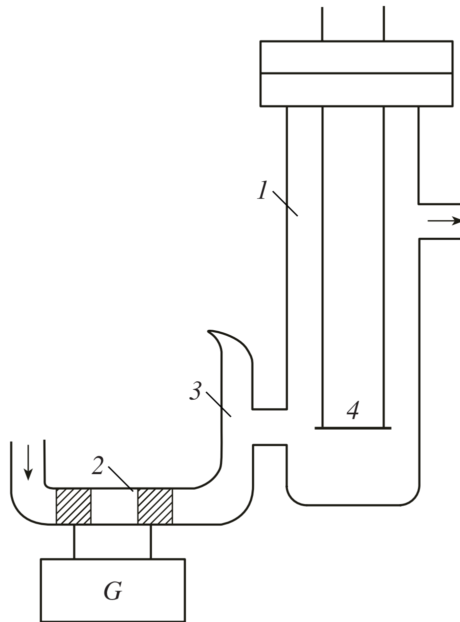

Fig. 1. Schematic sketch of the experimental system: (*1*) reactor, (*2*) discharge tube, (*3*) Wood horn, and (*4*) the sample.

generator; 99.995%-purity hydrogen was passed through a silica gel filter. Dissociation of the hydrogen molecules ($H_2 \longrightarrow 2H$) was conducted with the use of a high-frequency discharge in the gas. The radiation emission of the discharge was absorbed by the Wood horn (Fig. 1). The lack of illumination of the metal films with optical radiation of the gas discharge was checked using indications of a photoelectric multiplier. When diffusing into the reactor, the vibration- and electron-excited molecules produced in the discharge region experienced not fewer than 10^3 collisions with the gas molecules and, as a result, lost the excess energy [12]. In some individual experiments, it was established that the electrons and ions of the plasma recombined, when diffusing, and did not penetrate into the reactor. (At the voltage 100 V applied to the gap between the Au film and the electrode above it, the electric current in the gas was below 1×10^{-13} A.) In the reactor, the concentration of hydrogen atoms was 3×10^{13} cm^{-3}, as measured with the use of a hot probe.

Prior to the measurements, the samples were kept in atomic hydrogen atmosphere for three hours. This procedure results in the removal of adsorbed molecules (of oxygen, water, etc.) from the metal film, due to the formation of volatile hydrides and the sputtering of the adsorbed layer during the reaction [13, 14]. In some experiments, the samples were contacted with a thermocouple. It was established that the increase in their temperature due to the reaction at the surface of the gold film was about 0.2 K.

We now introduce the notation: let R_n be the resistance of the MSM structure, when incorporated into the circuit so that the metal film is connected with the "minus" pole of the voltage source, and R_p be the resistance of the same MSM structure, when the metal film is connected with the "plus" pole of the voltage source. In the experiments, we traced the time variations in the resistances R_n and R_p of the MSM structure after turning on and off the source of hydrogen atoms, the potential difference V (chemically produced voltage) generated at the contacts of the MSM structure during the reaction, and the short-circuit current I_0 initiated by the chemically produced voltage in the structure shorted against the microammeter. The resistances R_n and R_p were measured with the d.c. bridge UPIP-60 M. The quantity V was measured with the same bridge by the compensation method or with the use of the voltmeter F116. In "blank" experiments, with the use of a semiconductor diode placed into the reactor, it was established that there was no electromagnetic noise. (The system was protected from such noise by screening of the reactor, discharge, and measuring instrument.)

4. RESULTS

In the atomic hydrogen atmosphere, the potential difference V between the metal film (gold, nickel) and semiconductor and the changes ΔR in the resistance of the MSM structure are produced only in the case of MSM structures involving *n*-type silicon. Under the same conditions with samples involving *p*-type silicon, these effects are unobservable. The effects are lacking also in the MSM structures with "thin" metal films ($d = 1 \times 10^{-8}$ m) or in the *n*-type silicon crystals with no deposited metal ($d = 0$, and the upper point contact is connected directly with the *b* face of the crystal). The above effects are observed at the thickness of the metal films $d = 3 \times 10^{-8}$ m. No dependence of the effects on the size of the Si crystals is observed. The hydrogen atoms in the gas atmosphere influence the resistance of the MSM structures, only if the metal film is connected with the "minus" pole of the current source. When the polarity of the applied voltage is changed, no effect is produced: $\Delta R_p = 0$. With increasing content of hydrogen atoms in the gas atmosphere, the quantities V and ΔR_n increase. With increasing temperature ($T = 295$–450 K), the quantities V and ΔR_n show a sharp (reverse) decrease and become zero at $T \geq 390$ K.

In the case of the reaction $H + H \longrightarrow H_2$ at the surface of the gold film deposited at the surface of the *n*-type silicon, we obtain a number of results. These are described below. After turning on the source of atomic hydrogen, the resistance R_n of the MSM structures shows a stepwise decrease (by the quantity ΔR_n), and the new resistance (R_n^*) in the atomic hydrogen environment remains unchanged with time (during time

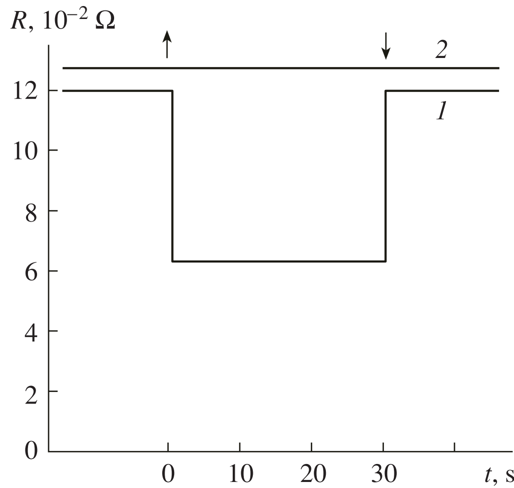

Fig. 2. The time dependence of the resistance of the Au film–n-Si contact after (upward arrow) turning on and (downward arrow) turning off the source of atomic hydrogen. The gold film is connected with (*1*) the minus and (*2*) plus poles of the power source. $U = 0.1$ V, $d = 3 \times 10^{-8}$ m, and $T = 295$ K.

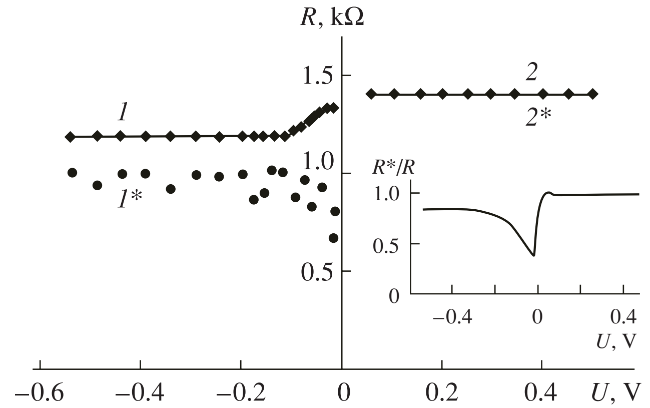

Fig. 3. Dependences of the resistance of the Au film–n-Si contact on the value and polarity of the voltage at this contact in (*1*, *2*) molecular and (*1**, *2**) atomic hydrogen. In measuring the resistance R in the atomic hydrogen environment, the source of hydrogen atoms was turned on for 7 s. The gold film is connected with (*1*, *1**) the minus and (*2*, *2**) plus poles of the current source. $d = 3 \times 10^{-8}$ m and $T = 295$ K. See text for explanations to the inset.

intervals of ~10^2 s). After turning off the source of atomic hydrogen, the resistance regains its original value in a stepwise manner. If we change the polarity of the voltage applied to the MSM structure, the hydrogen atoms in gas atmosphere do not influence the value of R_p (Fig. 2). The voltage U applied to the MSM structure influences the magnitude ΔR_n of the observed stepwise changes in the quantity R_n (Fig. 3, curves *1*, *1**). At the same time, a similar quantity ΔR_p remains equal to zero at different values of the voltage U (Fig. 3, curves *2*, *2**). The ratio of the resistance of the MSM structure with the turned-on source of atomic hydrogen, R^*, to the resistance with the turned-off discharge, R, depends on the value and polarity of the applied voltage U and shows a stepwise change at $U = 0$ (inset in Fig. 3).

After turning on and off the source of hydrogen atoms, the chemically produced voltage V generated at the contacts of the MSM structure during the heterogeneous reaction $H + H \longrightarrow H_2$ at the surface of the gold film and the short-circuit current I_0 initiated by this voltage show stepwise changes; then these quantities remain unchanged during the time intervals of ~10^2 s (Fig. 4). In atomic hydrogen atmosphere, the gold film acquires a positive charge, while the semiconductor a negative charge.

In the case of MSM structures with nickel films, under the same conditions, the quantities V and I are two orders of magnitude smaller than these in the MSM structures with gold films. In addition, the kinetic curves $R_n(t)$ obtained after turning on and off the source of hydrogen atoms are different for the structures with gold and nickel. After turning on the source of hydrogen atoms, the resistance R_n of the MSM structure with the nickel film shows firstly a stepwise increase and then a slow decrease. After turning off the source of hydrogen atoms, the resistance decreases stepwise and then slowly regains its initial value (Fig. 5, curve *1*). Similar slow changes in the resistance of this structure occur after turning on and off the illumination (Fig. 5, curve *1*'). With increasing temperature, the observed change ΔR_n in the quantity R_n sharply (reversibly) decreases, and at $T \geq 390$ K, turning on the source of hydrogen atoms has virtually no effect on the resistance R_n (Fig. 5, curve *2*). If the nickel film is connected with the "plus" pole of the current source, turning on the source

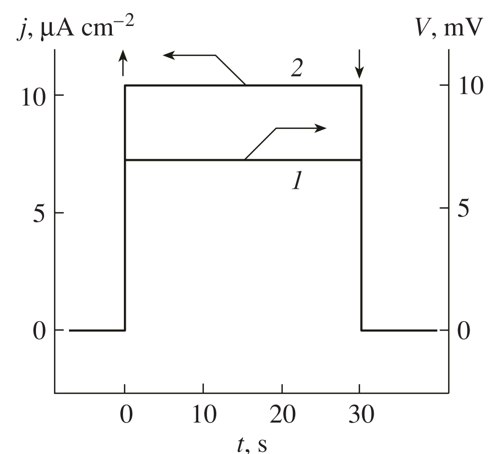

Fig. 4. The time dependence of (*1*) the potential difference between the gold film and n-type silicon and (*2*) the short-circuit current of the structure connected to a microammeter after (upward arrow) turning on and (downward arrow) turning off the source of atomic hydrogen. $d = 3 \times 10^{-8}$ m and $T = 295$ K.

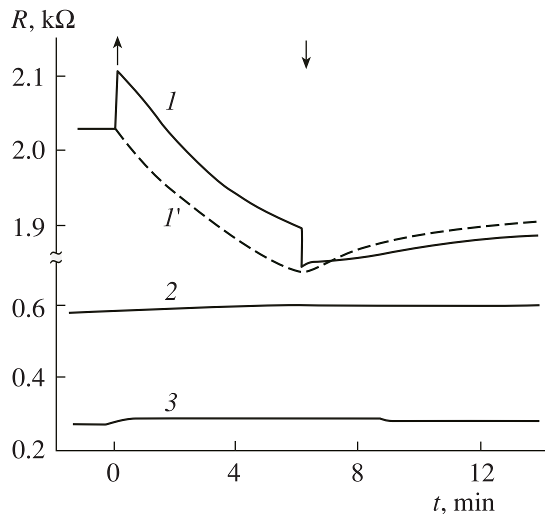

Fig. 5. Time dependences of the resistance of the Ni film–*n*-Si structure after (upward arrow) turning on and (downward arrow) turning off the source of atomic hydrogen. The nickel film is connected with (*1*, *1*', *2*) the minus and (*3*) "plus" poles of the current source. T = (*1*, *3*) 295 and (*2*) 390 K. Curve *1*' refers to the change in the resistance R_n with time after the turning on and off of the illumination. $d = 3 \times 10^{-8}$ m and $U = 1$ V.

of hydrogen atoms does not induce any changes in the resistance of the MSM structures (Fig. 5, curve *3*).

5. DISCUSSION

We may assume that the reaction is accompanied by luminescent emission of radiation, whose spectral composition corresponds to the infrared region beyond the response limits of the photoelectric detector. Penetration of this radiation into the semiconductor through the semitransparent metal film and then absorption of the radiation in the semiconductor have to be accompanied by generation of electron–hole pairs. However, the appearance of the potential difference V and the changes ΔR in the resistance of the MSM structure under the influence of hydrogen atoms are observed only for the NSM structures involving *n*-type silicon. Moreover, the quantity ΔR differs from zero only at a certain polarity of the applied voltage. These results cannot be conditioned by the effect of electromagnetic radiation on the semiconductor or by the thermoelectric effect associated with release of the reaction heat at the surface of the film.

The "thin" metal films ($d = 1 \times 10^{-8}$ m) are mosaic in structure, as suggested by the lack of the metal-type surface conductivity. The fact that no chemically produced voltage and no change in the resistance of the MSM structure under the influence of hydrogen atoms are observed in the MSM structures with "thin" metal films or without metal films ($d = 0$) means that, for these effects to occur, we need a continuous metal film forming an electric contact with silicon, whereas penetration of hydrogen atoms through the film to the silicon surface does not result in the these effects. In the case of "thick" films ($d = 10^{-7}$ m), these effects are lacking, since the condition $d \ll L$ is not satisfied; because of this, hot electrons lose the excess energy within the thickness of the film and do not reach the metal–semiconductor interface. With increasing temperature, the frequency of electron–phonon collisions increases. Therefore, at $T \geq 390$ K, the quantities V and ΔR_n are zero because of dissipation of the energy of hot electrons within the thickness of the metal film, since the inequality $d \ll \nu^{-1} v$ is violated.

Under the experimental conditions, after turning on the source of atomic hydrogen, the rate of the heterogeneous reaction $H + H \longrightarrow H_2$ at the surface of metals (Cu, Pt, Ni) shows a stepwise increase and then remains unchanged. After turning off the source of atomic hydrogen, the rate of the reaction shows a stepwise decrease by more than two orders of magnitude (these data were obtained by detecting the dynamic effect of the reaction) [6, 7]. Therefore, we can conclude that, in the case of MSM structures with gold films, the changes in the quantities ΔR_n, V, and I_0 after turning on or off the discharge occur simultaneously with the change in the rate of the heterogeneous reaction $H + H \longrightarrow H_2$ at the surface of the film.

Now we show that the above results cannot be attributed to the change in the temperature of the semiconductor because of the increase in the temperature of the gold film due to the exothermic process $H + H \longrightarrow H_2$ at the film surface. Differentiating expression (1), we obtain

$$\frac{1}{r} = \frac{dj}{dU} = -aj_s \exp(aU),$$
$$\frac{R_1}{R} = \frac{T_1}{T} \exp\left[a(U - u_c)\left(1 - \frac{T}{T_1}\right)\right]. \quad (6)$$

Here, r is the resistance of the contact between the gold film and semiconductor per unit area and R and R_1 are the resistances of the contact at the temperatures T and T_1 ($T < T_1$), respectively. As defined by formula (6), the dependence of the quantity R_1R^{-1} on the voltage applied to the contact is smooth, with no discontinuities. However, such dependence is inconsistent with the experimentally observed dependence of R^*R^{-1} on the voltage U: the experimental dependence involves a stepwise change in the ratio R^*R^{-1} at $U = 0$ (see inset in Fig. 3). This result suggests that the change in the temperature of the contact due to heat generation at the surface of the gold film does not produce any noticeable effect on the resistance of the contact. Consequently, the effect of atomic hydrogen on the resistance of the contact (see Figs. 2, 3) corresponds to the nonequilibrium electrical conductivity of the contact due to emission of nonequilibrium charge carriers from the gold film to the semiconductor. In this case, these charge carriers are electrons, since the effect depends on the polarity of the

applied voltage and occurs only if the "minus" pole of the voltage source is connected with the gold film.

Thus, the appearance of a positive electric charge in the gold film and the change in the resistance R_n of the MSM structure with n-type silicon are due to migration of hot electrons, excited during the heterogeneous reaction, through the film and metal–semiconductor interface. Due to the upward band banding at the surface of n-type silicon [11], the electric charges are separated at the interface during the reaction. The lack of similar nonequilibrium effects in the MSM structures with p-type silicon is attributed to the fact that the surface of p-type silicon captures holes, and as a result, there is a downward band bending at the surface [11]. That is why there are no conditions for separation of charges at the interface: hot electrons that have reached the plane of the contact are retained by the electric field of the contact and do not penetrate into the semiconductor.

According to the results obtained here, emission of hot holes from the gold film into the p- or n-type silicon is not observed. The reason is that the lifetime of hot holes in metals ($\tau_p \leq 10^{-14}$ s [15]) is at least two orders of magnitude shorter than the lifetime of hot electrons, and as a consequence, hot holes recombine with electrons within the film, not reaching the metal–semiconductor interface. In addition, the probability of generation of hot holes during the reaction can be small, since only the electrons, whose initial energy is close to the Fermi energy, gain the excess energy.

We use the equalities $I = UR_n^{-1}$ and $I^* = U(R_n^*)^{-1}$, where I and I^* are the currents through the MSM structure with the turned-off and turned-on source of atomic hydrogen, respectively. From expression (2), we find $\Delta I = I^* - I = e\eta JS$,

$$R_n^* = (R_n^{-1} + e\eta JSU^{-1})^{-1}, \quad \eta = \frac{U}{eJS}\left(\frac{1}{R_n^*} - \frac{1}{R_n}\right). \quad (7)$$

The above dependence $R_n^*(U)$ is consistent with the experimental curves $R_n^*(U)$ (Fig. 3, curve *1**). From expression (7) with the experimentally measured $R_n(U)$ and $R_n^*(U)$ (Fig. 3), we calculate the quantity η and determine its dependence on the voltage applied between the gold film and the semiconductor. In this case, the rate of the reaction is calculated by the formula $J = 0.25 n_a c\gamma$, where n_a is the concentration of hydrogen atoms in the gas environment, c is the average velocity of their thermal motion, and γ is the coefficient of heterogeneous recombination of hydrogen atoms at the surface of the gold film ($\gamma \approx 0.1$ [16]). It is found that the quantity η noticeably increases with the applied voltage U (Fig. 6). This result means that the probability β_2 of the propagation of a hot electron through the interface depends on U. The effect can be due to the fact that, as the strength of the applied electric field is increased [11], the potential barrier for electrons transferring from the metal to the semiconductor is lowered,

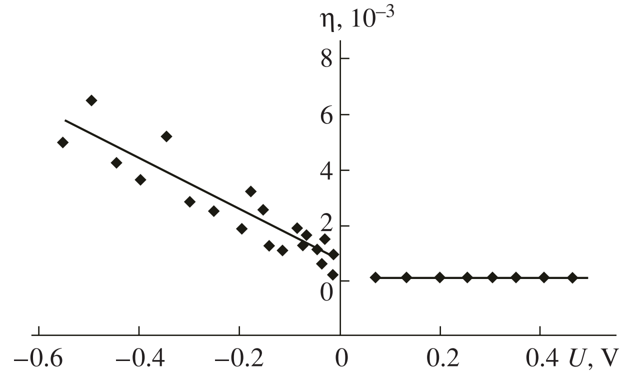

Fig. 6. The dependence of the coefficient η on the value and polarity of the voltage applied to the contact between the gold film and n-type silicon. $d = 3 \times 10^{-8}$ m and $T = 295$ K.

and, therefore, the portion of hot electrons diffusing through the interface increases. Another possible cause of the dependence $\beta_2(U)$ is limitation of the current by the space charge of electrons, probably due to trapping centers for electrons in the surface region of the semiconductor.

In the case of the MSM structure with the nickel film (Fig. 5, curve *1*), we use the parameters $S = 2$ mm^2, $R_n = 2$ kΩ m, $R_n^* = 1.8$ kΩ, $U = 1$ V, and $\gamma = 0.1$ [16] and obtain $\eta = 2.5 \times 10^{-2}$.

The slow change in the resistance of the MSM structures with Ni films after turning on and off the source of atomic hydrogen or illumination (see Fig. 5, curves *1*, *1**) is attributed to the capture of electrons by electron trapping centers at the Ni–Si interface and, hence, the limitation of the current by the space charge of electrons in the semiconductor. The traps are most likely formed due to diffusion of Ni atoms into the bulk of the semiconductor, in which the Ni atoms act as acceptor dopants [11]. Diffusion of Au atoms into Si with the formation of acceptor states seems to be less efficient because of the relatively large size of Au atoms. As a consequence, for the MSM structures with Au films, the kinetic curves $R_n(t)$ obtained with the time resolution $\Delta t \approx 1$ s are rectangular in shape (Fig. 2, curve *1*). Due to trapping of electrons by surface states, an inversion p-type layer is formed in the surface layer of n-Si [11]. Since nonequilibrium electrons generated during the reaction transfer from the nickel film into silicon, the resistivity of silicon, ρ_0, changes by the quantity $\Delta\rho = \rho - \rho_0 = \rho_0[\mu_p(p_0 - p) - \mu_e(n - n_0)](\mu_p p + \mu_e n)^{-1}$, where n and p are the concentrations of electrons and holes (at the time t at the distance x from the surface), n_0 and p_0 are their equilibrium concentrations (at $t \leq 0$), and μ_e and μ_p are the mobilities of the electrons and holes. Therefore, the initial increase in the resistance R_n (Fig. 5, curve *1*) is due to recombination of nonequilibrium electrons, transferring from the metal, with holes. Because of this, the concentration of charge carriers in

the blocking contact layer decreases for a short time. As the trapping centers become occupied, the concentration of charge carriers (electrons) in the blocking layer increases, resulting in a decrease in the resistance R_n with time.

6. CONCLUSIONS

The propagation of hot electrons through the metal–semiconductor interface is studied for the first time for electrons generated during a catalytic reaction. For chemoemission of electrons from the metal into the semiconductor to occur, the condition $L > d$ must be satisfied (L is the energy dissipation length of hot electrons in the metal and d is the thickness of the metal film deposited onto the semiconductor). In addition, the electric field at the contact may not retard the penetration of hot electrons into the bulk of the semiconductor. The measurements of the parameters of chemoemission, $\eta(U)$ and $R(t)$, provide some data on the degree of imperfection of the metal–semiconductor interface and on the trapping centers for electrons in the surface region of the semiconductor.

To accomplish efficient conversion of the energy released during the catalytic chemical reaction into the electric-current energy with the use of the metal–semiconductor structure, for the substrate for the metal film, it is necessary to use a planar p–n junction (or a heterojunction), in which the internal field draws hot electrons deep into the semiconductor.

ACKNOWLEDGMENTS

We thank S.N. Romashin, A.A. Yanovich, and T.V. Ivanov for their help.

This study was supported by the Russian Foundation for Basic Research, project no. 06-08-00079.

REFERENCES

1. W. Brenig, Z. Phys. B **23**, 361 (1976).
2. M. A. Kozhushner, V. G. Kustarev, and B. R. Shub, Dokl. Akad. Nauk SSSR **237**, 871 (1977).
3. B. N. Persson, Solid State Commun. **27**, 417 (1978).
4. V. F. Kharlamov, Yu. I. Tyurin, V. V. Styrov, and A. E. Kabanskiĭ, Teor. Éksp. Khim. **14**, 788 (1978).
5. V. V. Styrov and A. E. Kabanskiĭ, Zh. Éksp. Teor. Fiz. **76**, 1803 (1979) [Sov. Phys. JETP **49**, 916 (1979)].
6. V. F. Kharlamov, *Atomic Recombination on Solid-State Surface and Accompanying Effects* (Tomsk. Gos. Univ., Tomsk, 1994) [in Russian].
7. V. F. Kharlamov, Kinet. Katal. **46**, 497 (2005).
8. V. F. Kharlamov, Kinet. Katal. **20**, 946 (1979).
9. V. F. Kharlamov, A. V. Sedov, and S. N. Romashin, Pis'ma Zh. Tekh. Fiz. **30** (17), 48 (2004) [Sov. Tech. Phys. Lett. **30**, 732 (2004)].
10. E. M. Lifshitz and L. P. Pitaevskiĭ, *Physical Kinetics* (Nauka, Moscow, 1979; Pergamon, Oxford, 1981).
11. V. L. Bonch-Bruevich and S. G. Kalashnikov, *Physics of Semiconductors* (Nauka, Moscow, 1990) [in Russian].
12. A. Kallir and J. Lambert, in *Comprehensive Chemical Kinetics*, Ed. by C. Bomford and C. Tipper (Elsevier, Amsterdam, 1969; Mir, Moscow, 1973).
13. L. Yu. Frolenkova, V. F. Kharlamov, T. S. Rogozhina, and K. M. Anufriev, Kondens. Sredy Mezhfaz. Granitsy **3** (1), 49 (2001).
14. V. F. Kharlamov, L. Yu. Frolenkova, and T. S. Rogozhina, Zh. Tekh. Fiz. **71** (10), 90 (2001) [Sov. Phys. Tech. Phys. **46**, 1294 (2001)].
15. V. I. Veksler, *Secondary Ion Emission From Metals* (Nauka, Moscow, 1978) [in Russian].
16. V. A. Lavrenko, *Hydrogen Atom Recombination on Solid-State Surface* (Naukova Dumka, Kiev, 1973) [in Russian].

Translated by É. Smorgonskaya