Electron-Hole Pair Creation at Ag and Cu Surfaces by Adsorption of Atomic Hydrogen and Deuterium

H. Nienhaus,[1,3,*] H. S. Bergh,[1] B. Gergen,[1] A. Majumdar,[2] W. H. Weinberg,[1] and E. W. McFarland[1]

[1]*Department of Chemical Engineering, University of California, Santa Barbara, California 93106*
[2]*Department of Mechanical Engineering, University of California, Berkeley, California 94720*
[3]*Laboratorium für Festkörperphysik, Gerhard-Mercator-Universität, Duisburg, Germany*
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Hot electrons and holes created at Ag and Cu surfaces by adsorption of thermal hydrogen and deuterium atoms have been measured directly with ultrathin metal film Schottky diode detectors on Si(111). When the metal surface is exposed to these atoms, charge carriers are excited at the surface, travel ballistically toward the interface, and have been detected as a *chemicurrent* in the diode. The current decreases with increasing exposure and eventually reaches a constant value at the steady-state coverage. This is the first direct evidence of nonadiabatic energy dissipation during adsorption at transition metal surfaces. [S0031-9007(98)08122-8]

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The pathways of energy dissipation in exothermic reactions at metal surfaces are of fundamental interest but still poorly understood. Bond formation energies of up to several eV are transferred into the substrate. Since bulk phonon energies are typically 2 orders of magnitude smaller, nonadiabatic excitations of electron-hole (e-h) pairs may be a significant alternative to multiple phonon creation [1–4]. With surface reactions at thermal collision energies, there are a few examples of energy transfer into the electronic system accompanied by light emission (chemiluminescence) [5] and exoelectron ejection [6]. These effects are observed only with the exothermic adsorption of electronegative molecules on reactive metal surfaces. In addition, exoelectron emission requires that the metal has a low work function. Heretofore, there has been no direct experimental evidence for adsorption-induced e-h pair excitations at transition metal surfaces. Although the maximum energy of any hot charge carriers is smaller than the metal work function, precluding exoelectron emission, the energy may be sufficiently large to enable the charge carriers to be collected by crossing a smaller potential barrier.

We demonstrate in the present study that the direct detection of chemisorption-induced e-h pairs is feasible using the Schottky barrier of a transition metal-semiconductor diode detector. We chose the adsorption of atomic hydrogen on Ag and Cu film surfaces as model systems. These metals exhibit high reactivity to atomic hydrogen but negligible dissociative adsorption of H_2 [7]. The formation energy of the H-metal bond is large, about 2.5 eV in both cases [7]. To detect the hot charge carriers, we designed a sensor consisting of a large-area metal-semiconductor contact with an ultrathin metal film. The proposed mechanism of current production in the sensor is illustrated in Fig. 1(a) for the case of hot electrons. The transition metal film is evaporated on *n*-type Si forming a diode with a Schottky barrier, Φ. Figure 1(a) shows the Fermi level, E_F, the

conduction band minimum (CBM) and the valence band maximum (VBM). If the exothermic chemisorption of H atoms creates e-h pairs, hot electrons may travel ballistically through the film and cross the barrier. They can be detected as a current which we hereafter call a *chemicurrent*. Similarly, hot holes may be measured with a *p*-type diode. The charge carrier energies lie between the barrier height and the adsorption energy, i.e., between 0.5 and 2.5 eV above E_F. The mean free path (mfp) of electrons and holes in this energy range are typically on the order
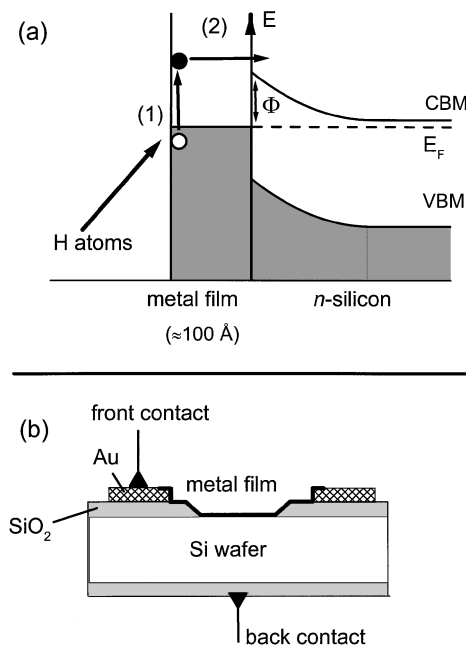

FIG. 1. (a) Principle of *chemicurrent* detection. H atoms react with the metal surface creating e-h pairs (1). The hot electrons travel ballistically through the film into the semiconductor (2) where they are detected. (b) Schematic cut view through the H sensing Schottky diode. The ultrathin metal film is connected to the Au pad during evaporation.

of 100 Å, as determined by thermal and field emission [8], internal photoemission [8], and ballistic electron emission microscopy [9]. The film thickness should be in the range of the mfp of the charge carriers.

The sensor design is shown in Fig. 1(b). The devices are microfabricated on n- and p-doped Si wafers with (111) orientation ($\rho_n = 5-10\ \Omega$ cm, $\rho_p = 1-20\ \Omega$ cm), and an Ohmic contact is provided on the back of the wafers by As^+ and B^+ ion implantation, respectively. Isolated from the silicon, thick Au contact pads are evaporated on a 4000 Å thermal oxide layer on the front of the device. A 0.3 cm^2 window is wet chemically etched through the oxide and between the isolated Au pads by use of buffered hydrofluoric acid leaving a clean and passivated Si(111) surface. The processing is performed under clean room conditions using ultrapure reagents. The samples are then transferred into an ultrahigh vacuum chamber ($p \approx 10^{-8}$ Pa) for metal deposition and measurements.

Copper and silver films are deposited by e-beam evaporation at substrate temperatures of 135 K. The nominal thickness is measured by a quartz microbalance. The etching of the oxide produces an angle of inclination between oxide and Si surface of typically 25°. The evaporated thin metal films are connected to the thick Au pad by virtue of this small inclination angle providing a zero-force front contact. This design allows electrical contact for current-voltage (I-V) measurements between the front and back contacts even with film thicknesses below 80 Å. The rectifying properties are improved by annealing the devices to room temperature and cooling back to 135 K. The measured I-V curves were analyzed using thermionic emission theory [10]. Effective barrier heights of 0.6–0.65 eV and 0.5–0.55 eV were determined for Cu and Ag films of 75 Å thickness on n-Si(111), respectively. On p-Si(111), Ag and Cu diodes showed barriers of 0.5–0.6 eV. Ideality factors between 1.05 and 1.5 indicate that the large-area diodes are laterally nonuniform and exhibit a barrier height distribution [11]. This corresponds to the nonuniform structure of the metal films. Atomic force microscopy revealed coalescing metal islands after annealing.

The devices were maintained at 135 K and exposed to a modulated, thermal hydrogen beam produced by a microwave plasma. Photons had to be extracted from the beam to avoid photoexcitation which can be orders of magnitude stronger than the chemicurrent. A special light blocking fixture was inserted into the plasma tube to prevent any photon transmission. Design and function of the device are described in detail elsewhere [12]. The content of atomic hydrogen, c_H, i.e., the number of atoms relative to the total number of particles in the beam was measured with an in-line mass spectrometer. It varied typically between 7% and 25%, where the variations were associated with plasma fluctuations. We also measured an average kinetic energy of the atomic hydrogen of between 300 and 350 K [12]. The total rate of atomic and molecular hydrogen impinging on the diode was approximately constant, 10^{13} particles/s. Hence, with a sensor

area of 0.3 cm^2, the atomic flux varied between 3 and 10 $\times$ 10^{12} H atoms/cm^2 s. The reaction-induced chemicurrent was detected between the front and back contacts using standard lock-in techniques. *No bias* was applied to the detectors during measurements. Because of the low temperature, the noise level was less than 0.5 pA.

Detector current responses in time (I-t curves) while exposing the devices to atomic hydrogen are shown for Ag/n-Si, Ag/p-Si, and Cu/n-Si diodes in Fig. 2. The atomic impingement rate, q_H, was 7.5 $\pm$ 2.5 $\times$ 10^{11} atoms/s. At $t = 0$, the beam shutter was opened. The current increases instantaneously upon exposure, decays exponentially, and eventually reaches a steady-state value. The dip observed in the I-t curve for Cu is due to a decrease in the atomic hydrogen flux due to plasma instabilities. The atomic hydrogen content, c_H, decreased from 15% at $t = 1600$ s to below the detection limit of 2% at $t = 2100$ s and then recovered to its original value. The total beam intensity (atomic and molecular hydrogen) remained constant. Thus, the chemicurrent is detected only if atomic hydrogen is present. Figure 2 shows that chemicurrents were detected for both p- and n-type Ag/Si diodes, implying that both hot electrons and hot holes are created.

The chemicurrent transient shown in Fig. 2 represents the occupation of empty adsorption sites by atomic hydrogen on the metal film. The hydrogen coverage, Θ, increases and the adsorption probability decreases with the decreasing availability of empty sites. The steady-state current observed in the long time limit is a consequence of a balance between H removal from the surface by abstraction and readsorption [13]. The chemicurrent, I, is
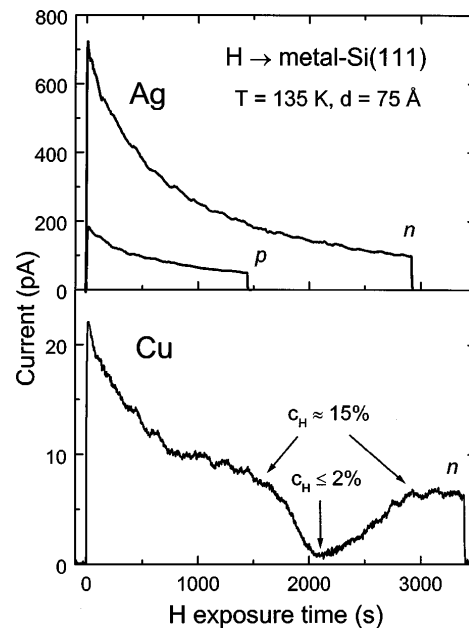

FIG. 2. Chemicurrent as a function of H exposure time for diodes with thin Cu and Ag films. The transients correspond to the filling of empty adsorption sites by atomic hydrogen on the metal surfaces. The steady-state currents are explained by a balance of abstraction and readsorption of atomic hydrogen.

expected to be proportional to the H atom flux and the fraction of unoccupied adsorption sites, i.e., $I = \alpha q_H(\Theta_s - \Theta)$, where Θ_s is the saturation coverage if no abstraction occurs and α is a constant.

If we assume that the adsorption of H and its abstraction by atomic hydrogen in the gas phase are governed by a Langmuirian and an Eley-Rideal mechanism, respectively [13], the time rate equation for I and Θ obeying first-order kinetics may be written as

$$dI/dt \propto -d\Theta/dt = -(q_H/A)[\sigma_a(\Theta_s - \Theta) - \sigma_r\Theta],$$
$$(1)$$

where A is the active diode area, and σ_a and σ_r are the cross sections for adsorption and abstraction, respectively. By considering the time limits for $t = 0$ and $t \to \infty$, the ratio of the cross sections may be determined from the maximum value, I_{max}, and the steady-state value, I_s, of the chemicurrent via $\sigma_r/\sigma_a = I_s/(I_{max} - I_s)$. Cross section ratios calculated from the data in Fig. 2 are 0.2 for Ag/n-Si and 0.4 for the two other diodes. Such large abstraction cross sections have been observed previously on other surfaces [13]. Equation (1) predicts an exponential decay of the chemicurrent with a time constant of $A/q_H(\sigma_a + \sigma_r)$. Single exponential fits to the data in Fig. 2 result in decay constants of 480 s for Ag/p-Si, 670 s for Cu/n-Si, and 750 s for Ag/n-Si. The observed variation is still within the rather large uncertainties of the flux. Cross section ratio and decay constant allow the calculation of the absolute cross sections if the active diode area, A, and the H atom rate, q_H, are known. With $A \approx 0.3$ cm^2, the analysis gives values for σ_a of approximately 5×10^{-16} cm^2 for Ag and 4×10^{-16} cm^2 for the Cu film. With an assumed initial adsorption probability of unity, the reciprocal of the cross section σ_a is equal to the adsorption site density. From our data, we obtain adsorption site densities of $(2-3) \times 10^{15}$ cm^{-2} for both Ag and Cu films. These values are in excellent agreement with the number of metal atoms per unit area which is 2.4×10^{15} cm^{-2} for Ag(111) and 3.1×10^{15} cm^{-2} for Cu(111) surfaces, and support our interpretation of the I-t curves. Furthermore, the present experiment shows a new way of measuring self-abstraction rates with only one atomic species.

It was also found that the chemicurrent is attenuated exponentially with increasing metal thickness in Ag/n-Si diodes. The attenuation length correlated well with the mfp of electrons in Ag, which further supports the idea of hot electron creation at the surface and ballistic travel through the metal film.

The quantitative difference between the n-type Ag and Cu Schottky diodes in Fig. 2 is striking. A sensitivity may be defined by dividing the initial chemicurrent at $t = 0$ by the H atom impingement rate. This gives the number of electrons detected per adsorption event which is 4.5×10^{-3} for Ag and 1.5×10^{-4} for Cu. On p-type diodes, we found the same sensitivity *ratio*. Thus, the difference does not correspond to a barrier height difference which is observed only with n-type Schottky

diodes. We attribute the sensitivity difference to two effects. First, the mfp of electrons in Cu films has been measured to be half that of Ag films [8]. Second, the interface properties of Ag/Si and Cu/Si are very different; e.g., although copper reacts with Si and may form a silicide [14], similar reactions are not known for Ag on Si. Since the diodes are annealed, Cu/Si interfaces are expected to be rougher and to have more scattering centers than Ag/Si interfaces. The enhanced roughness may reduce the transmission probability considerably, in agreement with reported results on mfp in silicides which are smaller than in metals [9].

The p-type Ag/Si diode is seen in Fig. 2 to be approximately 3.5 times less sensitive than the n-type device. This might be explained by differences in the mfp of holes and electrons in Ag, as observed previously in Au [8] and PtSi thin films [15]. In these studies, the attenuation lengths of holes were a factor of approximately 1.5 smaller than for electrons. Additionally, the sensitivity difference may be related to the energy spectra of holes and electrons excited by the surface reactions. The d bands of bulk Ag cannot contribute to the ballistic current since they are more than 2.7 eV below E_F [16]. The ballistic charge carriers thus have nearly free sp character. The probability of exciting an e-h pair is assumed to depend on the joint density of states (DOS) of occupied and empty electronic states. Since the DOS of Ag increases slightly with energy in the range of ±3 eV around E_F [16], electrons closer to the Fermi level are excited more effectively. Consequently, the energy distributions of ballistic holes and electrons are not symmetric around E_F and, on average, the ballistic electrons are expected to have higher kinetic energies than the hot holes. Such an asymmetry would lead to a significant sensitivity difference between p- and n-type devices.

Figure 3 shows I-t curves for atomic hydrogen and deuterium reacting with a 75 Å Ag film on n-Si(111). The oscillations in the decay curves are due to plasma
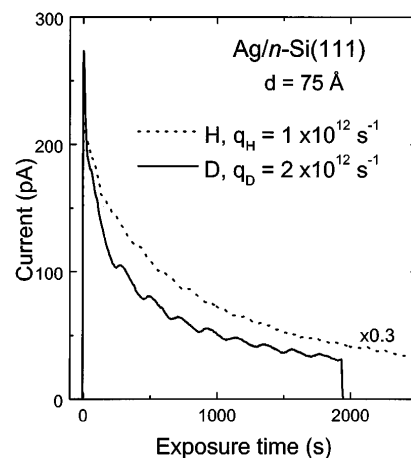

FIG. 3. I-t curves recorded from Ag/n-Si(111) diodes exposed to atomic hydrogen and deuterium. The chemicurrent due to atomic hydrogen adsorption is multiplied by a factor of 0.3.

fluctuations. Although the impingement rate of atomic deuterium was approximately twice as large as for atomic hydrogen, the measured chemicurrent with D exposure was smaller by a factor of 3, i.e., the sensitivity to D is 6 times smaller than to H atoms. The slight difference in the strengths of H and D metal bonds cannot explain this observed isotope effect. A reduced adsorption probability for D on Ag would also not account for this observation since this would affect the decay rate as well. The decay rates in Fig. 3 differ by a factor of approximately 1.8 which is exclusively attributed to the flux difference. The isotope effect implies different velocities and interaction times of the incoming H and D atoms by a factor of $\sqrt{2}$. The interaction time, however, is still in the 10^{-13} s range, at least 1 order of magnitude longer than time constants of electron transfer between substrate and the impinging atoms. For the same reason, we exclude internal exoelectron emission which requires quenching of resonant charge transfer into the affinity level of the approaching atom accompanied by a drastic change of the surface oxidation state [3,6].

The more relevant mechanism behind the isotope effect is likely to be the deexcitation of highly excited vibrational states formed under chemisorption. The maximum spacings between the vibrational levels are in the order of 100 meV. Therefore, higher order vibrational relaxation is needed to create hot electrons and holes with sufficient energy to traverse the Schottky barrier. The formation energies of D-Ag and H-Ag bonds are almost identical; however, the vibrational states in the anharmonic D-Ag potential are closer to each other than for H-Ag. Consequently, to create charge carriers with energies above the barrier, the transition between two vibrational levels must be of higher order for the D-Ag than for the H-Ag system. The transition probability decreases with increasing order, so that less electrons or holes with sufficient energy are excited when D instead of H is adsorbed. This explains the lower sensitivity of the device to D.

In summary, we report the first direct detection of hot electrons and holes excited by adsorption of atomic H (and D) on ultrathin Ag and Cu films as a *chemicurrent*. The current is measured in a large-area Schottky diode formed from these metals on Si(111). The devices are unique sensors which can discriminate atomic from molecular hydrogen as well as D from H atoms. The chemicurrents decay exponentially with exposure time and reach a steady-state value. This behavior corresponds to the occupation of free adsorption sites by H atoms and a balance between adsorption and abstraction. The currents are smaller if p-type semiconductors are used and if the devices are exposed to D rather than H. This effect opens a new way of monitoring reactions on metal surfaces and will certainly initiate further investigations to clarify the mechanism of the excitation.

*Author to whom correspondence should be addressed. Email address: nienhaus@uni-duisburg.de

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