Generation of hot charge carriers by adsorption of hydrogen and deuterium atoms on a silver surface

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The generation of hot charge carriers during adsorption of atomic hydrogen and atomic deuterium on Ag has been investigated by chemicurrent measurements using thin-metal film Ag/*p*-Si(111) Schottky diodes. The detected currents are due to nonadiabatic dissipation of chemical energy and exhibit a strong isotope effect. The chemicurrent efficiency is found to be 3.6 times larger for atomic hydrogen adsorption than atomic deuterium. The isotope effect does not depend on the metal film thickness of the device. The results are in excellent agreement with the electronic friction model of chemicurrents [Phys. Rev. Lett. **88**, 166802 (2002)] and give a temperature parameter of 1690 K for the Boltzmann-type energy distribution of the hot charge carriers excited by atomic hydrogen adsorption on Ag.

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In the past years, experiments using thin metal film electronic devices have demonstrated that chemical energy deposited by reactions on metal surfaces can be dissipated nonadiabatically by exciting electron-hole pairs in the metal film.[1–5] Schottky diodes have been most successfully used as a tool to probe chemically induced electronic excitations by measuring chemicurrents. Such currents are due to ballistic transport of excited charge carriers created at the metal surface towards the metal-semiconductor interface. If the kinetic energy of the hot charge carriers is larger than the Schottky barrier height they are able to traverse the barrier where they are detected as a reverse current in the diode.

Soon after the first experimental results, *ab initio* theories of chemicurrent generation based on density functional theory were presented.[6] The studies focus on the electron-hole pair production in Cu(111) surfaces exposed to atomic hydrogen or atomic deuterium. The simulations show that the excitation of hot charge carriers by the atom-surface interaction is attributed to electronic friction mechanisms. The resulting energy distributions of the hot electrons and holes in the metal are in principle of Boltzmann type, i.e., $\sim\exp(-\varepsilon/k_B T_{\mathrm{eff}})$ where ε is the excess energy relative to the Fermi level and T_{eff} is a parameter describing the energy spread of the distribution. It should be noted that the hot charge carriers are not thermalized and that the exponential distribution does not describe an equilibrium situation. The friction model proposes a strong isotope effect as it predicts an excitation efficiency which depends on the particle mass or, equivalently, on the vibrational frequency of the atom in the potential well. Basically, the temperature parameter T_{eff} is proportional to $1/\sqrt{M_i}$ where M_i is the mass of the isotope. In the case of Cu(111), chemicurrents by H adsorption are expected to be six times larger than with D exposure if the Schottky barrier height is in the range between 0.5 and 0.6 eV.[6] Since the diodes are used as high-pass energy filters the isotope effect is much more pronounced with larger barrier heights. The calculations give T_{eff} values of approximately 1400 K for hot electron distributions excited by atomic hydrogen impingement on Cu(111).[6]

Heretofore, reliable chemicurrent measurements of the isotope effect have been missing. They require accurate numbers of the atom flux variations and a precise investigation of how device properties such as the metal film thickness influence the measurements. The present study allows us to verify the predictions of the electronic friction model for chemicurrent generation as it provides reliable quantative data of the isotope effect. Schottky diodes made of Ag/*p*-Si(111) are used to investigate the chemicurrent strength when exposing the diodes to well-defined doses of atomic hydrogen and atomic deuterium. A large number of diodes with varying metal film thicknesses were prepared to study the influence of the device parameters.

Large-area Schottky diodes were fabricated on *p*-type Si(111) wafer pieces with Ohmic back contacts. The Si surfaces were cleaned and hydrogen terminated in a multistep wet chemical process using hydrofluoric acid as described in detail elsewhere.[4] The passivated samples were rapidly transferred into an ultrahigh vacuum chamber ($p \leq 5\times10^{-8}$ Pa) where Ag films were thermally evaporated at substrate temperatures of 110 K. The actual diode area was 8×9 mm^2. The diodes were annealed to room temperature to improve the metal film as well as the diode quality. The properties of the Ag/Si(111) diodes are studied in detail in Ref. 7. After softly approaching a Au front contact ball to the metal film the diode was characterized by current-voltage (I/V) measurements from which effective Schottky barrier heights and ideality factors could be extracted. Using an extrapolation scheme from Ref. 8, the homogeneous Ag/*p*-Si(111) Schottky barrier height was determined from a large number of I/V curves at different temperatures to be 0.46 eV which is in good agreement with data from the literature.[8,9] Diodes with *p*-type Si were used because they are found to have better reverse current characteristics than Schottky diodes on *n*-type Si although the barrier height is smaller. For chemicurrent measurements, hot hole detection with *p*-type diodes is equivalent to hot electron detection using *n*-type devices as long as the electronic density of states does not vary strongly in a small interval around the Fermi level.[10] This is the case for metals such as Ag or Cu. Accordingly, the energy distributions of chemically induced hot electrons and hot holes are identical. Exposures of atomic hydrogen did not change the I/V characteristics significantly. Very small changes of less

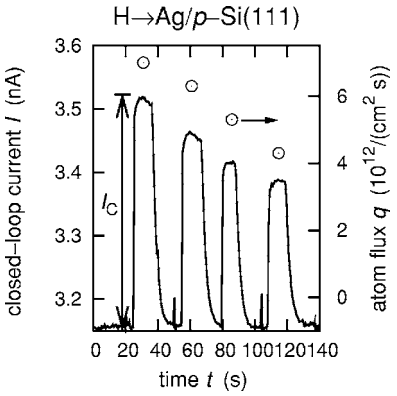

FIG. 1. Closed-loop currents detected from Ag/p-Si(111) Schottky diodes exposed to atomic hydrogen at a temperatures of 100 K. The current increase I_C during exposure is due to chemicurrents in the device. The background current is due to residual photocurrent. The open circles represent the atom flux values (right scale) during exposure.

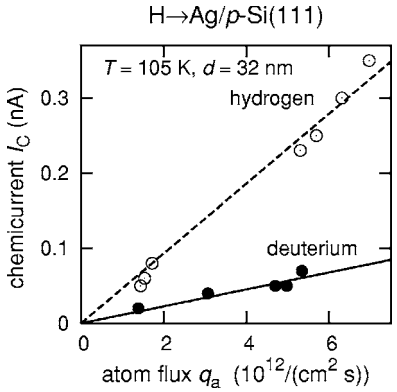

FIG. 2. Chemicurrent values from a Ag/p-Si(111) Schottky diode as a function of the atom flux for atomic hydrogen and atomic deuterium exposures. Impingement of the molecular species does not generate a chemicurrent. Atomic hydrogen exposure gives larger chemicurrents than such of atomic deuterium.

than 0.02 eV of the homogeneous barrier height were observed but did not influence the chemicurrent measurements.

Atomic hydrogen and atomic deuterium beams were generated by thermal dissociation in a hot-capillary source. The temperature at the end of the capillary was set to a temperature of 2300 K which gave a dissociation of 83% of the H_2 and 81% of the D_2 molecules.[11] Changing the front line pressure, the number of atoms leaving the source nozzle was varied from 1 to 7×10^{15} atoms/s.

Since the hot capillary is a strong photon emitter which induces photocurrents of 100 μA in the Schottky diodes, a light block was inserted in front of the nozzle. It is made of carbon-filled Teflon and uses angled passages to absorb photons while permitting hydrogen atoms to pass. Background photocurrent was easily reduced by five orders of magnitude. The distance between nozzle and diode is approximately 10 cm so that the atomic hydrogen flux onto the diode surface may be estimated at 1000 times smaller than the nozzle flux, i.e., between 1 and 7×10^{12} atoms/cm^2 s. The absolute atom flux is not essential to quantify the isotope effect accurately as long as the ratio between H and D flux is well defined.

Chemicurrents were recorded between front and back contact with no bias applied (closed-loop current) while the substrate temperature was held at 100 K to reduce the noise level. The measured closed-loop current in a Ag/p-Si(111) diode with a metal film thickness of 32 nm is shown in Fig. 1 where the exposure to atomic hydrogen is switched on and off with varying flux intensities. The latter are shown as open circles. The constant background of 3.16 nA is attributed to the residual photocurrent in the device. The current increase upon exposure is due to the chemicurrent I_C induced by spontaneous adsorption of atomic hydrogen on the Ag surface. A flux of 7×10^{12} hydrogen atoms/cm^2 s generates a chemicurrent of 350 pA in the device which corresponds to an efficiency of approximately 4×10^{-4} elementary charges per impinging H atom. The background photocurrent is not influenced by the hydrogen flux through the capillary as measured independently with a separate photodiode. Changes of the chemicurrent due to hydrogen adsorption on the surface may be neglected as the gas exposures are in the range of 1/100 of monolayer per data point and the total surface coverages are negligible.

The current increase I_C due to the chemicurrent is proportional to the atom flux as illustrated in Fig. 2 for a 32 nm Ag/Si diode. In addition, the chemicurrent is found to be 4.5 times stronger for this specific diode if it is exposed to atomic hydrogen compared to atomic deuterium which is in agreement to the predicted isotope effect. No chemicurrent is observed upon exposure to hydrogen molecules.

To quantify the isotope effect any influence of the metal film thickness must be excluded. Many Schottky diodes with Ag film thicknesses in the range between 6 nm and 35 nm were prepared and exposed to the atom beam. The determined chemicurrent efficiencies are plotted on a logarithmic scale as a function of the metal film thickness d in Fig. 3. Open symbols represent data for atomic hydrogen and solid ones for atomic deuterium. The chemicurrents are attenuated with increasing metal film thickness where the linear fits in Fig. 3 show first order exponentials ($\sim\exp[-d/\lambda]$). The attenuation constant λ is determined as 24±7 nm irrespective of the isotope. Thus, the significant isotope effect does not

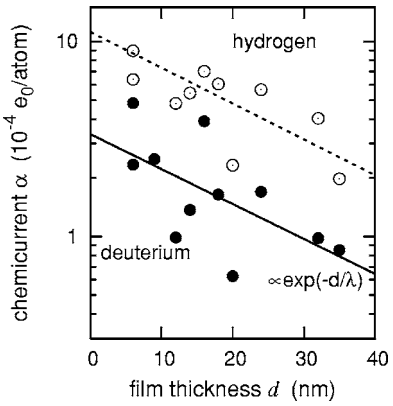

FIG. 3. Chemicurrent efficiencies as a function of Ag film thickness. The isotope effect is independent of the film thickness.

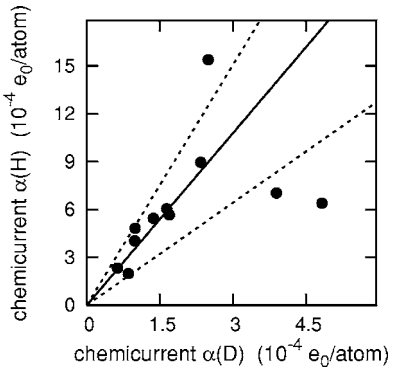

FIG. 4. Chemicurrent efficiencies of various diodes for exposures of H and D atoms. The solid line is a fit to the data and gives an efficiency ratio of 3.6. The dashed lines give the confidence interval of the data assuming a log-normal distribution of the efficiency ratios.

depend on device properties. Any effects which may be expected due to attenuation constants which should change with hot charge carrier energies are too small to be significant within the error margins.

In Fig. 4 the chemicurrent efficiencies of all diodes are plotted in one diagram. Assuming that the chemicurrent data scatter according to a normal distribution, the statistical error of the efficiency ratio $\gamma = \alpha(\mathrm{H})/\alpha(\mathrm{D})$ may be described by a log-normal distribution. The slope of the solid line in Fig. 4 corresponds to the expectation value of this ratio and is found to be $\gamma = 3.6$. The dashed lines in Fig. 4 indicate the 1σ-confidence interval which is $[2.1, 5.0]$. It is obvious from Fig. 4 that the data from Schottky diodes with small metal film thicknesses and high chemicurrent efficiencies have the largest scatter. This finding may be explained by the strong variations of the morphology of very thin Ag films on Si. These tend to form large coalescing islands which influence the chemicurrent strength due to different height distributions.[7] Excluding the three data points with large chemicurrents outside the confidence interval in Fig. 4 demonstrates the small scatter of the other data and yields $\gamma = 3.7 \pm 0.7$.

Applying the Boltzmann-type energy distributions of excited charge carriers from the electronic friction model to our system of deuterium and hydrogen the isotope efficiency ratio is related to the Schottky barrier height Φ_B and the temperature parameter T_{eff} as

$$\ln \gamma = \frac{\Phi_B}{k_B T_{eff,\mathrm{H}}} \left(\sqrt{\frac{M_D}{M_H}} - 1 \right). \quad (1)$$

Inserting $\gamma = 3.7 \pm 0.7$ and $\Phi_B = 0.46$ eV yields $T_{eff,\mathrm{H}} = 1690 \pm 300$ K for hot holes excited by H adsorption on Ag surfaces which is in excellent agreement with the prediction of the first principle calculations. The data, therefore, strongly support the electronic friction model of nonadiabatic energy dissipation during adsorption of H atoms on metal surfaces.

In addition, Eq. (1) gives the relationship between the Schottky barrier height and the efficiency ratio. If the effective temperatures of hot hole and hot electron distributions do not largely deviate, the H/D-chemicurrent efficiency ratio may be estimated for *n*-type Ag/Si(111) diodes with Schottky barrier heights of 0.7 eV. For a temperature parameter of 1690 K a value $\gamma_n \approx 7$ is expected which agrees very well with the high efficiency ratios observed in the first chemicurrent studies.[2]

In conclusion, chemicurrents have been measured in Ag/*p*-Si(111) Schottky diodes which were exposed to atomic hydrogen and to atomic deuterium. The currents are due to nonadiabatic dissipation of chemical energy during spontaneous adsorption of the atoms on the clean silver surfaces. Exposures to atomic hydrogen generate currents which are 3.7 times larger than exposures to atomic deuterium indicating a strong isotope effect in nonadiabatic energy dissipation. This value is independent of the metal film thickness of the device. The experimental results are in excellent agreement with electronic friction calculations which predict Boltzmann-type energy distributions of the hot charge carriers. Temperature parameters of 1690 K are deduced for atomic hydrogen adsorption on Ag surfaces.

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