Chemically induced charge carrier production and transport in $Pd/SiO_2/n$-Si(111) metal-oxide-semiconductor Schottky diodes

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The energy transfer associated with reactions at metal surfaces produces energetic electrons and holes. Using ultrathin films of Pd on metal-semiconductor (MS) and metal-oxide-semiconductor (MOS) diode structures, we have investigated reaction-induced electrical phenomena associated with a variety of molecular and atomic interactions with the Pd surfaces. Distinct electronic signals are observable for species as diverse as atomic oxygen, xenon, and molecular hydrocarbons. Both MS and MOS devices allowed the detection of the chemically induced excitation of electron-hole pairs for highly exothermic chemisorption. Electronic signals from gas species with low adsorption energies were only observed in MOS devices with a thin oxide layer between the active metal film and the semiconductor. The density and distribution of interfacial states in the MOS devices have been found to be an important factor in understanding the origin and transport pathways of these "chemicurrents." A dynamic model is introduced to explain the displacement currents in the MOS devices during low-energy gas-surface interactions.

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I. INTRODUCTION

For almost 30 years metal-oxide-semiconductor (MOS) structures have been intensively investigated and used as gas-sensitive devices.[1–9] The principle of operation of MOS sensors has been explained by chemically mediated changes in the electric field across the oxide that modifies the space-charge layer in the semiconductor and the device electrical properties. Practically, the flatband voltage, the capacitance-voltage (C-V) characteristics, or photocurrents may be monitored in MOS diodes as a function of the gas exposure.

The details of how the gas species interact with the gate metal to give rise to the alterations in the oxide electric fields are still speculative. In the best-studied case of hydrogen detection by Pd-MOS diodes or field-effect transistors, hydrogen atoms created by breaking of hydrogen bonds at the catalytic metal are assumed to penetrate the Pd film and polarize the metal-oxide interface.[4] This mechanism may occur if the device is maintained at temperatures well above 400 K. The sensitivity of MOS devices with noble metal gates for reactive molecular species such as NO_2 has been explained by the penetration of gas particles through pores, voids, or grain boundaries of the assumed, discontinuous metal film.[1,5–7] For ammonia detection using Pt-SiO_2-Si diodes, a capacitive coupling of adsorbed molecules on the discontinuous gate metal film to the space-charge layer was proposed to understand the gas-sensitive field effect.[10]

Recently, ultrathin-film metal-semiconductor (MS), Schottky diodes have been shown to be active sensors for atomic and molecular gas phase species.[11–16] Gas-surface interactions are monitored not indirectly by a change in the device properties (passive sensing), but rather by direct detection of charge carriers produced from the gas-metal interaction. On these devices, when an adsorbate interacts with the surface, the adsorption energy may appear as an energetic electron-hole (e-h) pair generated in the metal surface. The excited electron can travel ballistically through the thin metal film and traverse the Schottky barrier if the kinetic energy of the electron is larger than the barrier height Φ_B and if the film thickness is comparable to the ballistic mean free path. Once inside the semiconductor, the electron is detected as a "chemicurrent" analogous to the photocurrent in a photodiode. Chemicurrent detection is very effective at low temperatures between 130 and 200 K. The currents are attenuated exponentially with increasing metal film thickness according to the mean free path concept of ballistic charge carriers in metals.

Gergen *et al.* showed that, by adding a thin oxide layer between the metal and the semiconductor, the modified MOS device had an increased sensitivity and had a response to a variety of weakly interacting gas species not detectable on the standard MS Schottky diode sensor.[14] The mechanisms for carrier generation and transport in these devices remain unclear. The original explanation of ballistic charge transport over the Schottky barrier appears valid for the detection of species with large adsorption energies including O, H, as well as molecular NO and NO_2. The mechanism of carrier generation and detection on the same devices for weakly interacting species such as alkanes, alkenes, and Xe is less clear since their average adsorption energies are below the average Schottky barrier.

In the present work we study the reaction-induced chemicurrents in Pd/n-Si(111)-Schottky and $Pd/SiO_2/n$-Si(111)

MOS diodes at low temperatures. The devices are exposed to gas species with large as well as very low adsorption energies. We propose a mechanism for current generation in the MOS diodes which includes the excitation of charge carriers in the metal. It explains the observed variation of the space-charge layer in the semiconductor without the need of gas particle penetration through the gate metal film.

II. EXPERIMENTAL DETAILS

A. Device fabrication and properties

The devices were fabricated on 17.5×12 mm^2 phosphorus-doped *n*-Si(111) wafers (resistivity $\sim1-10\ \Omega$ cm). The samples were prepared using a standard RCA cleaning procedure, followed by a 1-min dip in an aqueous solution of buffered HF and subsequent rinse in deionized (DI) water to form an oxide-free hydrogen-terminated Si surface.[17] On the back side of the silicon wafers, 150 nm of Ti followed by 150 nm of Au were evaporated to achieve a functional Ohmic contact. Two 400-nm Pt pads isolated from the silicon substrate by a 300-nm-thick evaporated SiO_2 film were used as front contacts. For MOS diodes an ultrathin silicon oxide layer was grown between the front contacts by means of a 5–10-min dip in an aqueous solution of 30% H_2O_2. Using angle-dependent x-ray electron spectroscopy, the thickness of the SiO_2 layer was determined as approximately 0.7 nm. All device preparations have been performed under clean room conditions.

The backside ohmic contact of the diode platform was mounted with indium to a molybdenum sample holder and transferred into the ultrahigh vacuum (UHV) chamber ($p<5\times10^{-8}$ Pa). Pd films (5–80 nm) were deposited on the front of the platforms by *e*-beam evaporation at low temperature of 125 K to form the Schottky diode contact. Low-temperature deposition was selected in order to inhibit surface diffusion, which results in a continuous, polycrystalline, pinhole-free film at a smaller thickness than what would be achieved at higher temperatures.[18] The dependence of sensitivity on film thickness was investigated by sequential fractional monolayer exposures, followed by subsequent thermal evaporation of Pd under UHV on the same device.

Atomic force microscopy (AFM) at room temperature under atmospheric pressure was performed to determine the film morphology. A 6-nm-thick Pd film of a MS Schottky diode exhibits a relatively "flat" surface with an average roughness of less than 2 nm. Polycrystalline Pd films of the same thickness on the oxidized Si surface are comprised of continuously interconnected islands of approximately 10 nm diameter hemispherical elements, in agreement with the expected island growth of transition metals on oxide surfaces.[19]

Due to the ultrathin oxide layer, the MOS diodes have rectifying properties similar to the standard MS Schottky diodes. Effective Schottky barrier heights were extracted from current-voltage (*I-V*) and capacitance voltage (*C-V*) measurements at low temperatures using standard theory for metal-semiconductor contacts.[20] From the *C-V* data, barrier heights of 0.8 eV for Pd/*n*-Si and 0.88 eV for Pd/SiO_2/*n*-Si diodes were found, indicating that there is an additional potential barrier of 0.88 eV in the case of the MOS device. This may be attributed to negative charges at the metal-oxide interface.

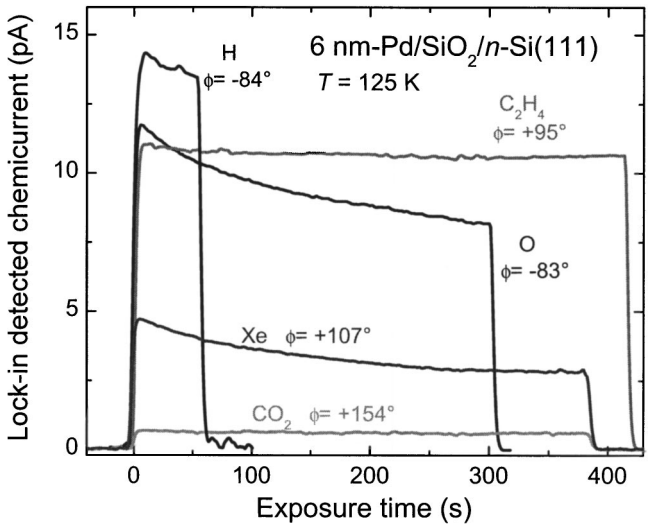

FIG. 1. Lock-in detected chemicurrent signals from Pd(6 nm)/SiO_2(0.7 nm)/*n*-Si(111) MOS diodes as a function of exposure time to H, O, C_2H_4, CO_2, and Xe.

B. Current measurements

Chemicurrents and photocurrents in the devices were measured under UHV conditions at temperatures of 125 K. The diodes were connected in series with a current preamplifier (SRS 570), whose output was connected either to a lock-in amplifier (SRS830) or an analog-to-digital (A-D) converter (LeCroy 9361) for signal averaging. Photocurrents were measured by illumination of the diodes with modulated light from laser diodes with wavelengths of 1550 nm [infrared (IR)] and 660 nm [visible (vis)].

To investigate the diode response to gas exposure, the active sensors were positioned in line to a shuttered collimated gas beam modulated at 4 Hz (50% duty cycle). The room temperature thermalized beam had a flux that varied between 2 and 5×10^{12} gas particles cm^{-2} s^{-1}. The sensors were exposed to molecular and atomic hydrogen and oxygen, several hydrocarbons (C_2H_4, C_3H_6, etc.), xenon, and carbon dioxide. Mixed beams of atomic and molecular gas species were produced and delivered by a three-stage differentially pumped beam source.[21] Hydrogen and oxygen atoms were produced by dissociation of molecules within a microwave plasma at gas pressures between 15 and 80 Pa. The plasma source was especially designed to extract any photons from the gas beam since the plasma emits intense ultraviolet light with a photon energy of 10.2 eV and the Schottky diodes are sensitive photodetectors.

III. RESULTS

Figure 1 shows the phase-sensitive demodulated lock-in amplifier output from Pd(6 nm)/SiO_2/*n*-Si(111) MOS diodes exposed to O, H, C_2H_4, Xe, and CO_2. The shutter was opened at $t=0$ and closed after exposures of between 60 and

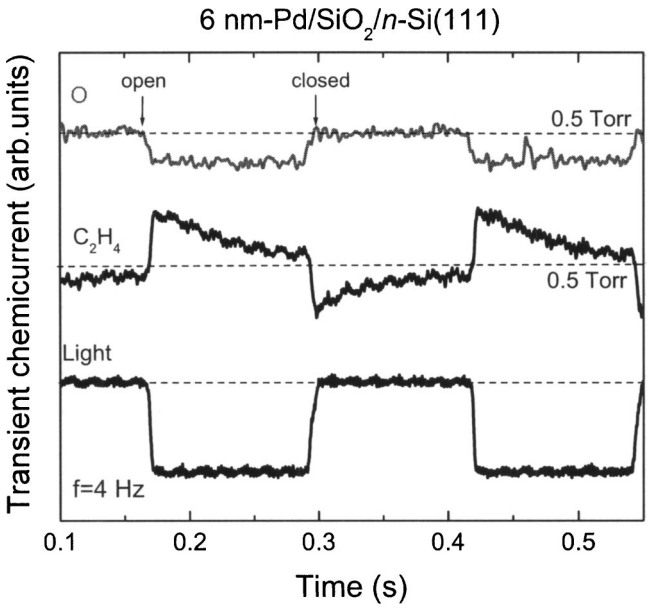

FIG. 2. Time-averaged single pulse currents recorded at Pd-MOS diodes during exposure to O, C_2H_4 and white light. The signals were modulated at 4 Hz and the dashed lines indicate the signal base line. The gas pressure of 0.5 Torr in the first beam chamber is a relative measure of the gas particle flux.

420 s. Upon exposure to the reactive atomic species O and H, a decaying chemicurrent is observed similar to what is found with Pd/*n*-Si(111) and other MS Schottky diodes.[11] The current transients reproduce the chemical kinetics of the surface reaction, which may be modeled by spontaneous adsorption and abstraction mechanisms.[16] For the much less reactive gas species C_2H_4, CO_2 and Xe currents are detected from MOS diodes that cannot be observed on Pd/*n*-Si MS devices. In addition, only the Xe-induced signal exhibits a slight decay, consistent with the formation of an adlayer of

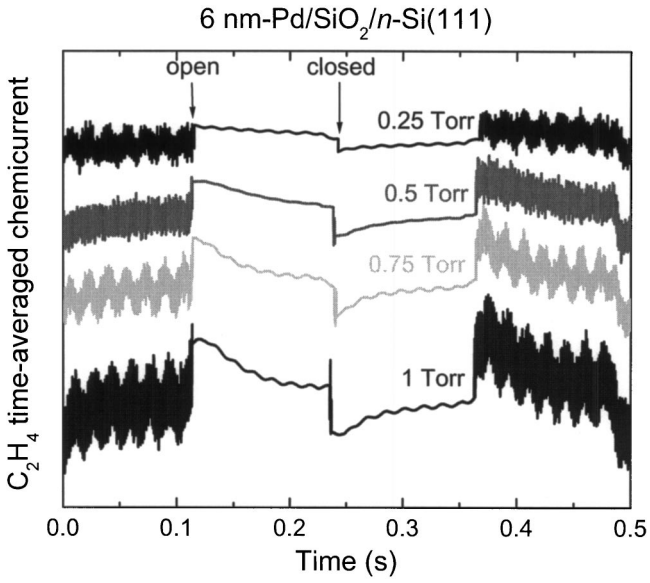

FIG. 3. Time-averaged single pulse chemicurrents measured during Pd-MOS diode exposure to C_2H_4 beams with first beam chamber pressures from 0.25 to 1 Torr.

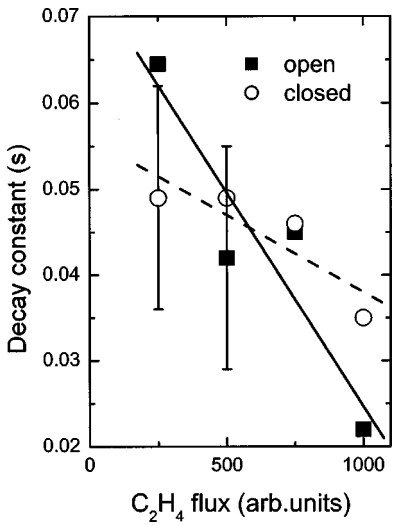

FIG. 4. Variations of the time constants of the decaying forward (shutter open) and reverse currents (shutter closed) with C_2H_4 flux.

Xe adsorbed on Pd at a temperature of 125 K. The phase-sensitive currents for the molecules are approximately constant over the exposure time.

The phase φ of the signals in Fig. 1 is a measure of the direction of the current movement relative to the incident beam pulse impingement.[22] In the case of the energetic atomic species (O and H), a negative phase was measured, which is identical to the photocurrent phase corrected for the difference in beam transit times (0.5 ms), indicating a reverse bias current that is expected for a chemicurrent due to hot electron generation in the metal and transport over the Schottky barrier. For species (C_2H_4,CO_2,Xe) interacting with low energy with the surface, the phase of the signal was reversed, corresponding to a forward bias current movement that cannot be explained by the original chemicurrent picture.

To clarify the response of the MOS diodes, individual chemicurrent and photocurrent signal pulses at 4 Hz were captured and averaged for noise reduction. The averaged signals from O, C_2H_4, and vis-light exposure are shown in Fig. 2. The dashed lines indicate the zero current base line. The foreline pressure is a qualitative relative measure for the gas flux. With the O atom and light exposure, a continuous chemi- and photocurrent, respectively, is observed vanishing as soon as the shutter is closed.

It is evident that the current direction of the signal induced by the interaction of C_2H_4 (similar traces observed for CO_2 and Xe) is opposite to that of the more reactive species and to that of light. The apparent forward bias current (reversed phase) observed by lock-in detection is revealed here to be a displacement current similar to charging and discharging of a capacitor. When the device is exposed to C_2H_4, the positive space charge in the semiconductor is reduced by charge displacement. When gas exposure is stopped, charge movement occurs to reestablish the initial equilibrium.

The charging and discharging processes upon exposure to C_2H_4 were studied as a function of the gas flow. Figure 3 shows four current traces where the middle parts were smoothed to reduce the noise level. The intensity of the cur-

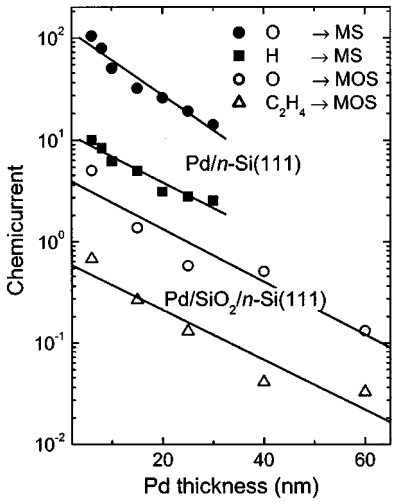

FIG. 5. Thickness-dependent chemicurrent (log scale) for Pd-MS and Pd-MOS diodes upon various gas exposures. The attenuation constants of the linear fits are 13 nm for O→Pd/Si and 17 nm for others.

rent scales with the molecular flux. To study the relationship between the time constants of the decaying forward and reverse currents, single exponential functions were used to fit the experimental data. In Fig. 4, the time constants of the approximation are plotted as a function of the relative particle flux for charge flow after opening and closing the beam shutter. The solid and dashed lines are linear fits to the solid and open data symbols, respectively. Although the error margins are large, there is an obvious tendency that the time constant of the decaying forward current when the shutter is opened (solid squares) depends on the molecule impinging rate. A larger gas flux leads to a faster decay of the forward current. However, the time constant of the backflow of charge (open circles) is less sensitive to the gas flux increase.

Measurements of the response of both MS and MOS devices to a chopped beam of O, Xe, or C_2H_4 during constant dc irradiation with IR or vis laser light showed no modulation of the dc photocurrent signal (if present), suggesting that no pulse-to-pulse change in the device electrical characteristics was occurring.

In order to clarify the nature of the chemically induced electrical phenomena, chemicurrents were studied as a function of the Pd film thickness. In Fig. 5 the results from Pd/*n*-Si(111) MS diodes upon exposure to H and O atoms and from $Pd/SiO_2/n$-Si(111) MOS diodes upon exposure to O and C_2H_4 are plotted on a semilogarithmic scale with arbitrary units. The detected currents are exponentially attenuated with film thickness. As guidelines, single exponential functions $[\sim\exp(-d/\lambda)]$ were fitted to the data to get an estimation of the respective attenuation constant λ. We find $\lambda \approx 13$ nm for the MS diodes upon O exposure and $\lambda \approx 17$ nm for the other gas-diode combinations. These values are in good agreement with electron attenuation lengths of 17 ± 3 nm from photoemission measurements on Pd/*n*-Si junctions using photon energies below 1.1 eV by Crowell *et al.*[23]

Although the scatter of the data in Fig. 5 is rather large, the attenuation of the MS diode chemicurrents may be better described by two exponential functions, implying the existence of smaller λ values for the thinner films than for the thicker films. This observation may be due to the formation of a thin Pd silicide layer in the absence of thin SiO_2 intermediate layer.[24] Hence, the two different attenuation lengths for MS diodes may be attributed to, first, ballistic charge transport in the Pd-silicide layer and then transport through the Pd metal on top of the silicide.

IV. DISCUSSION

The adsorption energies of atomic hydrogen and atomic oxygen on Pd are significantly greater than the internal Schottky barrier height of the MOS and MS devices. Thus, the electron currents detected moving from the metal surface into the semiconductor from both MS and MOS Pd/Si diodes from these energetic atomic adsorptions are consistent with the chemicurrent picture of hot electron transport and transmission over the Schottky barrier. The signal attenuation with thickness is also consistent with what is known of the hot carrier mean free path.[24] Thus, for energetic reactions, the currents in both the MS and MOS devices are generated by chemically induced excitation of hot charge carriers.

The interaction energies of Xe, C_2H_4, or CO_2 with Pd are between 0.2 and 0.5 eV. These energies are less than the Schottky barrier height in MS devices and, hence, the diodes do not show sensitivity to those weak interacting species. The adsorption energies are also less than the (higher) Schottky barrier of the MOS devices. To explain the presence of any signal at all and the fact that the electron current direction and transient behavior are different from those observed with high-energy interactions, a different mechanism is required. The critical difference between the two device types is the presence of the interfacial oxide, which must be responsible for the apparent displacement currents.

Previous work with MOS diodes has attributed sensitivity to changes in the device characteristics to chemically medi-

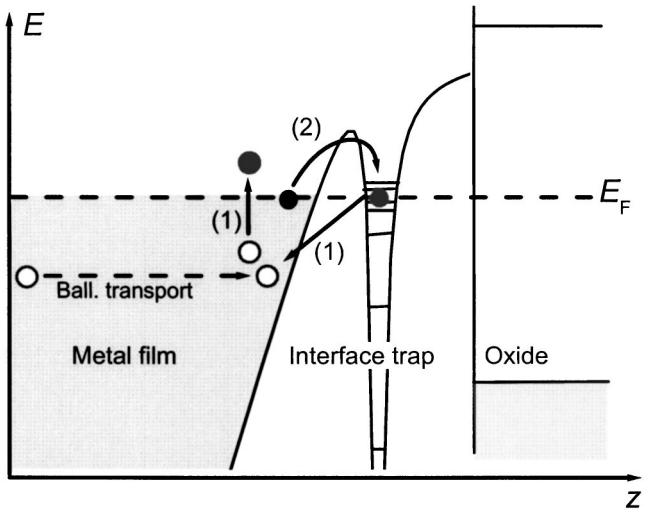

FIG. 6. Dynamic model for observed displacement currents. (1) Discharging of acceptor-type interface states by chemically induced ballistic holes. (2) Charging of interface states.

ated phenomena by gas particles, which diffuse to the metal-oxide interface and polarize the semiconductor, leading to a charge displacement in the space-charge layer by the field effect. The sensitivity of such field-effect gas sensors decreases only slightly with increasing metal film thickness.[10]

In the present study, the MOS diodes were exposed at low temperatures (125 K) so that diffusion-based processes are inhibited. Additionally, no pulse-to-pulse changes were observed in the *I-V* or *C-V* characteristics of the devices that correlated to adsorption of the chopped molecular beams. This, together with experiments performed using simultaneous dc photocurrent irradiation and chopped molecular ethylene or Xe beams that showed no modulation in the photocurrent signal, exclude an indirect mechanism, whereby the presence of the absorbate significantly alters the Schottky barrier or device performance. In addition, no significant changes of the *I-V* or *C-V* characteristics were observed with metal film thickness.

Furthermore, if changes in the work function or metal surface chemical potential were driving the charge transport, the observed current should be independent of the thickness of the metal that forms the Schottky contact. However, the thickness dependence of the chemicurrent displayed in Fig. 5 shows an exponential behavior and is consistent with attenuation of ballistic charges in both types of sensors.[16]

To explain the experimental findings in the MOS devices, we propose a dynamic model including ballistic transport of charges excited at the metal surface by the gas-surface interaction as shown in Fig. 6. There is evidence from the *C-V* measurements that localized negative charges exist at the metal-oxide interface. We assume that such charges are present in interface traps which act as acceptor-type states.

Electron-hole pairs created by gas adsorption have energies proportional to the reaction energy. The energy distribution of hot electrons and hot holes are approximately symmetric around the Fermi energy. For low interaction energies, the hot electrons have insufficient energies to overcome the Schottky barrier of the *n*-type diode, and are scattered within the metal film and eventually thermalized. However, the hot holes that reach the interface may recombine with electrons localized at the metal-oxide interface trap. As illustrated schematically in Fig. 6, the recombination occurs close to the Fermi level by an Auger process (1), creating an electron-hole pair that is rapidly thermalized. The trap may be recharged if metal electrons at the Fermi energy are transferred into the unoccupied trap state [pathway (2) in Fig. 6]. This process may happen either by tunneling, if the potential barrier between the metal electron state and the trap state is small, or by thermoemission across a larger barrier.

Thus, the occupation of the trap states changes when the beam shutter is opened and the diode is exposed to charge generating molecules. This forward current vanishes as soon as a detailed balance between the Auger process (1) and recharging process (2) is reached. When the shutter is closed, process (1) is stopped, but process (2) is still active and leads to the initial trap state occupation. Since the countercharge on the semiconductor side changes according to any variations of the trap charge, the on- and off-switching of process (1) leads to the observed flow of electrons in and out of the space-charge layer of the semiconductor.

To model the single-shot experiments shown in Fig. 2 and 3 quantitatively, simple rate equations are applied. Interface states are assumed to be acceptor type, i.e., they are charged negatively in thermal equilibrium and are neutralized by the Auger process (1). If A gives the total number of interface states per unit area, the number of negative charged interface states, A^-, varies in time during exposure according to

$$\frac{\mathrm{d}A^-}{\mathrm{d}t} = -k_1 P_h A^- + k_2(A - A^-), \tag{1}$$

where k_1 and k_2 are the rate constants for the processes of discharging and charging [(1) and (2) in Fig. 6]. The weighting factor P_h gives the probability that a hot hole exists at the interface state, i.e.,

$$P_h = \begin{cases} N_h/A & \text{for } N_h \leqslant A \\ 1 & \text{else.} \end{cases} \tag{2}$$

Assuming that the hot charge carrier creation is due to reaction of the adsorbate with the metal substrate, the number of hot holes produced per unit area, N_h, depends on the reactant flux, q, the average lifetime of the hot holes, τ_h, and device properties (e.g., metal film thickness, attenuation constants). Taking these factors into consideration, $N_h = \gamma \tau_h q \propto q$, where γ is a constant. Integration of Eq. (1) yields

$$A^-(t) = \frac{A}{k_1 P_h + k_2}(k_2 + k_1 P_h \exp\{-(k_1 P_h + k_2)t\}) \tag{3}$$

under the condition that $A^-(t=0)=A$, and $A^-(t\to\infty) = k_2 A/(k_1 P_h + k_2)$ gives the steady-state number of charged interface acceptors.

The detected current density of the pulse after the beam shutter is opened may be written as

$$j_+(t) = e_0 \frac{\mathrm{d}A^-}{\mathrm{d}t} = -e_0 A k_1 P_h \exp\{-(k_1 P_h + k_2)t\}. \tag{4}$$

For $t=0$, the current is proportional to the gas particle flux. The time constant depends on the particle flux as well. The total detected charge in one infinitely long charging pulse may be calculated as

$$Q_+ = e_0[A - A^-(t\to\infty)] = e_0 \frac{k_1 P_h}{k_1 P_h + k_2} A, \tag{5}$$

which is $e_0 A$ at maximum.

Recharging of the interface states occurs when the exposure is interrupted. The repopulation of the interface states obeys the simple rate equation

$$\frac{\mathrm{d}A^-}{\mathrm{d}t} = k_2(A - A^-), \tag{6}$$

which describes the time-dependent number of negatively charged interface states,

$$A^-(t) = A - \frac{1}{e_0} Q_+ \exp\{-k_2 t\}. \tag{7}$$

The current density during recharging is then

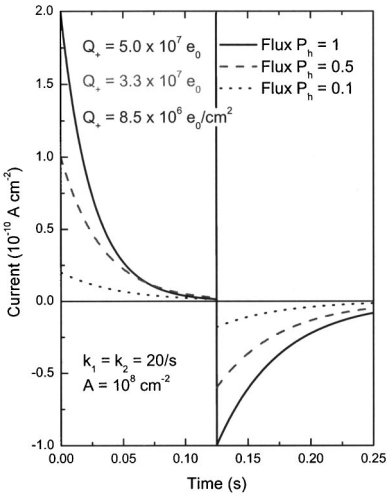

FIG. 7. Calculated chemicurrent traces for various parameter settings. At $t=0$, gas exposure starts; at $t=0.125$ s, the gas shutter is closed.

$$j_{-}(t) = k_2 Q_{+} \exp\{-k_2 t\}, \tag{8}$$

with a charge balance of

$$Q_{-} = e_0[A - A^{-}(t=0)] = Q_{+}. \tag{9}$$

From Eq. (8), it is obvious that the time constant of the recharging process is flux independent, in agreement with the experimental observations. Hence, the modulated beam generates an alternating current in the MOS diode, which gives an average signal at the output of the lock-in amplifier.

Figure 7 displays currents traces calculated following Eqs. (4) and (8) for $k_1=k_2=20/s$, $A=10^8$ cm^{-2}, and $P_h=1$ (solid line), 0.5 (dashed line), and 0.1 (dotted line) with Q^+ values of 5.0×10^7, 3.3×10^7, and 8.5×10^6 e_0/cm^2, respectively. At $t=0$, the gas exposure begins and the traces represent the discharging of the interface states due to chemically induced ballistic holes. At $t=0.125$ s, gas exposure stops and recharging of the interface states occurs.

The choice of the parameters is motivated by literature data. The reciprocal of the k values corresponds to the lifetime of deep levels in SiO_2. Such lifetimes have been determined by use of time-dependent capacitance-voltage measurement at metal-semiconductor interfaces[25] and emission time spectroscopy at heterostructures, e.g., at Si-SiO_2 interfaces.[26] They depend on the character of the deep level and the temperature, and lifetimes may vary by orders of magnitude, typically between seconds and microseconds. The k value of $20/s$ is in agreement with this interval. To estimate the interface trap density A, experimental values of the Si-SiO_2 interface may be considered, which range between 10^{10} and 10^{13} cm^{-2} eV^{-1} for traps far from the band edges.[26] Assuming that traps that are important for the process are in a thermal energy interval ($\approx$10 meV) around the Fermi level, an interface density of 10^8-10^{11} cm^{-2} is determined, close to the assumed A value in the model.

The P_h number cannot be extracted from other experimental data since the number of created hot holes per unit area is unknown. Therefore, a convenient value close to unity was assumed for P_h. However, if A is underestimated in the model, it may be corrected by smaller P_h values. Smaller P_h values would reduce the influence of the gas flux on the forward current time constant. Indeed, the experimental data in Figs. 3 and 4 exhibit a much smaller dependence of the decay time with particle flux than the calculated data in Fig. 7.

The decay of the lock-in current during Xe impingement may be explained within the proposed model if the adsorption rate of the gas particle cannot be neglected. In that case, the number of unoccupied surface sites must be included. Then, the current may be written as

$$j_{LI}(t) = \alpha_{eff} e_0[1 - \Theta(t)]q. \tag{10}$$

Depending on the adsorption process, the adsorbate coverage θ is time dependent. If a Langmuirian-type adsorption process and a first-order desorption is assumed, the rate equation becomes

$$\frac{d\Theta}{dt} = \sigma_a(1-\Theta)q - k_d\Theta, \tag{11}$$

with the time-dependent coverage given by

$$\Theta(t) = \frac{\sigma_a q}{\sigma_a q + k_d}(1 - \exp\{-(\sigma_a q + k_d)t\}), \tag{12}$$

where σ_a denotes the cross section for adsorption and k_d is the rate constant of desorption. The steady-state coverage for $t\rightarrow\infty$ is

$$\Theta_s = \frac{\sigma_a q}{\sigma_a q + k_d}, \tag{13}$$

which vanishes if the desorption rate is much larger than the adsorption rate. This is the case for CO_2 and C_2H_4 in Fig. 1, where the lock-in signal is independent of exposure time. For Xe at low temperature, a slow decay of the current is observed, leading to a steady-state coverage of approximately 17%.

V. CONCLUSIONS

The electronic responses of Pd/n-Si(111) MS and Pd/SiO_2/n-Si(111) MOS Schottky diodes were studied, associated with high-energy reactions on the Pd thin film of hydrogen and oxygen atoms and from low-energy interactions of Xe, C_2H_4, and CO_2. Chemisorption associated with large adsorption energies gives rise to excited electrons that surmount the Schottky barrier and are observable in both MS and MOS diodes. For gas adsorption with reaction energies of less than 0.5 eV, displacement currents are detected in MOS devices only. These currents indicate electron movement from the semiconductor towards the metal surface (forward direction) when gas exposure is started. A rapid, flux-dependent decay in the current is observed during exposure. After the exposure is terminated, a transient current is observed in the opposite direction, which also decays rapidly. These observations are consistent with a dynamic model that combines chemically induced electron-hole pair generation, hot hole transport, and discharging and recharging of localized states at the metal-oxide interface.

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