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A MIS device structure for detection of chemically induced charge carriers

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Abstract

Chemically induced electronic excitations were detected from adsorption of molecular ethylene and atomic oxygen on large-area Au/Al$_2$O$_3$/n-Si metal/insulator/semiconductor (MIS) diodes. The devices were fabricated with oxide thicknesses varying between 0 and 8 nm. For devices with an oxide layer less than ∼3 nm and relatively energetic surface adsorption reactions, electrons are excited by non-adiabatic energy transfer above the Fermi level and travel ballistically into the semiconductor. For low energy reactions and thicker oxides, charge transport in the device is dominated by ballistic "hot" holes created below the Fermi level which travel to the metal-insulator junction to electron donor states resulting in an effective forward-bias charging current. The energy-band structure of silicon as well as the density of interfacial states of the metal-insulator junctions strongly influences the electronic characteristics of the device. These MIS devices are suitable as molecular sensors for the detection of chemical species with low adsorption energies, such as hydrocarbons.
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1. Introduction

Energy and charge transfer during chemical reactions at surfaces are of fundamental and practical interest. During an adsorption process, the bond formation energies may exceed several eV, and the transfer and dissipation of the excess energy may involve one or more of the following processes: (1) phonon production [1,2]; (2) exoelectron emission [3,4]; (3) photon emission (chemiluminescence) [5,6]; and (4) electron–hole pair (e–h) production [7,8]. Recently, direct experimental evidence has been reported for excitations of energetic electron–hole pairs in metal surfaces during gas adsorption. These charge carriers can be observed using Schottky diodes with ultrathin metal films [9–13]. Electrons excited in the thin films to energies greater than the Schottky barrier height are transported over the barrier into the semiconductor and move through an external circuit as a "chemicurrent" that is analogous to a photocurrent. Both, hot electrons and hot holes have been observed from adsorption of atomic hydrogen and atomic oxygen on Schottky diode sensors deposited on n$^-$ and p$^+$ doped silicon. Recent work has shown that a measurable

signal is observed more ubiquitously, and currents have been detected upon the adsorption of a large number of chemical species including atoms (e.g., H, O, Xe) and molecules (e.g., NO, C$_2$H$_4$, C$_6$H$_6$) where each species has a unique signal amplitude and transient behavior such that sensing applications are possible [14]. The detailed mechanisms of adsorption-induced e–h pair excitations and detection on the metal surfaces remain incompletely understood.

The detection principle is schematically shown in Fig. 1 for a (left) metal-semiconductor (n-type) contact (Schottky diode) and a metal/insulator/metal (MIM) tunnel contact (right). An adsorbate interacting with the metal surface (either by chemisorption or physisorption) may dissipate the adsorption energy, E_{ads}, by excitation of an electron–hole pair. The excited charge carriers travel from the surface toward the device interface without significant attenuation when the thickness of the metal film is on the order of the mean free path of the carriers ∼10 nm. In the n-type Schottky diode, hot electrons are detected as a "chemicurrent" if their excess energy is larger than the local, effective Schottky barrier, Φ, which is the difference between the conduction band minimum (CBM) and the Fermi energy E_F at the interface. The chemicurrent is typically detected in the absence of an applied bias and is analogous to photocurrent in a photodiode. Schottky diodes have fixed barrier heights which are predominantly determined by material parame-

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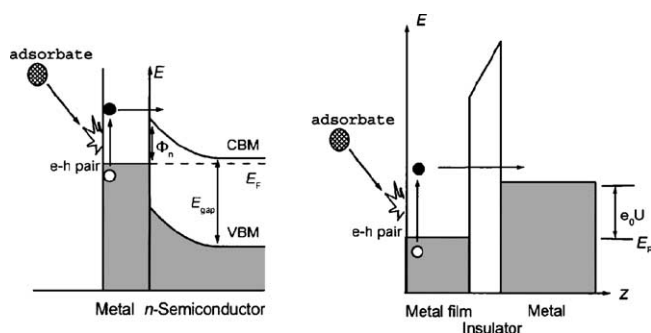*E-mail address:* mcfar@engineering.ucsb.edu (E.W. McFarland).

Fig. 1. Principle of chemicurrent detection with n-type Schottky diode (left), and metal-insulator metal device structure (right). Electrons in the metal are excited by the interaction of the adsorbate with the surface and move ballistically from the surface to the device interface.

ters and which cannot be adjusted by an external electrical potential. Depending on the metal and the interface properties, the Schottky barrier ranges between 0.2 and 1 eV. Tunnel devices such as metal/insulator/semiconductor (MIS) or the MIM structure shown in Fig. 1(right) allow the variation of the barrier by an external voltage U and may be used to detect less energetic interactions and, possibly, to obtain energy resolution.

Gold surfaces are considered to be relatively non-reactive and previous work reported that hydrocarbons do not chemisorb on polycrystalline Au films [15]. Only highly energetic reactions, such as atomic oxygen adsorption, have been observed on Au [16]. Surprisingly, it has recently been shown [17] that supported gold systems can be unusually active and/or selective for a number of reactions of commercial importance, such as complete oxidation, hydrochlorination, and hydrogenation reactions. The extraordinarily high catalytic selectivity of gold deposited as nanoparticles on selected metal oxides for the oxidation of CO or olefins [18–20] has attracted a growing interest from the scientific community.

To date, only Schottky diodes fabricated from ultrathin metal films deposited on hydrogen terminated silicon or germanium as metal-semiconductor (MS) junctions or deposited on chemically oxidized (~1 nm) silicon as metal-oxide-semiconductor junctions have been used for observation of reaction associated chemicurrents [14,21]. The Schottky barrier height of the junction acts as an energy filter for ballistic electrons and is a function of the interfacial states and defects as well as the metal and semiconductor type [22].

We are investigating the use of metal/insulator/semiconductor structures for detection of surface reaction associated charge carriers where the insertion of the electrically insulating layer between the ultrathin catalytic electrode (Au) and the semiconductor (n-Si) layer provides a device structure which can be biased over a wide-energy range in order to explore electron energetics. In this paper, we addressed the following questions. (1) Can a large-area Au based MIS device be fabricated and used to detect electronic excitations associated with gas adsorption? (2) What are the characteristic signals detected during exposure to species with different adsorption energies (ethylene, atomic oxygen)? (3) What is the dependency of the detection sensitivity on the insulator layer thickness and applied bias voltage?

2. Experimental

The devices were fabricated on n-type Si(1 1 1) wafers (phosphorous doped, 1–10 Ω cm). The Si surfaces were first treated according to the RCA method [23] and buffered hydrofluoric acid etching (pH = 5) to produce atomically flat, hydrogen terminated hydrophobic surfaces. The back side of the Si substrates were metalized with Ti(20 nm)/Au(200 nm) to provide an ohmic contact. A more detailed description of our Schottky diode sensor design can be found in [11–13,23]. The Al$_2$O$_3$ layers (<8 nm) were deposited on the clean Si surfaces by electron beam evaporation under oxygen atmosphere (1–2 × 10^{-4} Torr). On top of the Al$_2$O$_3$ films, 200 nm thick Au pads were used as front contacts. Finally, a thin gold film (9.0 nm) was deposited between the pads providing a total active area of ~0.55 cm^2. The film thickness was monitored and calibrated using a quartz microbalance and ellipsometry. The fabrication process was performed under clean-room conditions and using ultra-pure reagents. Immediately after preparation, the devices were transferred into an experimental chamber described in detail elsewhere [10]. The chamber provided a temperature controlled sample holder in ultrahigh vacuum (base pressure 1.5 × 10^{-10} Torr) where the electrical and chemical measurements were made.

The complex impedance of the diode was determined by the analysis of its response to a 1 μA alternating current signal at 1 kHz using lock-in detection (Stanford Research, SRS830). The reverse bias capacitance measured in the dark is extracted from the equivalent Rs-Cs series circuit representation [24,25]. The dc bias was supplied by a Potentiostat (EG&G 273). For the MS diodes, the depletion region capacitance can be expressed as [24,26,27]:

$$\frac{1}{C^2} = \frac{2(V_{d0} + V)}{q \varepsilon_s A^2 N_d} \tag{1}$$

where V_{d0} is the diffusion potential at zero bias, V the reverse bias voltage, A area of the diode, N_d is the doping concentration, ε_s the semiconductor dielectric constant, and q is the elemental charge. V_{d0} and N_d can be obtained from the linear fits of data. The zero bias barrier height is defined as:

$$\phi_B = V_{d0} + \frac{kT}{q} + \xi \tag{2}$$

where ξ is the Fermi energy measured relative to the conduction band edge. For the MIS diode, V_{d0} includes two terms related to the oxide charge and flat-band voltage. The oxide charge density can be calculated by [24]:

$$Q_{ox} = V_{ox} C_{ox} - \frac{Q_s}{2} \tag{3}$$

where V_{ox} is the voltage drop across the oxide layer, Q_s the Si surface space charge density at zero bias, and C_{ox} is the capacitance of the oxide layer. In this analysis, Q_{ox} is the oxide charge distribution and encompasses all charged defects and impurities distributed throughout the oxide, including surface states [27].

The chemicurrent was measured during exposure to a mechanically chopped (4 Hz) beam of atoms or molecules. The three-stage differentially pumped beamline can deliver molecules or excited atomic or ionic species from an in-line microwave plasma cavity. The beam system is described in detail elsewhere [10]. The flux was adjusted to be approximately $2–5 \times 10^{13}\,cm^{-2}\,s^{-1}$. The chemically induced electronic signal was measured between the front and back contacts of the devices during gas exposure through connection to a low-noise current preamplifier (Stanford Research, SRS57), which served as input to a lock-in amplifier. All chemicurrent measurements were performed with the device cooled to 125 K.

3. Results and discussion

3.1. Capacitance–voltage (C–V) measurement

A plot of $1/C^2$ versus bias voltage is shown in Fig. 2(a) for (i) an oxide-free Au(9 nm)-MS diode and, (ii) a Au(9 nm)-MIS diode with 2 nm Al_2O_3. The calculated barrier heights are 0.75 and 0.83 eV, respectively. The Schottky barrier height obtained for the Au-MS diode is in good agreement with Detavernier et al. [28] who reported 0.74 eV by ballistic electron spectroscopy. From the slope of the linear fit, a doping concentration of $1.34 \times 10^{16}\,cm^3$ and an intercept voltage with $1/C^2 = 0$ of 0.96 eV are obtained. A unique feature of the MIS structure is the presence of the oxide charge which in the device with 2 nm Al_2O_3 is $1.87 \times 10^{12}\,cm^{-2}$. Fig. 2(b) shows the device capacitance measured as a function of oxide thickness. As expected, the capacitance varies approximately as 1/oxide-thickness.

3.2. Detection of chemically induced electrical signals

Fig. 3(a) shows the zero-bias chemicurrent signal (I_0) from the oxide-free Au/n-Si device following exposure to atomic oxygen. The exothermic chemisorption of atomic oxygen produces excited electrons with excess energy sufficient to surmount the MS Schottky barrier and generate a net reverse bias chemicurrent. The peak current measured corresponds to approximately 7.8×10^{-4} electrons/adsorbed O atom. The atomic oxygen signal measured decays with increasing Au–O coverage as expected from the surface reaction kinetics [13]. The atomic oxygen signal measured with the zero-bias MIS devices, I_0, is significantly smaller (1.4×10^{-5} electrons/adsorbed O atom) than the MS signal due to ballistic electron attenuation in the oxide, Fig. 3(b).
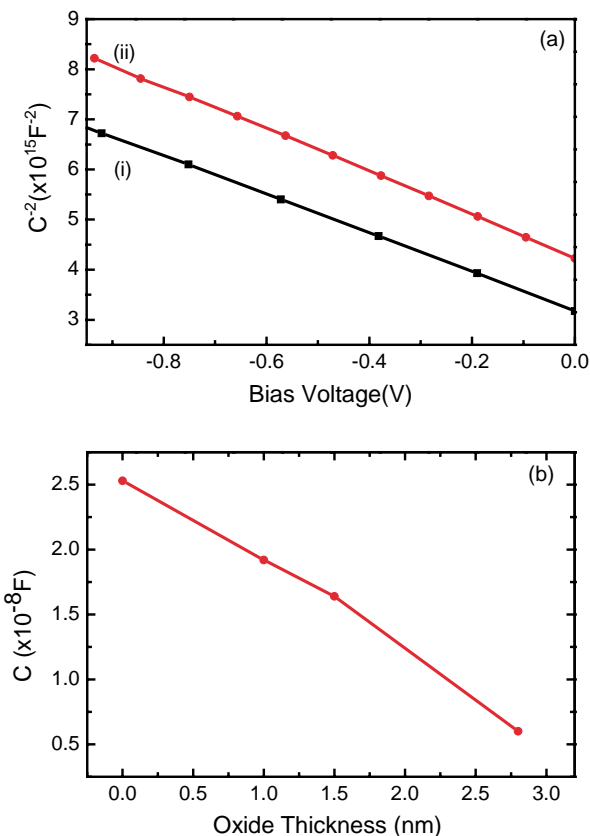

Fig. 2. (a) Reverse bias C^{-2}–V characteristics of the (i) oxide-free MS diode, (ii) MIS diode. (b) Capacitance versus oxide thickness for the Au(9 nm)/Al_2O_3(x)/n-Si(1 1 1) MIS device structure.

Upon exposure of the MS device to ethylene, no signal was detected, Fig. 3(a). The C_2H_4 adsorption energy on Au ~ 0.28 eV [29] is below the barrier height, and the absence of a signal is consistent with the hot electron carrier transport mechanism. Fig. 3(b) shows the ethylene adsorption signal (I_e) detected in the Au/Al_2O_3/n-Si device with a
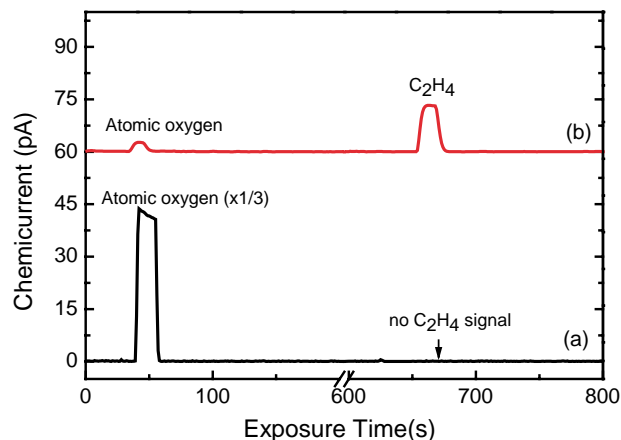

Fig. 3. Zero bias device response upon exposure to atomic oxygen and ethylene (a): Au(9 nm)/n-Si(1 1 1) MS diode, (b): Au(9 nm)/ Al_2O_3(3 nm)/n-Si(1 1 1) MIS diode.
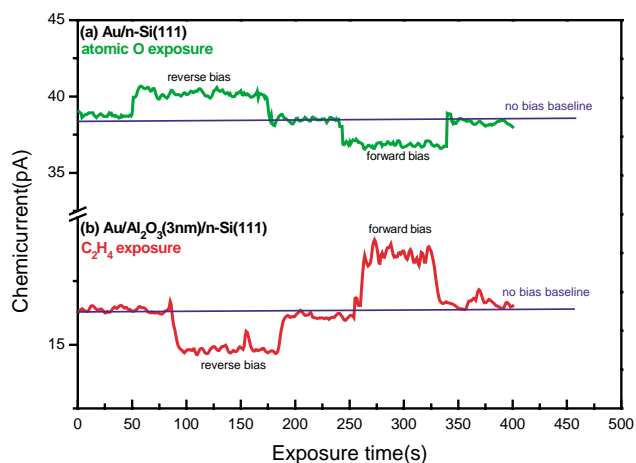
Fig. 4. Bias dependence of the chemicurrent signal for (a) Au/*n*-Si(1 1 1) MS diode, and (b) Au(9 nm)/Al$_2$O$_3$(3 nm)/*n*-Si(1 1 1) MIS diode. Reverse bias voltage refers to negative voltage on metal and positive on *n*-Si, forward bias refers to positive voltage on metal and negative on *n*-Si.

3.0 nm thick oxide. A surprising strong signal (2.0×10^{-5} electrons/adsorbed C$_2$H$_4$) is observed, approximately 10% that of the atomic oxygen response detected by the Au-MS device.

3.3. Electron–hole identification

The bias dependence of the chemicurrent signal for the MS and MIS devices is shown in Fig. 4(a) and (b), respectively. Using the zero bias chemicurrents (Fig. 3) as a reference, the atomic oxygen signal increases under reverse bias (negative potential applied on Au surface) and decreases under forward bias (positive potential applied on Au surface) for both the MS (Fig. 4(a)) and MIS devices (data not shown). This behavior is consistent with an increase of the effective barrier height under forward bias condition and a

decrease of the effective barrier height under reverse bias condition. By increasing the effective barrier, a smaller fraction of the electrons generated upon exposure to atomic oxygen have enough energy to be detected as a chemicurrent. For the weakly interacting C$_2$H$_4$, no signal was observed on the MS device with or without bias. On the MIS device however, the effect of the applied bias voltage on the strength of the ethylene chemicurrent signal was opposite to what was observed for atomic oxygen in the MS and MIS devices (Fig. 4b). The C$_2$H$_4$ signal increases under forward bias and decreases under reverse bias. Moreover, the phase of the lock-in detected currents was found to be approximately 180 degrees out of phase with respect to the oxygen atom signal.

The behavior under bias and the lock-in phase shift is consistent with an effective forward bias chemicurrent produced by the C$_2$H$_4$ compared to the reverse bias chemicurrent observed from atomic oxygen. Previous work with p-type Schottky devices [30] showed that both ballistic electrons and ballistic holes are produced from energetic chemisorption of atomic species. It is likely that with adsorption there is a distribution of excitations around the Fermi level with both hot electrons and hot holes mobilized. The energy filtering with an n-type MS Schottky device selects the hot electrons while a p-type MS Schottky device selects the hot holes. With the n-type silicon MIS device there is no pathway for holes transported through the interface to the back contact, and a net charging of the interface can occur.

3.4. Oxide thickness dependence

The magnitude of the measured ethylene and oxygen signals as a function of Al$_2$O$_3$ thickness is shown in Fig. 5. The oxygen signal decreases rapidly with increasing oxide thickness as the ballistic electron flux is attenuated exponentially. The ethylene signal, however, increases from 0 in
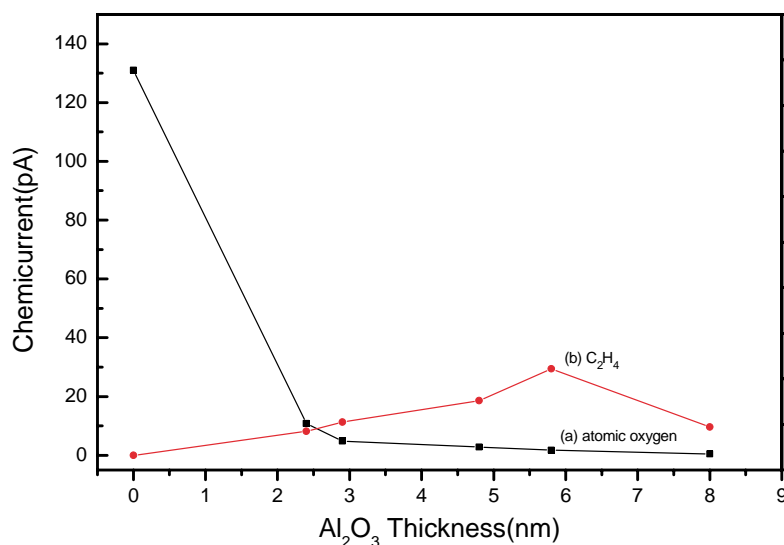

Fig. 5. Dependency of the MIS sensitivity on the Al$_2$O$_3$ insulator layer thickness (a) atomic oxygen and (b) ethylene.
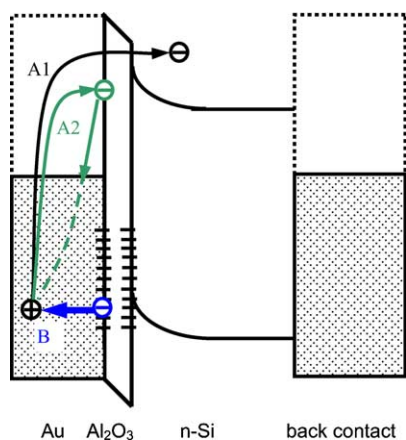
Fig. 6. Schematic principle of hot carriers transport excited by high and low energy adsorption processes detected by a MIS device.

the absence of an oxide (MS diode) to a maximum value of $\sim$30 pA (4.6×10^{-5} electrons/adsorbed C_2H_4) at approximately 6 nm. It is interesting to note that in the thickness region between 2.5–8.0 nm, the ethylene signal is larger than the atomic oxygen signal.

3.5. Carrier transport mechanisms

In an MS device, when the gas species impinges on the metal surface, electron–hole pairs (e–h) are produced from somewhere near the Fermi level of the metal. The excitation of these e–h pairs leads to hot electrons with energies above the Fermi level, and hot holes with energies below the Fermi level. If the e–h pair is generated in a metal/semiconductor structure, both hot electrons and hot holes may travel ballistically through the thin metal film to the metal-semiconductor interface. In an n-type device only the excited electrons can be effectively transmitted into the semiconductor conduction band and appear as a measurable current. Due to the prevalence of majority carriers at the semiconductor surface, the magnitude of the minority carrier injection is negligible compared to the majority carrier contribution [27] leading to the conclusion that the predominant hot carriers excited by adsorption processes on metal/n-Si are electrons.

For the low energy processes, the excited electrons have no pathway to reach the semiconductor conduction band and they are rapidly thermalized; as a consequence, no signal is observed during ethylene adsorption on n-type MS structures. Compared to an MS device, the MIS diode has a different band structure, surface charge, surface states, defect levels, etc. at thermal equilibrium. When electron–hole pairs are produced at the surface of the metal film in a MIS diode, there are two competitive transport pathways for the excited electrons and holes: the ballistic transport of electrons through the metal towards the conduction band of the semiconductor (Fig. 6, pathways A1 and A2), and hot-hole transport to the metal-insulator interface (Fig. 6, pathway B). It is the net current that is measured. Due to the high

density of electron donor states below the Fermi level at the metal-oxide interface, the predominant current observed is the transport of ballistic holes to the interface where they beutralize electron donor states resulting in an effective discharging of the interface. The compensatory forward bias diode current is the observed chemicurrent signal in these devices.

4. Conclusions and summary

Large-area Au/Al$_2$O$_3$/n-Si MIS structures have been successfully fabricated and used to detect electron–hole pairs produced during the adsorption of gas phase species on polycrystalline Au films. Both MS and MIS device structures showed sensitivity for energetic adsorption of atomic species; however, only MIS (and metal-oxide-semiconductor) structures could be used for the detection of gases with relatively low adsorption energies. The presence of electron donor states at the metal-oxide interface provides a trap for ballistic hot holes and the compensatory forward bias current is the observed chemicurrent. This current is opposite in direction to the chemicurrent produced when hot electrons are transmitted over the interface barrier into the semiconductor conduction band. We expect that the MIS devices will be sensitive to a similar wide variety of atomic and molecular species observed with metal-oxide-semiconductor structures [14] with the additional feature of bias capability to control the sensitivity.

Most chemicurrent experiments to date have been conducted in vacuum using cooled device structures to demonstrate the device principles and explore sensitivity limits. Operation at higher pressures is possible provided the incident flux of the desired species producing chemicurrent is greater than any background species that also produce charge carriers. For practical sensor applications device arrays with multiple types of metals will give differential sensing capabilities (depending on the gas/metal interaction activity). MIS devices operated under different bias conditions may also be useful in distinguishing different adsorbates. Cooling is required only to reduce noise and may be provided by simple Peltier type coolers.

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