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Selective H atom sensors using ultrathin Ag/Si Schottky diodes

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Schottky diodes with ultrathin silver films on *n*-Si(111) are used for selective detection of atomic hydrogen. The exothermic adsorption of H atoms on the Ag surface creates hot electrons which may travel ballistically through the metal film and traverse the Schottky barrier. The chemically induced current is measurable (≈ 0.001 electrons/H atom) as a chemicurrent. After saturation of the adsorption sites, this chemicurrent achieves a steady-state value due to a balance of removal of adsorbed hydrogen and readsorption. The detection limit of the sensors is approximately 10^{10} H atoms $\text{cm}^{-2} \text{s}^{-1}$. The detectors are completely insensitive to H_2 molecules. © 1999 American Institute of Physics. [S0003-6951(99)00526-4]

Atomic hydrogen has become an important process gas in different modern technologies, e.g., for passivation of defects in semiconductors, for cleaning of semiconductor surfaces, in synthetic diamond production, and in hydrogen storage and fuel applications. In addition to discharge tubes, small and ultrahigh vacuum (UHV) compatible atomic hydrogen sources based on thermal dissociation of H_2 molecules are also available.^{1,2} They provide extremely pure beams with high atomic hydrogen fluxes. On the other hand, inexpensive H atom detectors are needed which are insensitive to H_2 molecules. To date, two types of sensors have been introduced. The first class are calorimeters which measure temperature changes during exothermic recombination of atoms at catalytic surfaces.³⁻⁵ The minimum detectable fluxes reported were approximately 10^{13} H atoms $\text{cm}^{-2} \text{s}^{-1}$. High thermal stability is crucial for the proper functioning of these devices. The second type of sensor uses electrical conductivity changes of thin semiconductor or metal-oxide films under atomic hydrogen exposure.⁶⁻⁹ The devices are small, easy to manufacture, and exhibit high sensitivities of between 10^9 and 10^{12} atoms $\text{cm}^{-2} \text{s}^{-1}$. The sensitivity, however, changes with increasing hydrogen exposure as hydrogen permanently alters the sensor characteristics. This memory effect limits their accuracy and long term applicability.

Recent experiments have demonstrated that exothermic adsorption of atomic hydrogen on transition metal surfaces creates electron-hole (*e-h*) pairs in the metal due to nonadiabatic energy transfer mechanisms.¹⁰ Based on these experiments, sensitive, and selective H atom sensors have been developed¹¹ which detect the created hot electrons with thin silver film Schottky diodes on *n*-Si. The principle of operation is explained in the energy level diagram of Fig. 1. The Schottky barrier height, Φ , the Fermi level, E_F , and the

variation of the conduction band minimum (CBM) and of the valence band maximum (VBM) are shown. Hydrogen atoms impinge on the Ag film and the exothermic adsorption creates *e-h* pairs. Hot electrons may travel ballistically through the metal film and traverse the Schottky barrier if the excitation energy exceeds the Schottky barrier height. The local barrier height at the adsorption site may differ considerably from an effective Φ extracted, e.g., from current-voltage measurements due to a distribution of barrier heights typically observed in large area metal-semiconductor contacts.^{12,13} Hot electrons reaching the semiconductor without being scattered at the interface are detected as a *chemicurrent* in the device and the current is proportional to the rate of adsorption.

The actual device is fabricated on $6 \text{ mm} \times 18 \text{ mm}$ *n*-Si

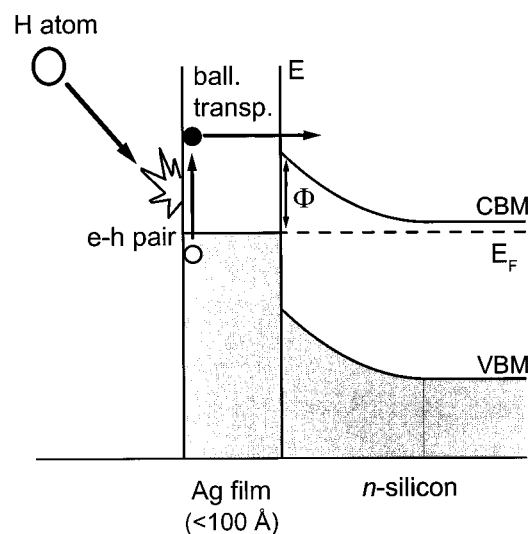


FIG. 1. Principle of H atom detection: exothermic adsorption of H on Ag creates *e-h* pairs. Hot electrons travel ballistically through the metal film into the semiconductor and are detected as a *chemicurrent*.

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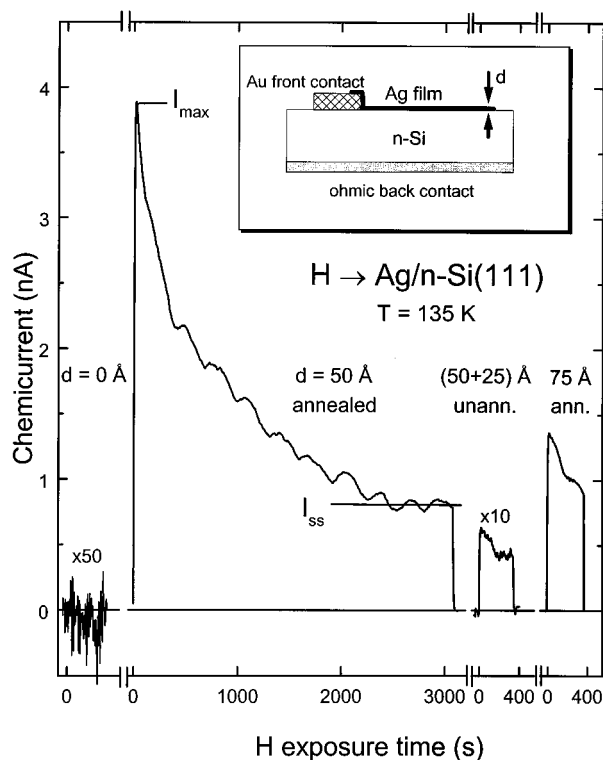


FIG. 2. Inset: schematic cut through an atomic hydrogen detector. Main panel: current responses from four sensors at different stages of Ag deposition. At $t=0$, the beam shutter was opened and the atomic hydrogen flux was approximately 3×10^{12} atoms $\text{cm}^{-2} \text{s}^{-1}$.

wafers with (111) surface orientation and a resistivity of 5–10 Ω cm. An ohmic contact is prepared on the backside of the wafers by As^+ ion implantation and subsequent thermal activation. After cleaning the surface with organic solvents and strong inorganic acids, a 3000 \AA thick thermal oxide layer is grown on the surface. By use of photolithography a window is etched into the oxide to evaporate a 2000 \AA thick Au film with a Cr interlayer on Si. This Au pad will provide electrical contact to the ultrathin Ag layer. Then, the residual oxide is wet chemically removed by buffered hydrofluoric acid leaving a H-terminated Si(111) surface.¹⁴ Within a few minutes, the sample is transferred into UHV ($p < 10^{-8}$ Pa). Low-energy electron diffraction (LEED) revealed sharp 1×1 spots indicating excellent hydrogen termination of the Si(111) surface. A thin Ag film is evaporated *in situ* onto the samples at a substrate temperature of 135 K. The low temperature prevents surface atom diffusion so that a coalesced Ag film covers the passivated Si surface as well as the Au pads. The deposition rate is measured by a quartz microbalance. After deposition, the samples are annealed to room temperature to reduce the Ag film roughness and the number of scattering centers in the film. The annealing improves considerably the transport properties for hot electrons and hence the performance of the sensors, as will be demonstrated later. Silver deposition removes the hydrogen termination at Si(111) surfaces and forms Schottky contacts on *n*-type Si with effective barrier heights typically between 0.67 and 0.74 eV.¹² A complete sensor is shown schematically in cross section in the inset of Fig. 2.

The sensors were maintained at 135 K and exposed to a modulated, thermal hydrogen beam produced by a micro-

wave plasma. To avoid photoexcitation, photons were extracted from the beam by a special light blocking fixture described elsewhere.¹⁵ The number of atoms relative to the total number of H and H_2 particles in the beam, i.e., the atomic hydrogen content, was determined with an in-line mass spectrometer and varied typically between 7% and 30%. With an active sensor area of approximately 0.3 cm^2 , the flux of H atoms ranged between 2 and 5×10^{12} atoms $\text{cm}^{-2} \text{s}^{-1}$. The reaction-induced chemicurrent was detected between the back and Au front contacts using standard lock-in techniques and with *no bias* applied to the detector.

Current responses as a function of time (I/t curves) while exposing the detector to atomic hydrogen are shown in Fig. 2 for different Ag deposition stages. At an exposure time of zero, the beam shutter is opened. In the absence of a Ag film ($d=0$ \AA), there is no response to atomic hydrogen even if the beam partly hits the Au front contact. Hence, any signal is due to hydrogen–silver reactions. The zero thickness experiment shows a noise level of 4 pA. After deposition of 50 \AA of Ag and annealing, a strong current response is observed as soon as the beam shutter is opened. The current jumps to a maximum value, I_{max} , of 3.8 nA, decreases exponentially, and reaches a constant steady-state value, I_{ss} , of 0.73 nA within 2500 s. The small current oscillations are due to fluctuations in the plasma. The decay of the chemicurrent is due to the occupation of empty adsorption sites by atomic hydrogen, whereas the steady-state value represents a final balance between removal of adsorbed hydrogen by gas-phase atomic hydrogen (abstraction) and readsorption.¹⁰ The ratio $I_{\text{ss}}/(I_{\text{max}} - I_{\text{ss}})$ corresponds to the ratio σ_r/σ_a of the cross sections for abstraction and adsorption. In the steady state the sensitivity of the detector to atomic hydrogen is constant and independent of the total exposure. Hence, this is the most preferred state of the sensor. Here, for $t \rightarrow \infty$, with an atomic hydrogen flux of approximately 3×10^{12} atoms $\text{cm}^{-2} \text{s}^{-1}$, 2200 adsorption events lead to one detected electron. Moreover, the noise level of 4 pA gives a theoretical detection limit of 2×10^{10} atoms $\text{cm}^{-2} \text{s}^{-1}$ which is comparable to the sensitivity of thin-film conductivity sensors.

The importance of the annealing step is demonstrated in the two I/t curves at the right in Fig. 2. If 25 \AA of Ag is added to the exposed 50 \AA sensor and the device is not annealed to room temperature, the maximum chemicurrent decreases to 65 pA. Annealing this device results in a 75 \AA sensor for which a maximum chemicurrent of 1.4 nA is observed. Apparently, annealing reduces the number of defects in the Ag film and significantly increases the mean free path of hot electrons.

The observed chemicurrent is entirely due to reactions of H atoms with the Ag surface and is proportional to the atomic hydrogen content in the beam, as shown in Fig. 3 where the chemicurrent variation in the 75 \AA Ag/*n*-Si device with changing H atom content of the beam is displayed. The total flux of atoms *and* molecules remained constant at approximately 10^{13} $\text{cm}^{-2} \text{s}^{-1}$. The decrease of the H_2 dissociation rate in the discharge tube from maximum to almost zero was caused by plasma instabilities which occurred within a few minutes. The H atom content was measured directly with the mass spectrometer (solid circles) or determined indirectly from variations in the photon emission from the

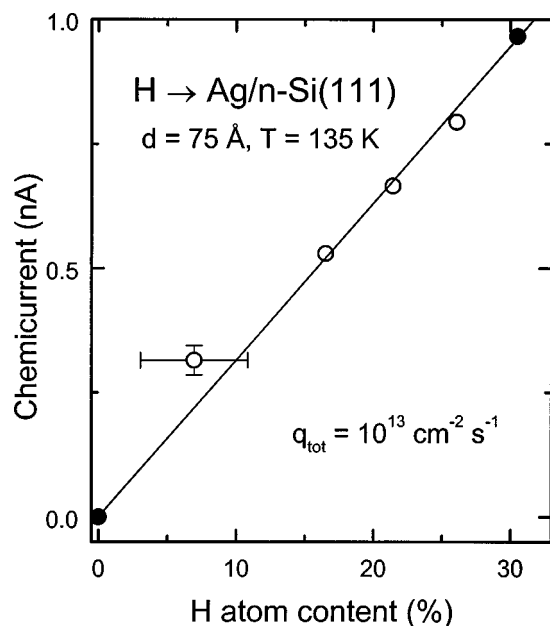


FIG. 3. Chemicurrent as a function of H atom content in the hydrogen beam. The detectors are sensitive to H atoms only.

plasma and in the plasma tube pressure (open circles). Both photon production and plasma pressure were found to be proportional to the dissociation rate. No current was observed in the presence of only molecular H_2 . This finding agrees well with studies on silver single crystal surfaces where the dissociative chemisorption of H_2 was found to be negligible.¹⁶

The steady-state chemicurrent and therefore the sensitivity of the detectors may be increased if desorption of hydrogen becomes a second significant mechanism to remove adsorbed atoms from the surface. On hydrogenated Ag single-crystal surfaces, thermal desorption studies revealed low desorption temperatures of approximately 180 K.¹⁶ Thus, increasing the detector temperature above this value is expected to increase the steady-state current. This is experimentally confirmed, as demonstrated in Fig. 4 where the current I_{ss} of the 50 Å Ag/n-Si(111) device is shown as a function of sensor temperature. Between 150 and 215 K the steady-state current increases from 0.73 to 1.9 nA. An additional enhancement of the sensor performance is achieved by reducing the noise level. This may be accomplished by increasing the barrier height at the Au/Si interface, e.g., by *in situ* evaporation of the contact pad, or by reducing the contact area.

In summary, large area Ag/n-Si(111) Schottky contacts with ultrathin Ag films have been used for selective and sensitive detection of atomic hydrogen. The detection mechanism is based on $e-h$ pair creation in the Ag film by exothermic adsorption of hydrogen. The created hot electrons may travel unscattered through the thin metal layer and be detected as a chemicurrent in the device. Upon initial exposure of the sensor to atomic hydrogen a maximum current proportional to the number of empty adsorption sites is ob-

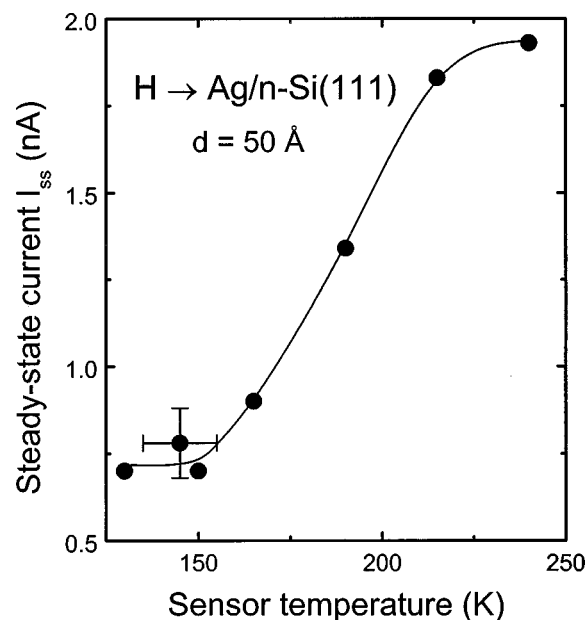


FIG. 4. Steady-state current as a function of sensor temperature. The sensitivity increases above 150 K due to enhanced thermal desorption of hydrogen from the Ag surface.

served. The current decays to a steady-state value determined by the balance between removal of adsorbed hydrogen by abstraction or by desorption and readsorption. The detection limit was found to be approximately 10^{10} H atoms $cm^{-2} s^{-1}$.

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