Hydrogen Sensing Mechanisms of Metal−Insulator Interfaces

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FIGURE 1. Brief description of the hydrogen sensitive Pd-MOS structure. (a) An oxidized Si wafer (p-doped in this case) is covered with Pd. The structure is electrically connected on both sides. (b) When exposed to hydrogen, a shift, ΔV, is observed in the capacitance (C) versus voltage (V) characteristics of the Pd-MOS structure. (c) Hydrogen atoms which have diffused through the Pd film and adsorbed at the Pd−SiO$_2$ interface form a dipole layer which gives rise to the observed voltage shift.

Introduction

The hydrogen sensitivity of palladium−silicon dioxide−silicon (Pd−MOS) structures was demonstrated about 25 years ago. One of the most interesting features of the Pd−MOS device as a hydrogen sensor is its very large dynamic pressure range. Such devices are now used in several practical applications and in commercially available equipment, both as single sensors and in sensor arrays. We recall that the hydrogen sensitivity of the device occurs due to a hydrogen induced polarization at the Pd−SiO$_2$ interface as schematically shown in Figure 1. During the years, several types of devices have been developed, both with insulators other than silicon dioxide and catalytic metals other than palladium. Furthermore, it has been demonstrated that sensors with thin, discontinuous catalytic metals can detect molecules, like ammonia, which are not detected by sensors with thick continuous palladium gates.[1−3] Although several insulators have been used in hydrogen sensitive Pd−insulator−semiconductor structures,[1,4,5] the vast majority of work has been made with silicon dioxide as insulator.

This review is concerned with the hydrogen sensing properties of Pd−SiO$_2$−Si structures with thick Pd films ($\geq$100 nm), and, more specifically, with the adsorption of hydrogen at the Pd−SiO$_2$ interface, and how this adsorption is related to the chemistry of the exposed Pd surface. It will focus on work performed in our own laboratory and discuss several recent findings. Although several interesting observations have been made previously,[6−10] there exists no comprehensive picture of the hydrogen adsorption at the interface yet. Such a picture is now emerging for Pd−SiO$_2$ through studies under ultrahigh vacuum conditions (UHV).[9−11] The present review takes the results of these studies as the starting point for a critical discussion of hydrogen adsorption at the palladium−silicon dioxide interface. It should be pointed out that such careful studies have not yet been performed for other palladium−insulator interfaces.

To understand the hydrogen sensing of MOS devices, a fundamental requirement is a good knowledge of hydrogen adsorption at the Pd−SiO$_2$ interface. We will describe the physical features of the dominating hydrogen interface sites, as we have learned to understand them, mainly from experiments performed under well-controlled conditions in UHV. We will also connect to experiments under atmospheric conditions. The conclusions which we will present will thus not be limited to a narrow pressure

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Mats Eriksson was born in 1963 in Stockholm, Sweden. He received a M.Sc. in 1987 and a Ph.D in 1997 from Linköping University. He has studied fundamentals of hydrogen sensing with Pd-MOS structures in ultrahigh vacuum. He has studied adsorption processes and catalytic reactions on catalysts with different degrees of dispersion. He has also performed kinetic modeling of catalytic reactions.

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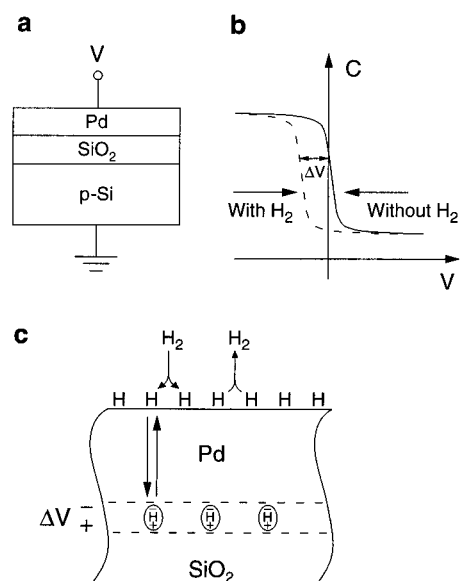
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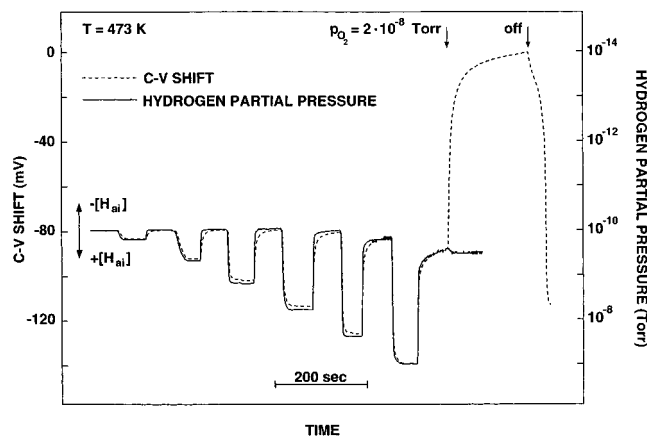† Formerly Petersson.

FIGURE 2. Experimentally recorded CV shift during hydrogen pulsing. Reprinted with permission from ref 10. Copyright 1996 Elsevier Science. At the end of the sequence an oxygen exposure is made. Also shown is the hydrogen partial pressure measured by mass spectrometry. The results confirm that the hydrogen-induced CV shift is proportional to the logarithm of the hydrogen pressure, and that a Pd-MOS device may detect hydrogen pressure changes on the 10^{-14} Torr scale. The zero level corresponds to an empty interface (see the text).

interval of no practical interest, but should also apply under "normal" working conditions for the sensor.

Hydrogen Sensing: Pertinent Features

Response versus Hydrogen Pressure. A striking feature of a Pd−MOS hydrogen sensor is its very large sensitivity range, in terms of hydrogen pressure. Actually, true saturation has never been reported, neither has the lower limit been observed through just a lowering of the applied pressure. The background hydrogen pressure always seems to set the lower limit. It has been shown that in inert atmospheres the hydrogen response, ΔV, is approximately proportional to the logarithm of the applied pressure over at least 10 decades of pressure.[12] The logarithmic pressure dependence is supported by results from a hydrogen exposure sequence in UHV, as shown in Figure 2.[10] The background hydrogen pressure of around 10^{-10} Torr sets the lower limit for the hydrogen detection. Interesting to note from Figure 2 is, however, the effect that during oxygen exposure the interface will be depleted of background hydrogen due to the formation and subsequent desorption of water from the surface.[10] Thus, it is possible to extrapolate a lower limit for the hydrogen sensitivity. At 473 K this limit is around 10^{-14} Torr, giving a dynamic pressure range for the response of about 14 orders of magnitude! A lower temperature will move the sensitivity limit to even lower hydrogen pressures.[9]

From these experimental facts it is clear that the hydrogen adsorption isotherm at the interface *cannot* be described by a conventional Langmuir isotherm, as has been done quite frequently in the literature. Already 13 years ago, Dannetun et al.[12] pointed out that a more proper description is that of a Temkin isotherm. By allowing the heat of adsorption at the interface to vary

with the hydrogen concentration, n_i, i.e., to describe it as

$$\Delta H_i = \Delta H_{i,0}(1 - \kappa n_i) \tag{1}$$

the characteristic features of a logarithmic pressure dependence may be obtained. With similar assumptions, Fogelberg et al.[9] estimated the initial heat of adsorption to be $\Delta H_{i,0} = 0.8 \pm 0.1$ eV/hydrogen atom, since this value gave a modeled steady-state isotherm that, at a temperature of 473 K, approached zero coverage at around 10^{-14} Torr. Eriksson et al.[13] gave the value 0.86 eV/atom in a more accurate estimation from the same experimental data.

It could always be argued that several states of Langmuir character (i.e., with constant heats of adsorption) together would add up to yield an isotherm of Temkin character, and this has, e.g., been done by Rye and Ricco in the case of hydrogen sensitive Pd−thin oxide−silicon diodes.[11] Our present belief, however, is that the *dominating* state should be regarded as one state, with a varying heat of adsorption, and that there is no need to involve several different states.

Hydrogen Induced Dipole Moment. The presence of hydrogen can be detected as a voltage shift of the capacitance−voltage (CV) characteristics of a Pd-MOS structure. In Figure 1 this CV shift is described to be due to a dipole layer formed by the interfacial adsorption of hydrogen. Thus, an effective dipole moment can be associated with every adsorbed hydrogen atom. The magnitude of the CV shift, ΔV, can then be described as

$$\Delta V = \frac{n_i \mu}{\epsilon} = \frac{n_i Q d}{\epsilon} = \frac{\sigma_i d}{\epsilon} \tag{2}$$

where μ is the effective dipole moment, Q the dipole charge, σ_i the charge concentration, d the effective charge separation,[14] and ϵ the permittivity. μ can roughly be determined from experiments. This was done by Fogelberg et al.[9] by measuring the rate of change of ΔV during a controlled hydrogen exposure of a device, which had initially been depleted of interface hydrogen through an oxygen exposure. A value of $\mu = 2$ Debye (D) was obtained (assuming the permittivity of vacuum in eq 2) and found to be consistent with other data.[9] This value is unreasonably large for hydrogen atom adsorption on metals.[15] Thus, a more likely adsorption site is one on the oxide side of the interface, where much larger dipole moments could be obtained. A likely adsorption site candidate is on the terminal oxygen atoms of the oxide. Furthermore, approximately the same value of the induced dipole moment seems to be valid over the full dynamic sensitivity range of the device. This, we believe, is a strong argument for the assumption of a "single-state" model.

Electrostatic Model for the Hydrogen Dipole−Dipole Interaction

We have recently presented an electrostatic model, resulting in a Temkin isotherm behavior of the hydrogen adsorption at the interface, based on a "single-state"

assumption.[13] The model assumes that adsorbed hydrogen atoms behave as laterally mobile dipoles, and, thus, the mean dipole charge distribution can be treated as two homogeneously charged sheets. When a new dipole forms at the interface, it will feel the repulsive electrostatic field from the already existing dipole layer. The potential difference between the charge sheets is identical with ΔV of eq 2. Now, the work involved in forming a new dipole will lead to a reduction of the heat of adsorption:

$$\Delta H_i = \Delta H_{i,0} - q\Delta V = \Delta H_{i,0} - q(\mu n_i/\epsilon) \qquad (3)$$

where q is the elementary charge. This equation is of the same type as eq 1; i.e., the adsorption energy decreases linearly with hydrogen concentration. Comparing eqs 1 and 3, we see that $\kappa = q\mu/\epsilon\Delta H_{i,0}$ and can thus be determined from experimental data. Furthermore, eq 3 suggests that there is a direct correlation between the observed CV shifts and the variation of the interface heat of adsorption.

When the interface adsorbate coverage becomes high enough so that the adsorption energy is reduced to the vicinity of the absorption energy of the Pd bulk, $\Delta H_i \approx 0.1$ eV/atom,[16] a significant amount of hydrogen will start to accumulate in the bulk. This leads to an expansion of the Pd lattice (and eventually to a complete Pd-hydride formation) and the formation of blisters, which severely affect the performance of the sensor.[17] Therefore, a *practical* upper limit, ΔV_p, exists for the sensor response:

$$\Delta H_{i,min} = \Delta H_{i,0} - q\Delta V_p \approx \Delta H_b \qquad (4)$$

i.e., ΔV_p [V] $\approx \Delta H_{i,0} - \Delta H_b$ [eV] ≈ 0.8. This limit is reached at a corresponding hydrogen concentration, $n_{i,p}$, at the interface:

$$n_{i,p} \approx (\Delta H_{i,0} - \Delta H_b)(\epsilon/q\mu) \qquad (5)$$

It should be noted that $n_{i,p}$ is only an approximate, *practical* limit. The total concentration of adsorption sites, N_i, at the interface could therefore exceed $n_{i,p}$.

Since we know the value of the dipole moment, we are now in position to estimate $n_{i,p}$. From eq 5

$$n_{i,p} \approx (0.86 - 0.1)\frac{8.86 \times 10^{-12}}{2 \times 3.3 \times 10^{-30}} = 1 \times 10^{18}\ m^{-2} \qquad (6)$$

This model gives both an estimation of the maximum obtainable concentration of hydrogen at the interface and an estimate of an upper practical limit of ΔV, which are in accordance with previous observations. For instance, Fogelberg et al.[9] estimated that the concentration of interface sites is much less than that of a clean Pd surface which has a site concentration of around $1 \times 10^{19}\ m^{-2}$. A concentration of interface sites of the order of 1×10^{18} m^{-2} has also been discussed by Hughes et al.[18]

Comments on ΔV_{max}. Equation 2, i.e., the relation between the observed voltage shift and the interface hydrogen coverage, has commonly been written in the literature as

$$\Delta V = \Delta V_{max}\Theta_i \qquad (7)$$

with

$$\Theta_i \equiv n_i/N_i \qquad (8)$$

where Θ_i is the hydrogen coverage at the interface. To our knowledge, there is no measurement reported where a true saturation of the hydrogen response has been measured. Thus, ΔV_{max} is commonly estimated from some fitting procedure of experimental data to an assumed Langmuirian model. Since, as we have demonstrated, a Langmuirian model is not in general applicable, we believe that this is an incorrect way of obtaining the proportionality between hydrogen coverage (or concentration) and ΔV. Furthermore, the observed maximum response of ΔV depends on the quality of the interface, since it may easily happen that the condition for dipole formation is not fulfilled for the full fraction of the surface, e.g., due to a blocking of interfacial sites, thus reducing the effective concentration of available sites at the interface. This will result in a proportionality constant ("ΔV_{max}") between ΔV and Θ_i which varies from device to device and with device treatment. Values of ΔV_{max} between 0.4 and 1 V have been reported in the literature.

Coupling between the Interface and the External Surface

Surface vs Interface. The transfer of adsorbed hydrogen atoms between the surface (s) and the interface (i) of the metal takes place via hydrogen in the bulk (b) of the metal:

$$H_s \leftrightarrow H_b \leftrightarrow H_i$$

It is generally assumed (for Pd) that the transfer of hydrogen across the metal is fast; i.e., for metal films of the order of 100 nm the diffusion across the metal film is rapid compared to other experimental time constants, so that the surface and interface are in a quasi-equilibrium.[1,6] This is a reasonable assumption, and naturally so under steady-state conditions. However, under transient conditions, where the interface goes toward more or less complete hydrogen depletion, extremely long time-constants may be observed. Such time constants can be accounted for by introducing an energy barrier for hydrogen entering the interface state.

If we introduce the coverage of adsorbed hydrogen at the surface, as was done for the interface in eq 8,

$$\Theta_s \equiv n_s/N_s \qquad (9)$$

where n_s is the number of adsorbed hydrogen atoms, and N_s the number of adsorption sites, then in equilibrium,

$$c_i\Theta_s(1 - \Theta_i) = d_i\Theta_i(1 - \Theta_s) \qquad (10)$$

where c_i and d_i are rate constants of Arrhenius type.

One very important assumption, supported by experiments,[10,19] is that hydrogen atoms coming from the interface are not blocked by other reactive adsorbates such as O and OH. Thus, eq 10 can be used also in the presence of oxygen.
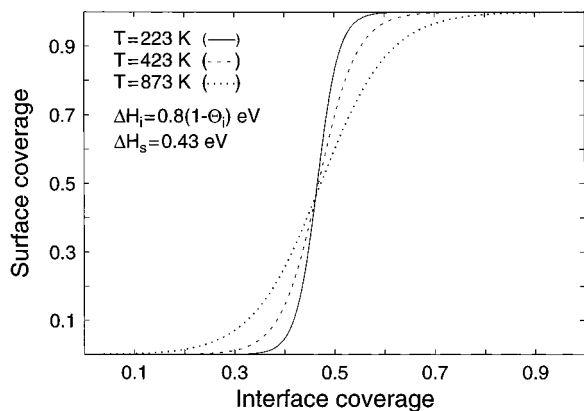
FIGURE 3. Relation between surface coverage and interface coverage at three different temperatures. The heat of adsorption of the surface is independent of coverage while that of the interface decreases with coverage according to $\Delta H_i = \Delta H_{i,0}(1 - \Theta_i)$, i.e., $a = 1$ in eq 11. The maximum operating temperature for Pd−SiO$_2$−Si devices is around 500 K, while sensors based on SiC can be used at temperatures up to around 1000 K.[31]

The heat of adsorption for hydrogen at the surface is assumed to be constant, ΔH_s, and at the interface to follow eq 1. We then find that[9,20]

$$\frac{\Theta_i}{(1 - \Theta_i)} = e^{-(\Delta H_s - \Delta H_{i0})/k_B T} e^{-a\Theta_i \Delta H_{i0}/k_B T} \frac{\Theta_s}{(1 - \Theta_s)} \quad (11)$$

with $a = \kappa N_i$.

In eq 11 it is assumed that the adsorption sites at the surface and interface have the same entropy term in the free energy of adsorption.

Figure 3 shows the relation between the interface hydrogen coverage and the surface coverage, using experimentally determined parameters.[9,20] The result, e.g., clearly demonstrates the fact that hydrogen can be detected at the interface even if the coverage at the surface is extremely small. Thus, initially, hydrogen rather adsorbs at the interface than at the surface.

Hydrogen on the Surface. The coverage of hydrogen at the surface is determined by the chemistry on the metal surface. It has been shown that, for metals such as palladium and platinum, the adsorption of hydrogen can be modeled by[9,20]

$$\frac{dn_s}{dt} = 2FS_H \frac{N_s - n_s}{N_s} - d_s \frac{n_s^2}{N_s} - \frac{dn_i}{dt} \quad (13)$$

where F is the hydrogen molecular flux (which is proportional to the hydrogen pressure, P_{H_2}), S_H the initial sticking coefficient for hydrogen adsorption, and d_s is the desorption rate constant. It may be noted that the hydrogen adsorption is of first order (instead of the conventional second order) in terms of the self-blocking term. Experimentally, this has been shown to be valid for dissociative hydrogen adsorption on many metals and assumed to be due to the large mobility of hydrogen on the metal surface.[15] Thus, in steady state, the surface coverage of
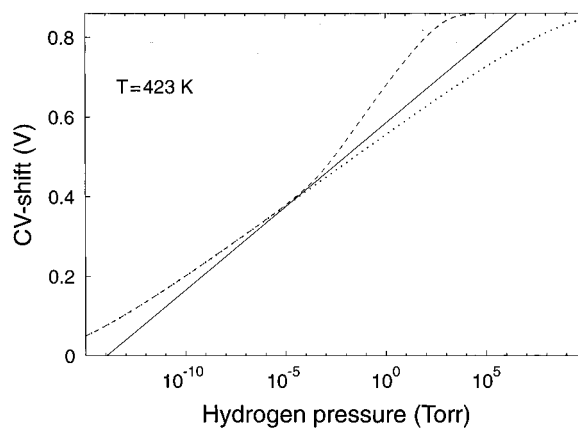

FIGURE 4. Modeled magnitude of CV shifts versus hydrogen pressure with $\Delta H_{i,0} = 0.86$ eV/atom, $\Delta H_s = 0.43$ eV/atom, and $a = 1$. Dotted line corresponds to an isotherm assuming second-order adsorption and desorption at the Pd surface. Dashed line corresponds to first-order adsorption and second-order desorption. This, we believe, is the best theoretical representation of the response for a Pd−SiO$_2$−Si device. Full line corresponds to the Nernst equation. The shadowed region is inaccessible since hydride formation will occur for the corresponding hydrogen pressures.

hydrogen in a vacuum (or inert atmosphere) is given by

$$\Theta_s = -\frac{FS_H}{N_s d_s} + \sqrt{\left(\frac{FS_H}{N_s d_s}\right)^2 + \frac{2FS_H}{N_s d_s}} \quad (13)$$

Interface Hydrogen Isotherm. Having a model for the interface hydrogen adsorption, the coupling between the surface and the interface, and a model for the hydrogen adsorption at the surface, we may simulate the "response" of the Pd-MOS device as a function of hydrogen pressure. This is done in Figure 4, where the interface hydrogen adsorption isotherms for both first- and second-order hydrogen adsorption at the surface, respectively, are plotted. Clearly, surface kinetics are important for the response of the device. It is evident for the first-order case that the apparent reaction order actually changes from being initially second order to becoming first order at higher pressures. We believe that the first-order case in Figure 4 today represents the best theoretical description of the *dominating* state in the hydrogen response of a Pd-MOS device in inert atmospheres.

A different model of the hydrogen response has been presented by Robins et al.[21] They suggested that the Pd−SiO$_2$ interface acted as an electrochemical half-cell for the hydrogen reaction H$_2$ $\rightleftarrows$ 2H$^+$ + 2e$^-$, yielding a Nernst relationship with the slope $2.3 k_B T/2q$ V/(concentration decade), independent of the kinetics on the Pd surface. In Figure 4 we have also plotted an adsorption isotherm for a second-order process that follows the Nernst equation. Thus, in inert atmospheres, and for an intermediate coverage range, the slope of the Nernst expression gives a reasonable description of the ΔV vs log (p_{H_2}) dependence. Note, however, that the Nernst equation describes a thermodynamic equilibrium and an unlimited "adsorption site" situation. Such conditions are not generally met for chemical sensing with metal−insulator−semiconductor devices.
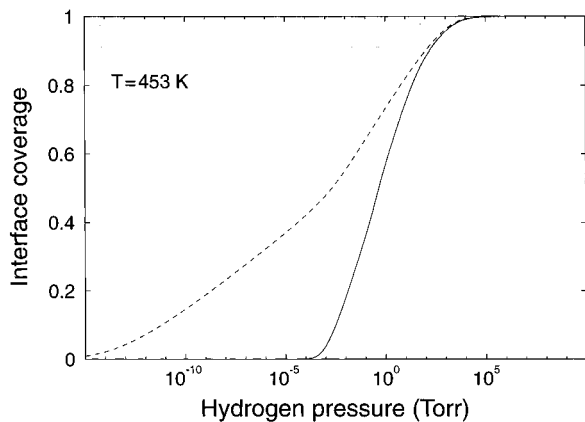
FIGURE 5. Modeled interface hydrogen adsorption isotherm (i.e., normalized CV response) for hydrogen in 152 Torr of oxygen (full line). For comparison, the adsorption isotherm in inert atmosphere is also shown (dashed line).

That surface kinetics play an important role in determining the hydrogen response will become even more evident when we treat the case of hydrogen in "air", i.e., hydrogen in oxygen. Therefore, we believe that the failure of the Nernst equation to describe the experimental data by Robins et al.[21] is also due to its neglect of the water-forming reaction on the Pd surface.

Importance of Surface Chemistry to the Response

H_2 in O_2. In oxygen, the rate of hydrogen adsorption will have to be modified according to[10]

$$\frac{dn_s}{dt} = 2FS_H \frac{N_s - 4n_O - 4n_{OH} - n_s}{N_s} - d_s \frac{n_s^2}{N_s} - r_{OH}\frac{n_O n_s}{N_s} - r_{H_2O}\frac{n_{OH}n_s}{N_s} - \frac{dn_i}{dt} \quad (14)$$

with obvious notations. One may, for example, note that adsorbed oxygen (and OH) blocks four hydrogen adsorption sites. Matching rate equations for oxygen adsorption and hydroxyl coverage can now easily be set up in a model where it is assumed that oxygen desorption is negligible, and the water coverage always is low. Such a model has been found to reproduce experimental data very well, both in terms of the water production rates of the Pd surface and in terms of the hydrogen response, under UHV conditions.[10]

With these modifications of the surface kinetics, the hydrogen response in oxygen can also be plotted under atmospheric pressure conditions. Such a response curve is shown in Figure 5. For instance, utilizing this model it can been shown that the results of Morita et al.[22], who measured the hydrogen response for Pd-MOS devices at 373 K and under atmospheric conditions, can be reproduced well.[23] Morita et al.[22] obtained a good fit of their data to a pure Langmuir isotherm. This is, we believe, more by coincidence, than implying a microscopic physical model for the hydrogen interaction of the device.

Kinetic Limitations. An even more drastic influence on the hydrogen response may occur in the presence of
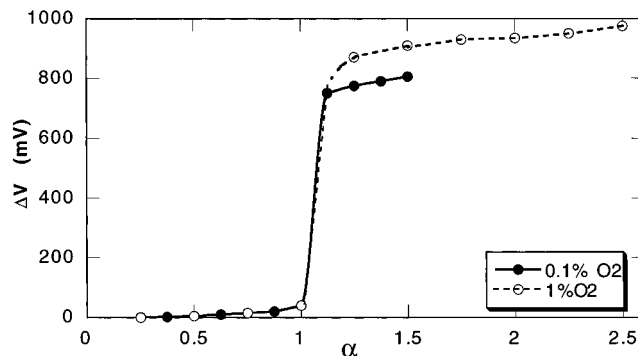

FIGURE 6. The response of a Pt—TaSi$_x$—SiO$_2$—SiC structure to hydrogen in two different oxygen concentrations at atmospheric pressures. Reprinted with permission from ref 26. Copyright 1997 The Electrochemical Society, Inc. The temperature is around 873 K. $\alpha = P_{H_2}/2P_{O_2}$. The nominal thicknesses of Pt, TaSi$_x$, and SiO$_2$ are 400, 10, and 125 nm, respectively.

CO. It has been shown that both hydrogen adsorption and hydrogen desorption may be totally blocked by adsorbed CO.[24,25] Thus, it is possible to both prevent hydrogen from entering the Pd and to entrap hydrogen in the Pd film. Consequently, the sensor does not show any response to changes in the hydrogen pressure.

A second example of a strong kinetic influence on the response is that of mass transport limitations in the gas phase. Under certain circumstances the response to hydrogen may become almost binary, with a transient from a small, almost zero voltage shift, to a very large shift, over a narrow range in pressure. An example is given in Figure 6, where the response of a Pt—TaSi$_x$—SiO$_2$—SiC capacitor operated at 600 °C shows an injection limited transition occurring at the stoichiometry of the reaction.[26] A very interesting consequence of such behavior is that the catalytic properties of the sensor surface become more or less unimportant, as long as the reaction rate is high enough to fall in the mass transport limited region. On the other hand, the sensor can now only give an almost binary response.

Other Interface States

In this review we have strongly emphasized the importance of one type of hydrogen site at the Pd—SiO$_2$ interface, namely, that giving rise to the Temkin isotherm behavior. It is, however, a fair question to ask whether there are other sites contributing to the response. For instance, since hydrogen can be detected on the surface, why not at the Pd side of the interface? Figure 7 shows the response to a hydrogen/deuterium exposure at 223 K. The transient response clearly indicates the existence of two different adsorption states. At 473 K only the "normal" Temkin like state is seen (insert, Figure 7). The new state, seen at lower temperatures, seems to have a heat of adsorption similar to (or slightly lower than) that of the Pd surface, and, furthermore, a dipole moment giving an increase in the work function of the metal, exactly as the hydrogen adsorption state of a clean Pd surface in vacuum.[27] The presence of this state has only been clearly identified at low temperatures during tran-
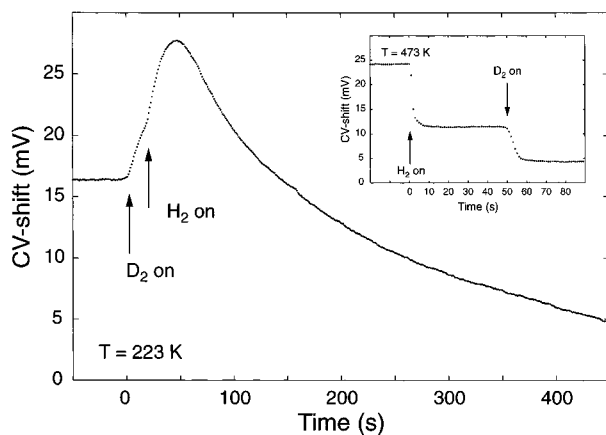
FIGURE 7. CV shift of a Pd-MOS device at low temperature. $P_{H_2} = 4.5 \times 10^{-9}$ Torr and $P_{D_2} = 7.5 \times 10^{-9}$ Torr. The insert shows a similar exposure but at normal operating temperatures. (The zero level is arbitrary in the drawings.) Clearly, at least two states seem to be involved in the response at the lower temperature. (The mixed isotopic exposure is of no concern in this context.)

sient measurements, but, in principle, it should also influence the steady-state response at normal operating temperatures at pressures above the ppm level. The total contribution of this state is, however, much smaller than that of the ordinary state, due to a significantly smaller dipole moment.[27]

Transient measurements at atmospheric pressures have sometimes indicated contributions from states with opposing dipole moments. Still, no thorough characterization of such states has been performed.

Emerging Model of the Metal—Insulator Interface

The obvious conclusion from previous and present studies is that there are hydrogen adsorption sites at the metal—insulator interface with different heats of adsorption. The most comprehensive way to describe the hydrogen adsorption at Pd—SiO$_2$ interfaces is to assume an interaction between adsorbed hydrogen atoms leading to a coverage dependent heat of adsorption. By assuming that these adsorption sites are located at the oxide surface, and that the adsorbed hydrogen "atoms" are sufficiently mobile laterally, the interaction energy is suggested to be purely electrostatic and equal to the voltage shift itself (in eV).

There are, however, some experimental observations which are difficult to reconcile with these considerations alone. These observations relate to the kinetics, i.e., the charging and discharging of hydrogen adsorbed at the Pd—SiO$_2$ interface. For instance, discharge time constants can be of the order of hours, and they are not explained by the largest observed heat of adsorption (0.86 eV/atom). However, by including an extra energy barrier of about 0.7—0.8 eV/atom (with reference to the vacuum level) between the Pd and the SiO$_2$ surfaces, reasonable time constants can be obtained. The presence of such an energy barrier is not unreasonable, considering that the hydrogen atoms have to leave the Pd surface to adsorb at the oxide surface. In a vacuum, the atomic hydrogen
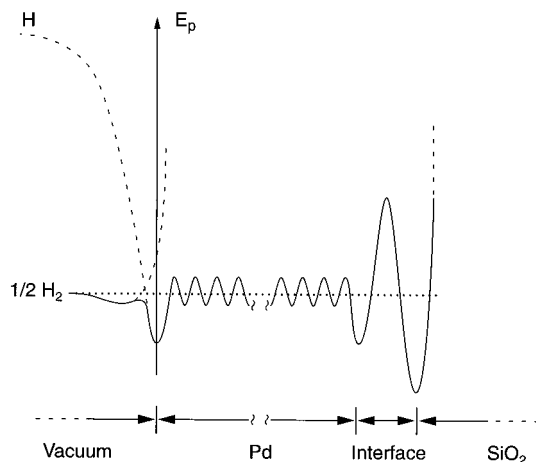

FIGURE 8. Schematic illustration of the energetics of the model for hydrogen sensing with Pd—SiO$_2$—Si devices. The surface heat of adsorption is 0.43 eV/atom; the initial interface heat of adsorption of the dominating state is around 0.86 eV/atom and decreases linearly with coverage due to an increased electrostatic interaction (cf. text). The heat of adsorption on the Pd side of the interface is probably somewhat less than that of the surface. The energy barrier between the two interface states is 0.7—0.8 eV/atom. The dipole moment of the dominating state is around 2 D while that of the Pd interface state is smaller by two orders of magnitude, and of opposite direction.

potential energy rises steeply outside a metal surface to reach a value of 2.25 eV/hydrogen atom. Thus, together with the additional hydrogen adsorption site described above, we arrive at a potential energy diagram for hydrogen adsorption at the interface indicated in Figure 8. It is important to point out that there is no one-to-one correspondence between the two interface adsorption states; they differ not only in induced dipole moment, but probably also in concentration.

The hydrogen response over more than 10 pressure decades was measured by Dannetun et al. and is shown in Figure 9.[12] It is now possible to add the effect of the hydrogen interface state on the Pd side to our first-order isotherm simulation, shown in Figure 4.[27] Assuming that this second state gives a maximum voltage shift of about 0.13 V, opposite to that of the main contribution, and has a heat of adsorption of 0.38 eV/atom, the model isotherm of Figure 9 (dashed line) is obtained. These values are reasonable in comparison to values for the hydrogen adsorption state on Pd.[15] Even though we do not wish to overemphasize the good agreement between the model and experiments in Figure 9, we believe that it may render some credibility to the general model of the hydrogen sensing mechanism of Pd— SiO$_2$ devices.

... and Its Relation to Some Previously Published Data

In evaluating the hydrogen response of Pd—SiO$_2$ structures, it is important to consider the influence of some critical experimental parameters. With the comments given below at hand, we believe that a majority of published results on Pd -MOS devices may be explained within our model of the hydrogen sensing at the Pd—SiO$_2$ interface.
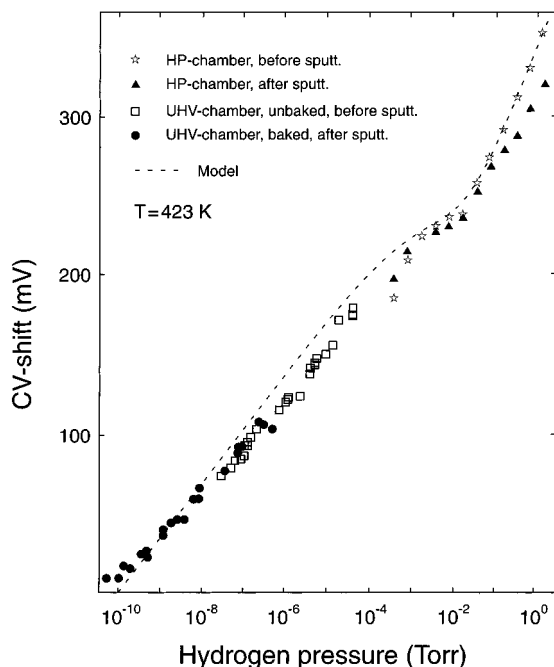
FIGURE 9. Magnitude of steady-state CV shift for a Pd-MOS device exposed to hydrogen pulses of increasing pressure. The measurements in the HP chamber were performed under atmospheric pressures with Ar as carrier gas (see ref 12 for further details). The dashed line corresponds to a simulated isotherm, assuming first-order adsorption and second-order desorption on the Pd surface, coupled to two interface states, one of Temkin character and one of Langmuir character (see the text for further details).

(a) Relative Pressure Range. Many workers seem to have used a Langmuir isotherm model in order to discuss their data.[1–3,5,22,28,29] It is easy to show that it is difficult to distinguish between a Langmuir and a logarithmic isotherm over a limited concentration range. A dissociative Langmuir isotherm and a logarithmic dependence look very similar even over 3–4 decades of (hydrogen) concentrations. Thus, reasonable fits to Langmuir adsorption isotherms have been obtained, yielding different values for the heat of adsorption and for the estimated ΔV_{max}.

(b) Absolute Pressure Range. If there is a distribution of heats of adsorption, the absolute hydrogen pressure is important. Measurements over say ~3 decades between 0.1 and 100 ppm H_2 do not yield the same heat of adsorption as measurements between 10 and 10 000 ppm.

(c) Background Pressure or Concentration of Hydrogen. Because of the large sensitivity of the Pd–SiO$_2$ structures to hydrogen, both in inert atmospheres and in oxygen, it can be difficult to determine a true zero level. The measured zero level will be influenced by trace amounts of hydrogen in carrier gases and in vacuum systems, which in turn influence the measured voltage shifts.

(d) Different Interfaces and ΔV_{max}. The details of the metal–insulator interface play an important role in the observed response. As has been stated earlier, ΔV_{max} is a very deceptive parameter and strongly dependent on the evaluation method. Furthermore, the quality of the interface may influence the estimated value of ΔV_{max} by both affecting the absolute concentration of available sites and the relative concentration between the oxidic and the metallic adsorption sites.

(e) Influence of the External Surface. As we have shown, the external surface enters into the behavior of the Pd–SiO$_2$ structure in several ways. One is related to fabrication and handling of the sample. More specifically, different amounts of contaminants may influence the reactivity of the surface. A second influence is of fundamental nature, and relates to the details of the rate-limiting catalytic reactions on the metal surface, which determine the source term for the adsorption isotherms of the interface. Thus, the chemistry of the metal surface strongly influences the response function.

A slightly different example is that of blistering of Pd films during high hydrogen pressures.[17] Several ways to overcome or minimize these effects have been suggested. For instance, with a Pd–Pt double layer, with the Pt facing the insulator, blistering can be avoided for pressure increases of at least a factor of 100, compared to that needed for blistering of a single Pd film.[30] Such an effect is completely understandable, simply due to the fact that the heat of absorption for hydrogen in bulk Pt is negative (i.e., endothermic), and thus a much higher pressure is needed, e.g., to form a hydride. In our model, this means that higher interface coverages may be obtained without blistering the metal film. A further interesting observation in the work of Choi et al.[30] is that it is the *outer* metal layer that determines the value of the shift at a certain hydrogen pressure. This is in complete accordance with our model, stating that it is adsorption sites at the insulator, coupled to the surface chemistry, which determine the response. What is between is of minor importance, as long as it may deliver hydrogen atoms to the interface.

Summary and Outlook

The presence of a hydrogen adsorption site at the Pd–SiO$_2$ interface with a large dispersion in the heat of adsorption gives the Pd–SiO$_2$ based devices a very large dynamic range for hydrogen detection, certainly up to 14 decades in hydrogen pressure. We suggest that this dispersion is due to an electrostatic interaction between adsorbed hydrogen atoms simply given by the potential ΔV built up by the adsorbed hydrogen dipoles. We pointed out that the experimentally observed isotherm is strongly dependent not only on the energy dispersion at the interface, but also on the chemical reactions on the metal surface. A model of the interface adsorption has emerged, being based on some recent experiments and model calculations. This model seems to be consistent with a wealth of previously published data.

A detailed knowledge about the hydrogen adsorption properties of the Pd–SiO$_2$ interface leads both to a better understanding of chemical sensors based on field effect devices, and to more accurate predictions when such devices are used to study heterogeneous catalysis or

surface phenomena. The model presented here will, we believe, also be helpful in elucidating the properties of other interfaces, some of which will show very similar properties as the Pd−SiO$_2$ interface, only with other parameters. Other interfaces, like those in Pt−TaSi$_x$−SiO$_2$−SiC structures, probably involve new physics and completely different hydrogen adsorption sites. To understand the hydrogen sensing mechanism of such structures is a future challenge which the present understanding of the Pd−SiO$_2$ interface may facilitate.

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