

## Effects of hydrogen absorption on the electrical conduction of discontinuous palladium thin films

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The continuation of work reported earlier (Morris and Wu 1994) on the development of a discontinuous thin palladium film hydrogen sensor confirms the effects first described and interpreted by Barr (1977). The basic principle is that quantum-mechanical tunnelling between the discrete metal islands of the film is modulated by barrier height increases due to the surface adsorption of hydrogen, and by gap reduction due to island lattice swelling. Transient thermal effects do not yet permit quantitative verification of the model.

### 1. Introduction

Discontinuous metal films are formed in the initial stages of deposition and growth of a noble metal on an insulating substrate, and they consist of discrete metal islands. The detailed theory of electrical conduction in discontinuous metal films is still a topic of active investigation (Neugebauer and Webb 1963, Abeles *et al.* 1975, Morris and Coutts 1977, Morris *et al.* 1990, Morris 1990), but the only aspect of the various models necessary to the interpretation of the experiments described here is the assertion of quantum-mechanical tunnelling as the electron transport mechanism between metal islands. It is also widely accepted that the single electron charging of an island requires an electrostatic activation energy of the order of

$$E = \frac{q^2}{4\pi\epsilon} \left( \frac{1}{r} + \frac{1}{r+s} \right) \quad (1)$$

where  $r$  is the radius of the island,  $s$  is the width of the gap between islands,  $q$  is the electronic charge, and  $\epsilon$  is the effective dielectric constant in the film. The film resistance  $R$  at temperature  $T$  may therefore be written approximately as

$$R = C \exp(A\phi^{1/2}s + E/kT) \quad (2)$$

where  $C$  and  $A$  are constants,  $k$  is Boltzmann's constant, and  $\phi$  is the effective barrier height between islands, related to the island's surface potential. Island diameters for films in the 1-5 nm range are typically 1-10 nm with gaps at around 2 nm.

When a discontinuous palladium film is exposed to hydrogen (Fig. 1):

- (1) gas molecules impinge on the surface of the metal islands (at a rate proportional to the hydrogen partial pressure  $p_H$  and  $T^{-1/2}$ )

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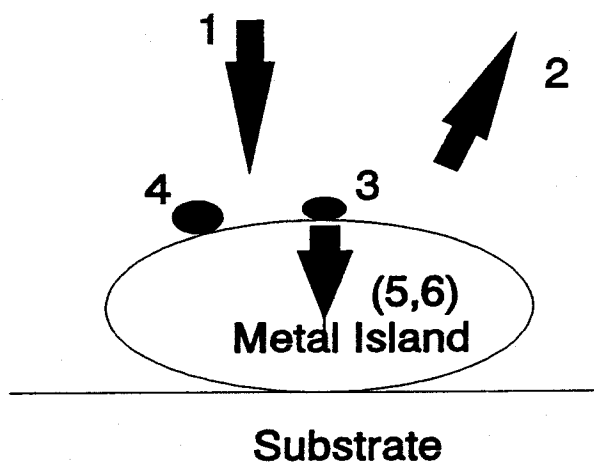


Figure 1. Hydrogen effects on discontinuous palladium films: 1 impingement, 2 re-evaporation, 3 physisorption, 4 chemisorption, 5 bulk diffusion and absorption, 6 solution or compound formation.

- (2) Most of these atoms or molecules are re-evaporated, because the hydrogen vapour pressure will be much greater than  $p_H$ ; there are four possible types of adhesion reaction for those that do not
- (3) physical adsorption
- (4) chemisorption (both surface effects have an  $\exp(W/kT)$  type of temperature dependence)
- (5) absorption
- (6) bulk compound formation (both bulk effects dependent on thermally activated diffusion).

Processes (3) and (5) are essentially reversible; (4) and (6) may be irreversible, but it was observed in prior work (Morris and Wu 1994) that film resistance returns to its original value with a difference of less than about 1.5% when the system is re-evacuated, the small discrepancy being attributed to continued annealing effects. The overall thermal variations of the absorption effects will obviously be very complex unless individual processes are dominant or can be isolated. The problem is to determine the surface concentration  $N_s(p_H, T_s, t)$ , and to adapt the diffusion distribution  $N_s \operatorname{erfc}(x/(4Dt)^{1/2})$  (with  $D = D_0 \exp(E_d/kT_s)$ ) to determine the lattice hydrogen concentration  $[H](p_H, T_s, t)$  as a function of time  $t$ ,  $p_H$  and substrate temperature  $T_s$ .

Barr (1977) assumed that the work function  $\phi$  of the palladium island would increase by  $\Delta\phi$  as hydrogen is adsorbed, and hence that the resistance of the film would increase, and that bulk absorption by the lattice (Feenstra *et al.* 1986, Batalla *et al.* 1989) causes a decrease  $\Delta s$  in the tunnelling gap width  $s$ , and a decrease in film resistance. Both effects should increase with hydrogen partial pressure.

From (2) we have

$$R = C' \exp(A\phi^{1/2}s) \quad (3)$$

where  $C' = C \exp(E/kT)$ ,  $\phi = \phi_0 + \Delta\phi$  and  $s = s_0 + \Delta s$ , which can be rewritten as

$$R = C' \exp[A(\phi_0 + \Delta\phi)^{1/2}(s_0 + \Delta s)] \quad (4)$$

Since  $\Delta\phi$  and  $\Delta s$  are very small, we have

$$\ln \frac{R}{R_0} \simeq A\phi_0^{-1/2} \left( \phi_0 \Delta s + \frac{s_0 \Delta \phi}{2} \right) \quad (5)$$

where  $R_0 = C' \exp(A\phi_0^{1/2}s_0)$ , or

$$\ln \frac{R}{R_0} \simeq A\phi_0^{1/2}s_0 \left( \frac{\Delta s}{s_0} + \frac{\Delta \phi}{2\phi_0} \right) \quad (6)$$

It is assumed that  $\Delta\phi \propto N_s(p_H, T_s, t)$  and that  $\Delta s \propto [H](p_H, T_s, t)$ .

Physical adsorption is reported to decrease the work function, and surface chemisorption to increase it (Hayward 1971). Chemisorption will increase with temperature, whereas physical adsorption decreases. Diffusion of physical adsorbed species into the bulk increases with increased temperature. So the work function effect  $\Delta\phi$  will increase with temperature, whereas the net effect on  $\Delta s$  will depend on the temperature dependence of the solubility of hydrogen in palladium.

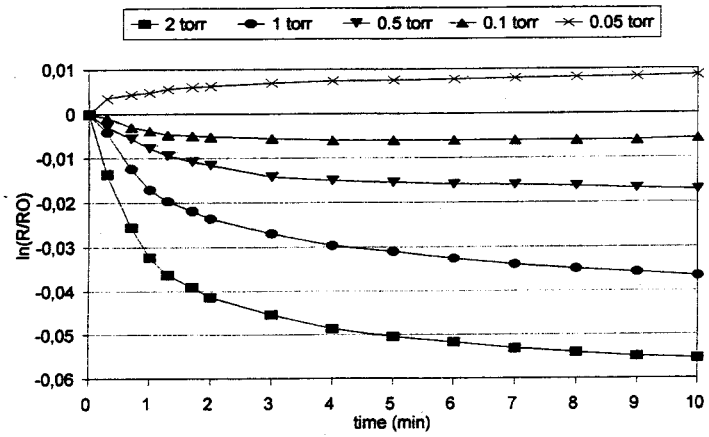
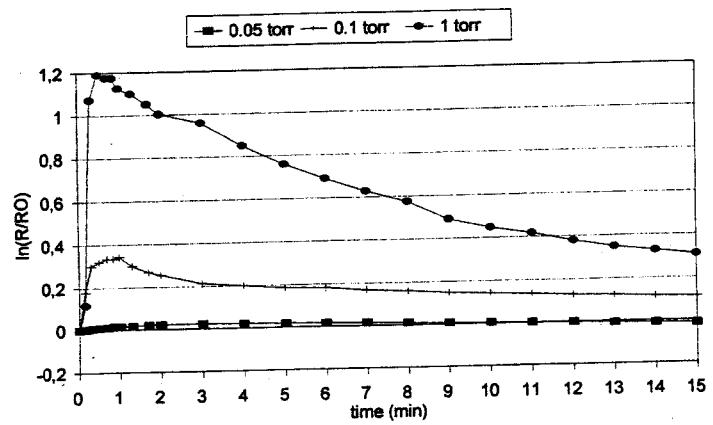
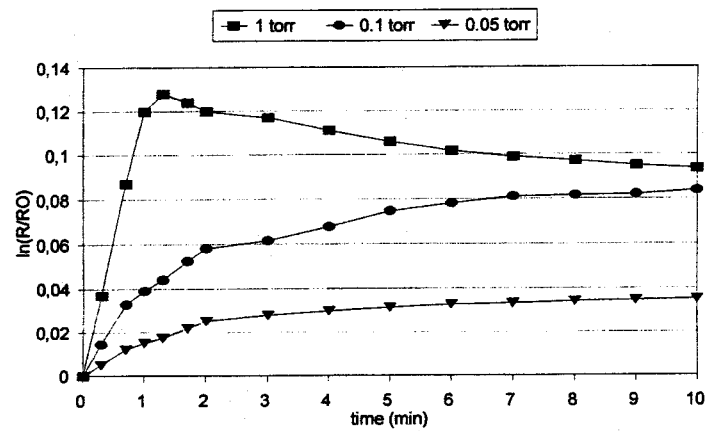
The exponential dependence of film resistance on both effects should yield a hydrogen sensor of great sensitivity. Furthermore, both are effectively surface effects (given the typical nm dimensions of the islands), so the response times are expected to be much lower than for sensors based on bulk effects, and comparable with those for Pd-gate MOSFETs.

The experimental procedures are the same as those previously reported (Morris and Wu 1994), except that the films are transferred to another vacuum system (with 2 hours of subsequent outgassing *in vacuo*) to permit low-temperature experiments. (Low temperatures were achieved by liquid nitrogen (LN2) cooling of the substrate holder, with control by heat lamp.) The primary objective was the enhancement and isolation of the gap width modulation, by higher deposition temperatures to increase island sizes.

Results are shown in Table 1 and Figs 2–9. Figs 2 and 6 demonstrate the dual effect clearly in both films selected as examples. The bulk absorption effect is significantly enhanced at higher pressures. Figures 3 and 4 show the effects of cooling

	Film					
	1	2	3	4	5	6
Substrate temperature (°C)	110	105	110	110	150	150
Average thickness (nm)	1.6	1.6	1.6	1.6	1.6	1.6
Initial resistance (MΩ)	4.3	45.0	21.8	122.5	15.5	2.3

Table 1. Film deposition data. Resistance values are not consistent with earlier films deposited under apparently identical conditions.

Figure 2. Film 6: resistance changes in  $H_2$  at 300 K; various pressures.Figure 3. Film 6: resistance changes in  $H_2$  at 269 K; various pressures.Figure 4. Film 6: resistance changes in  $H_2$  at 333 K; various pressures.

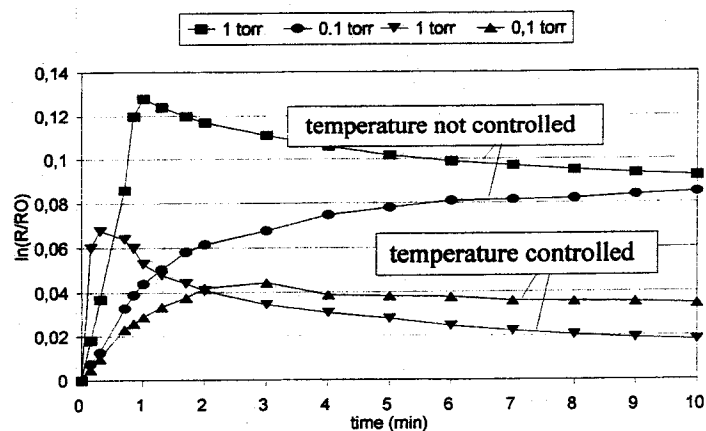


Figure 5. Film 6: resistance changes in H<sub>2</sub> at 333 K with temperature control.

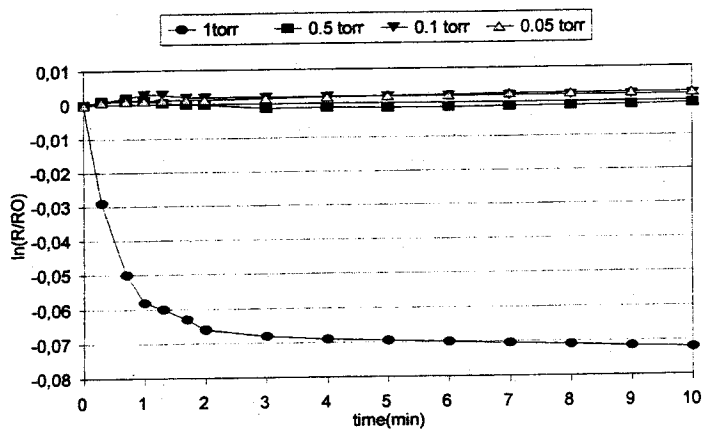


Figure 6. Film 5: resistance changes in H<sub>2</sub> at 300 K; various pressures.

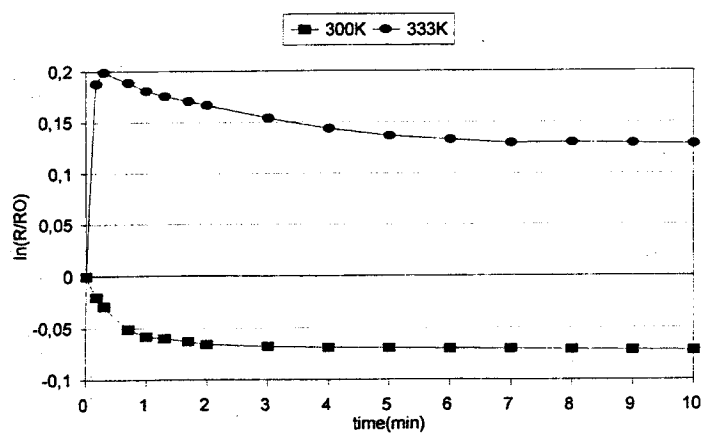


Figure 7. Film 5: resistance changes in 1 torr H<sub>2</sub> at 300 K and 333 K.

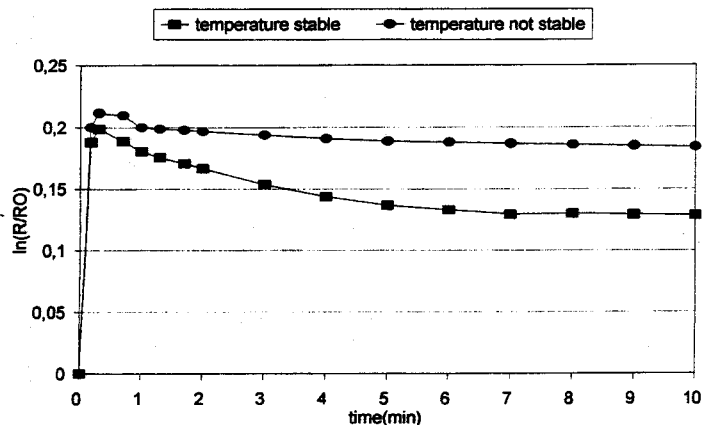


Figure 8. Film 5: resistance changes in 1 torr  $H_2$  at 333 K with temperature control.

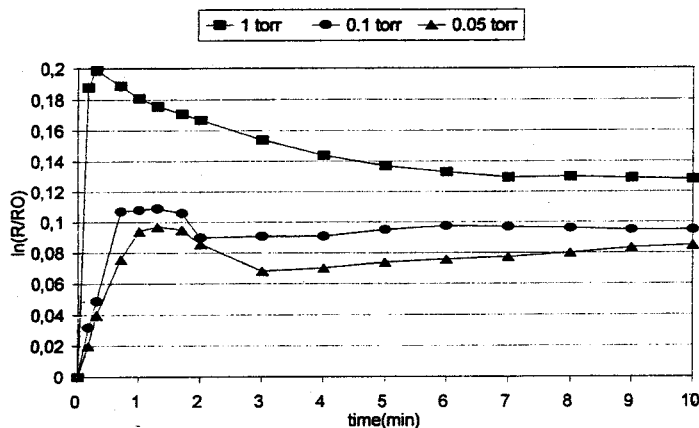


Figure 9. Film 5: resistance changes in  $H_2$  at 333 K with temperature control; various pressures

and heating the substrate, respectively. Both show the superposition of a cooling transient (Table 2) due to gas expansion (from supply pressure to essentially zero) on the expected resistance changes, but the enhancement of the negative (bulk) effect at low temperatures is nevertheless apparent. Table 2 demonstrates that the transient temperature decrease is proportional to the thermal capacity of the hydrogen introduced, i.e. to the partial pressure. Convection effects are also evident (and dependent on pressure) between the film and the LN2 substrate cooling system, the heat lamp and the vacuum chamber walls at room temperature. Attempts were made to compensate for these transients by manually adjusting the heat lamp power to maintain the set-point of the substrate temperature; Fig. 5 shows that these were not very successful. Figures 6–9 show similar effects in film 5.

	Test		
	1	2	3
Initial temperature $T_i$ (°C)	-4	-4	7
Initial resistance $R_i$ at $T_i$ (M $\Omega$ )	2.67	2.68	2.64
Hydrogen partial pressure (Torr)	0.05	0.1	1.0
Transient $T$ on H <sub>2</sub> admission (°C)	-6	-20	-101
Transient $R$ on H <sub>2</sub> admission (M $\Omega$ )	2.80	3.40	5.67

Table 2. Temperature changes upon admission of the H<sub>2</sub> to film 6.

### 3. Conclusions

Both types of resistance change are observed, consistent with the model. The negative effect is enhanced by deposition at elevated temperatures, due to larger islands (and smaller gaps). Both effects increase with hydrogen partial pressure. The positive effect tends to be dominant at low pressures, with the negative being more readily apparent at higher pressures. In each region it appears that  $\log(R_{t \rightarrow \infty})$  may be directly proportional to partial pressure. The cooling effect of the hydrogen expansion can be eliminated by the use of an expansion chamber to bring the gas to thermal equilibrium before exposing the film. Minimization of convective effects will require the redesign of the substrate temperature control system and physical layout.

Practical sensors will need to be designed for maximum island sizes and small gaps, to maximize the hydrogen specific negative response and to minimize the electrostatic activation energy (i.e. negative temperature coefficient of resistance). Unfortunately, this structure is the most difficult to achieve, the most irreproducible and the least stable. A parallel project is addressing this problem.

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