

# The effects of hydrogen absorption on the electrical conduction in discontinuous palladium films

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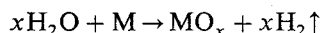
## Abstract

The effects of hydrogen absorption on the electrical conduction in discontinuous palladium films on glass substrates were investigated. A qualitative model is proposed to explain the experimental results, based on work function changes due to surface adsorption and chemisorption and on island expansion due to bulk hydrogen absorption.

## 1. Introduction

### 1.1. Hydrogen sensors

The measurement of hydrogen continues to be a challenging technological problem in spite of commercial instruments that are available. One important application of hydrogen detection is in the detection of corrosion



in the oil industry or power generation systems. Some other examples of the importance of detecting hydrogen gas are as follows: point detection of leaks in liquid-hydrogen-fueled rocket motors such as on the space shuttle; hydrogen leaks in semiconductor fabrication clean rooms; explosive mixtures of hydrogen in mixed radiative waste; chemical process control; and other places where dangerous levels of hydrogen could be present.

There are many existing hydrogen gas sensors based on different mechanisms. The pyroelectric gas sensor (Pd-LiTaO<sub>3</sub>) [1] is made of Z-cut, single-crystal LiTaO<sub>3</sub> wafers. Exposure to hydrogen gas has been shown to produce a signal difference between the palladium and reference electrodes. Besides its multilayer fabrication complexity, this pyroelectric sensor has proved to be extremely temperature dependent. The piezoelectric quartz crystal microbalance [2] has proved to be very useful as a hydrogen gas detection device. The concentration of a pollutant gas is measured by detecting a change in the crystal vibration frequency. Operation at low hydrogen concentrations is impeded, however, by interference from other ambient gases.

This phenomenon has turned out to be a significant disadvantage of the piezoelectric quartz crystal detector. According to Lundsgaard *et al.* [3], the electrochemical hydrogen sensor has shown high durability and reproducibility with a response detection limit of 2000 ppm in air at 25 °C. Device construction is very complex though. The metal-oxide-semiconductor field effect transistor (MOSFET) with a palladium gate is the predominant hydrogen-sensing technology under development at present [4]. Hydrogen modifies the surface potential of the palladium and hence shifts the threshold voltage of the MOSFET. The device has relatively good sensitivity (in the ppm range) and fabrication would be inexpensive using mature silicon-processing techniques. The devices are small and would be cheap, despite apparent constructional complexity. A fifth kind of hydrogen gas sensor in the literature is the palladium wire hydrogen sensor [5]. As hydrogen is absorbed by the palladium lattice, the wire resistance changes and provides a measure of hydrogen concentration. The response speed is slow (approximately 1 h), however, owing to the need for complete permeation of the hydrogen into the interior of the wire.

In this paper we describe the effect of hydrogen gas on the electrical conduction in discontinuous palladium films. This effect has the potential to be the mechanism of a new, inexpensive, sensitive hydrogen gas sensor.

### 1.2. Discontinuous metal films

Discontinuous metal films are formed in the initial stages of deposition and growth of a noble metal on an insulating substrate. The poor chemical bond between impinging atoms and the substrate surface leads to high surface mobility and to film formation as discrete metal islands instead of as a monolayer [6].

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Theoretical models to analyze experimental results of electrical conduction in discontinuous metal films are far from conclusive [7]. Several theories of electrical conduction in discontinuous metal films have been proposed in the past [8], such as thermionic emission, thermally activated tunneling, tunneling between allowed states, substrate-assisted tunneling, variable-range hopping, etc. All models match experiment only qualitatively. In view of the wide distribution of island sizes and separations, it is quite possible that two or more mechanisms take place simultaneously. Abeles *et al.* [9] suggested that the ratio of grain size  $r$  to grain separation  $s$  should remain constant as  $r$  and  $s$  vary and developed an elegant percolation conduction model. However, while there is evidence for this in cermets and granular films, structural studies with discontinuous metal films show no such correlation whatsoever between particle size and particle separation [7]. Morris and Coutts [8] developed an alternative approach to the percolation formulation.

The generally accepted fundamental basis of the theory of conduction in discontinuous metal films originates with Neugebauer and Webb [6]. Quantum tunneling was a natural choice for the conduction mechanism, because the separation of islands is on the order of a few nanometers when a significant current flows in a discontinuous metal film. It was also realized that a certain amount of work has to be done against electrostatic forces to transfer an electron from one island to another. In conclusion, only electrons with energies of the order

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

above the Fermi level of the initial island can tunnel to a nearby island, where  $r$  is the radius of an island,  $s$  is the width of the gap between islands and  $\epsilon$  is the effective dielectric constant in the film. The film resistance  $R$  at temperature  $T$  may therefore be written approximately as

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

where  $C$  and  $A$  are constants,  $q$  and  $k$  are the electronic charge and Boltzmann's constant respectively and  $\phi$  is the effective barrier height between islands, related to an island's surface potential. Island diameters are typically 1–10 nm with gaps around 2 nm.

Extensive investigations of the effect of the adsorption of hydrogen by palladium in a variety of forms have been made [10–12] and it has been found that hydrogen markedly affects the resistance of palladium wire, foil, continuous thin films and discontinuous thin films. The resistance increases in the first three cases, but discontinuous films give results which are very different.

Barr [12] has measured the conductance–temperature characteristics of discontinuous palladium films. The conductance–temperature characteristics for annealed films were found to exhibit a hysteresis effect on cooling and heating. An explanation of the effect of hydrogen adsorption on the electrical conduction in discontinuous palladium was given in terms of both work function variations and island expansions. The observation of a fast rise in resistance was attributed to a work function increase, the accompanying slower resistance decrease to the islands increasing in size owing to lattice expansion driven by bulk absorption. He did not present any data on the resistance variation with time and only temperatures below ambient were employed. From Barr's results it can be seen that a hydrogen sensor based on the lattice expansion effect would not only be more sensitive than the palladium wire sensor, but also faster and cheaper. The problem will be the complication of the work function change.

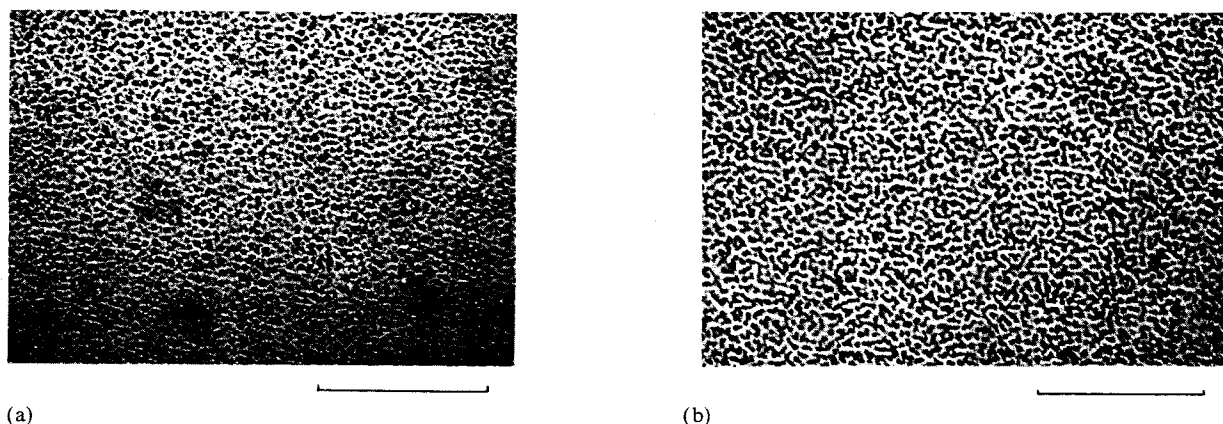
In this paper we present systematic measurements of the effects of the adsorption of hydrogen gas on the resistance of discontinuous palladium films. We also show the dependence of this effect on the structure of the films, hydrogen partial pressure, temperature and time. A qualitative model based on that of Barr is proposed to explain the experimental results.

## 2. Experimental procedure

All discontinuous films were deposited using an electron beam system in a turbo-pumped stainless steel high vacuum chamber with a base pressure of about  $10^{-7}$  Torr. Residual gas analysis was carried out with a Dycor quadruple residual gas analyzer. The distance between the evaporation source and the sample was 30 cm. The average thickness of the evaporated film was measured with an Inficon quartz oscillator to an accuracy of about 0.1 nm. The deposition rate was usually about  $0.01$ – $0.02$  nm s $^{-1}$  at a system pressure below  $10^{-6}$  Torr.

The substrates used were Corning 7059 glass 1 mm thick. They were cleaned by washing in an ultrasonic bath, using first a detergent solution (TUD, Transene ultrasonic detergent) and then deionized water, and were then dried by nitrogen gas. Final cleaning was carried out by baking in the vacuum system at a pressure on the order of  $10^{-7}$  Torr.

The discontinuous palladium films were evaporated after carefully outgassing the 99.995% pure source metal on the electron gun hearth. At room temperature palladium films 0.8–1.6 nm thick were deposited; at 100 °C films 1.5 nm thick were deposited. Films were deposited simultaneously on carbon-coated copper grids for transmission electron microscopy studies



(a)

(b)

Fig. 1. Electron micrographs of discontinuous palladium films deposited at  $3 \text{ \AA s}^{-1}$  to thickness of (a) 1.8 nm (deposited at  $100^\circ\text{C}$ ) and (b) 1.4 nm (deposited at  $24^\circ\text{C}$ ). Markers: 100 nm.

(Fig. 1). Experience suggests that the films on glass will exhibit less coalescence than those simultaneously evaporated on the carbon grids, which are nevertheless useful as a general guide to structural trends and to confirm the discontinuous structure.

After depositing the palladium film, aluminum electrodes 1000 nm thick were deposited, as two squares about 5 mm apart, for measuring the resistance across the film. The resistance was monitored by a Keithley 617 programmable electrometer after deposition.

All films were kept at their temperature of deposition for at least 2 h to enable low temperature annealing to take place. Substrate temperatures were measured using a very fine chromel–alumel thermocouple in contact with the surface of the substrate.

### 3. Model

All measurements of the effects of adsorption of hydrogen gas on the resistance of discontinuous palladium films were performed in the same vacuum system where deposition took place. We focus here on the dependence of these effects on the hydrogen partial pressure, test temperature and the structure (thickness) of the films.

All explanations of these effects were based on the following model. Electrical conduction in discontinuous palladium films is caused by quantum mechanical tunneling of electrons between adjacent metal islands. As shown in Fig. 2, when the hydrogen gas is introduced into the vacuum chamber, there are several processes which take place simultaneously. The measured effects depend upon their relative rates as functions of pressure and temperature. (1) Hydrogen molecules impinge on the surface of the metal islands. Some of these atoms or molecules are (2) re-evaporated. There are four possible

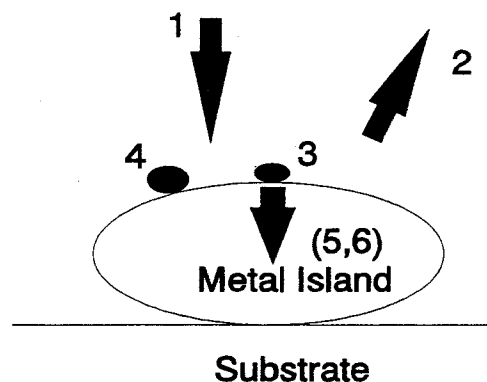


Fig. 2. Hydrogen effects on discontinuous palladium films: 1, impingement; 2, re-evaporation; 3, physisorption; 4, chemisorption; 5, 6, diffusion into the bulk.

types of adhesion reaction for those that are not: (3) physical adsorption, (4) chemisorption (both surface effects), (5) absorption and (6) bulk compound formation (both bulk effects). Processes 3 and 5 are essentially reversible, but processes 4 and 6 may be irreversible. Physical adsorption is reported to decrease the work function and surface chemisorption to increase it [13]. It was observed that after the discontinuous palladium films have been exposed to hydrogen, the 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.

Barr [12] 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. He also proposed a change in tunneling gap widths.

The lattice constant of palladium islands increases when hydrogen atoms are absorbed into the bulk [14,

15]. Therefore the island diameter increases and the inter-island separations will be reduced by  $\Delta s$ , raising the electron tunneling probability and thus producing a resistance decrease.

All processes should increase with hydrogen partial pressure. Chemisorption will increase with temperature, while physical adsorption decreases. Diffusion of physically adsorbed species into the bulk increases with temperature. Thus the work function effect  $\Delta\phi$  will increase with temperature, while the net effect on  $\Delta s$  will depend on the conflicting effects of physical adsorption and diffusion. All these processes are also functions of the structure of the film, *i.e.* of island and gap dimensions.

From eqn. (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

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

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

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

#### 4. Results

The results focus on three films for which they are typical in each category. Films 3 (2 G $\Omega$ , 1.0 nm) and 10 (0.17 G $\Omega$ , 1.4 nm) were deposited on unheated substrates; the substrate for film 4 (45 G $\Omega$ , 1.5 nm) was maintained at 373 K during deposition. In Figs. 3(a) and 3(b) the changes in  $\ln(R/R_0)$  vs. time are plotted for films 3 and 10 at various hydrogen partial pressure increases from  $t = 0$  as soon as hydrogen gas was introduced into the vacuum chamber. It can be observed that the higher the hydrogen partial pressure, the greater the eventual equilibrium change is and the faster the resistance of the film increases. In Fig. 3(b) an initial decrease in resistance is noted for the thinner, *i.e.* more discontinuous, of the two films.

The small initial decrease in resistance observed in Fig. 3(b) is attributed to the bulk lattice effect described above. It is noted again that this film is "more discontinuous" than the other. The continuous increase in resistance of the films with hydrogen partial pressure is related to the work function change and surface coverage. When the hydrogen partial pressure increases, the rate of surface impingement, rate of surface coverage (to first order) and rate of resistance rise all increase.

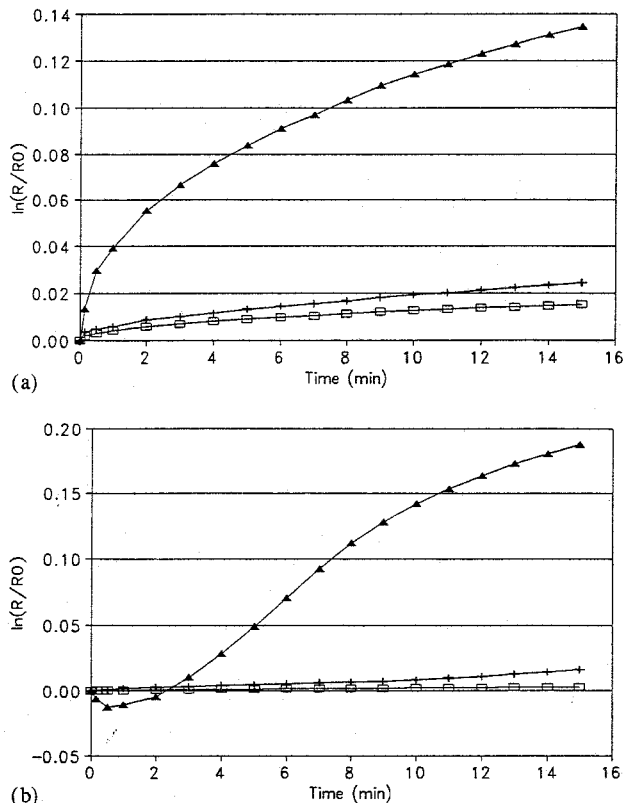


Fig. 3.  $\ln(R/R_0)$  vs. time (a) for film 10 ( $\square$ ,  $6.97 \times 10^{-6}$  Torr; +,  $1.97 \times 10^{-5}$  Torr;  $\blacktriangle$ ,  $5.00 \times 10^{-4}$  Torr) and (b) for film 3 ( $\square$ ,  $2.42 \times 10^{-5}$  Torr; +,  $3.79 \times 10^{-4}$  Torr;  $\blacktriangle$ ,  $2.28 \times 10^{-1}$  Torr) in response to hydrogen at 24 °C.

Then the equilibrium coverage of the adsorbed hydrogen atoms on the island surface increases and the change in the work function  $\Delta\phi$  is proportional to this coverage. By analogy with ordinary chemical reactions, chemisorption might be expected to proceed until a definite surface stoichiometry is achieved and then abruptly cease. This would correspond to a monolayer—normally one adsorbed species per surface metal atom. However, in Fig. 3 this clear-cut behavior is not observed. One important reason is that the heat of adsorption tends to decrease as more gas is adsorbed, whereas ordinary chemical compounds usually have fixed bond energies. It follows that if the surface is in equilibrium with the gas phase at any given temperature and pressure, it is always possible to increase the extent of adsorption. Our model follows that of Barr in attributing the resistance increase to  $\Delta\phi$  and surface coverage; but while the literature would suggest chemisorption for the  $\Delta\phi$  increase, the effect is also most totally reversible upon subsequent re-evacuation, subject only to small continued annealing effects.

The effect of temperature on the behavior of  $\ln(R/R_0)$  vs. time is more complicated than that of hydrogen

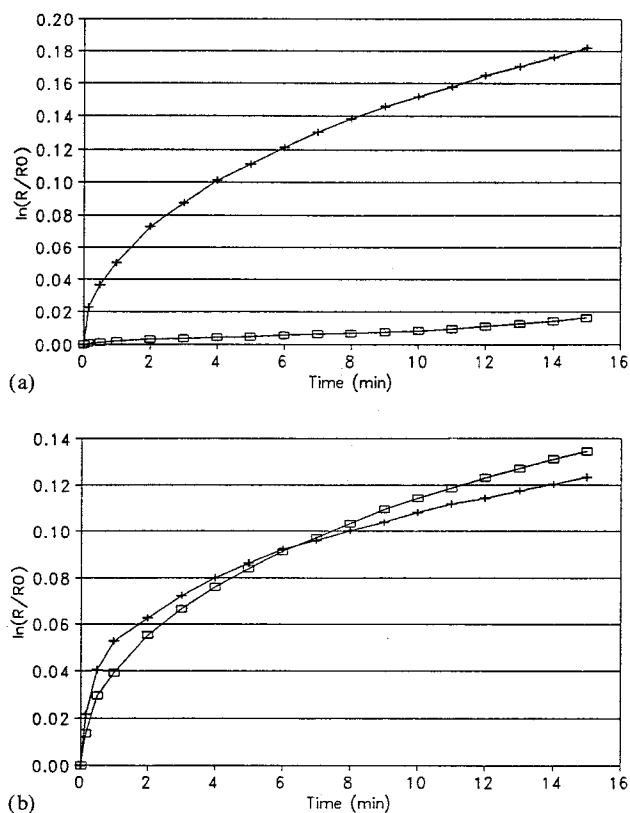


Fig. 4.  $\ln(R/R_0)$  vs. time (a) for film 3 ( $\square$ ,  $3.79 \times 10^{-4}$  Torr,  $T = 24^\circ\text{C}$ ;  $+$ ,  $3.64 \times 10^{-4}$  Torr,  $T = 103^\circ\text{C}$ ) and (b) for film 10 ( $\square$ ,  $5.00 \times 10^{-4}$  Torr,  $T = 25^\circ\text{C}$ ;  $+$ ,  $4.85 \times 10^{-4}$  Torr,  $T = 108^\circ\text{C}$ ) in response to hydrogen at  $p_H \approx 10^{-4}$  Torr at various temperatures.

partial pressure. Figure 4 shows  $\ln(R/R_0)$  vs. time at various test temperatures for the same two films as in Fig. 3. Figure 4(a) indicates that both the amount of change in the resistance due to hydrogen adsorption and the rate of change increase with the test temperature. In Fig. 4(b) the curves appear to begin consistently, *i.e.* tending faster to a high resistance at the higher temperature, but subsequently cross. Again the tentative explanation is that the bulk effect intrudes (more) in the high temperature curve.

In all the above figures increases in resistance were dominant. The reason that the decrease in resistance due to the island slowly increasing in size is absent may be that all these films were deposited at low temperature. When the films are deposited at low temperature, metal atoms are quenched by the substrate as they condense and lose energy rapidly. Their diffusion distance on the substrate is small and hence nuclei are closely spaced and the island size is small. Therefore small island sizes result, leading to lesser island size expansion effects when hydrogen gas is absorbed. In this case the term  $s_0 \Delta\phi$  in eqn. (5) dominates the behavior of  $\ln(R/R_0)$  vs. time.

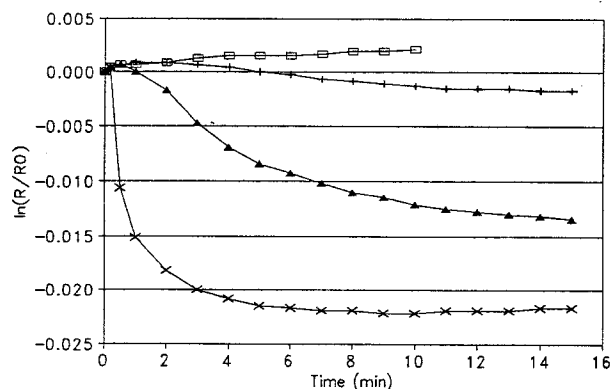


Fig. 5.  $\ln(R/R_0)$  vs. time for film 4 in response to hydrogen at  $24^\circ\text{C}$ .  $\square$ ,  $3.03 \times 10^{-6}$  Torr;  $+$ ,  $4.39 \times 10^{-5}$  Torr;  $\blacktriangle$ ,  $4.24 \times 10^{-4}$  Torr;  $\times$ ,  $1.90 \times 10^{-1}$  Torr.

Figure 5 shows  $\ln(R/R_0)$  vs. time with hydrogen pressure variation at ambient temperature for film 4 deposited at  $373\text{ K}$ . Figure 6(a) shows the same results in a different format and contrasted in Fig. 6(b) with data at high temperature. In Fig. 6(a) it is observed that (i) at very low hydrogen partial pressure  $p_H = 3 \times 10^{-6}$  Torr (background pressure  $5 \times 10^{-7}$  Torr) the resistance of the film increases slowly, (ii) at higher hydrogen partial pressure  $p_H = 3 \times 10^{-5}$  Torr the resistance starts to increase and subsequently decreases, (iii) at  $p_H = 1.5 \times 10^{-1}$  Torr the resistance decreases with time during the test period and (iv) at very high hydrogen partial pressure  $p_H = 1.5$  Torr the resistance starts to decrease and then increases. Figures 6(a) and 6(b) both show increases and decreases in resistance of the film, but with the decreases in resistance much more apparent than in films 3 or 10. The amount of decrease also appears to be smaller at higher temperature than at room temperature.

When deposited at relatively high temperature, the rate of surface diffusion of the metal atoms is appreciable and large island sizes are naturally expected because of an increase in surface mobility. Larger islands result in larger island expansions, hence larger changes (decreases) in inter-island gap  $s$ , unless the increase in gap width is proportionately greater than the increase in island size. In this case, however, the term  $\Delta s/s_0$  appears to be comparable with the term  $\Delta\phi/\phi_0$ . Which term determines the balance of behavior of  $\ln(R/R_0)$  vs. time depends on the hydrogen partial pressure and test temperature.

At low test temperature (room temperature), when the hydrogen partial pressure is low, the coverage of adsorbed hydrogen atoms on the surface of the metal island is small; hence few adsorbed hydrogen atoms diffuse into the metal islands. Thus the increase in work function dominates the behavior of  $\ln(R/R_0)$  vs. time. When the hydrogen partial pressure goes up, more

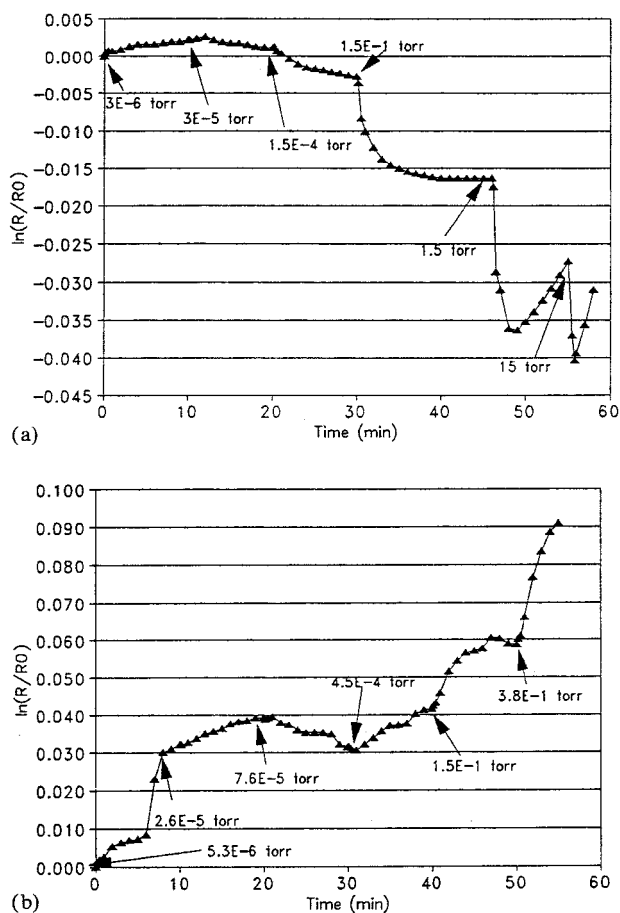


Fig. 6.  $\ln(R/R_0)$  vs. time for film 4 in response to continuous hydrogen pressure variation (a) at 24 °C and (b) at 100 °C.

hydrogen atoms are absorbed into the metal island and the effect of the island expansion becomes comparable with or greater than the effect of the work function increase.

The reason the effect of island expansion in Fig. 6 is weaker at higher test temperature than that at lower temperature may be due to a reduced physisorbed population. Thus at the same hydrogen partial pressure fewer hydrogen atoms are available to diffuse into the metal islands at elevated temperature and hence they cause less island expansion. This also agrees with Barr's results. In Barr's paper [12] all tests were done at low temperatures from liquid nitrogen temperature to room temperature, thus dominant bulk effects were observed. At low temperature physical adsorption increases with more adsorbed atoms diffusing into the bulk, thus causing more lattice expansion and gap decrease. Furthermore, when the temperature goes down, the diffusion coefficient also goes down and therefore the increases should proceed more slowly. Confirmation of these trends at temperatures above ambient is frustrated by the surface effect masking.

## 5. Conclusions

The effects of adsorption of hydrogen gas on the electrical conduction in discontinuous palladium films are being investigated. The experiments described were performed at ambient and elevated temperatures. Resistances were measured at various hydrogen partial pressures and temperatures. The resistance response to hydrogen adsorption-absorption is explained in terms of quantum mechanical tunneling incorporating both surface and "bulk" effects. This model can explain most experimental ( $\ln(R/R_0)$  vs. time) results qualitatively, but not without some unresolved questions. In particular, Fig. 3 does not support the presumption that the negative resistance change associated with the gap width decrease will be greater for thicker films. One possible explanation amongst others is that the fractional lattice expansion at a given hydrogen content is greater for smaller islands. Kuhrt and Anton [16] observed decreases in the lattice expansion with increasing deposited palladium thickness and claimed that this decrease may be due to depletion of palladium hydride or to a limitation in the diffusion process. Clearly more systematic data are required and it would be advantageous to establish two distinct regions where the competing effects might be effectively separated. Then the data must be matched to the model quantitatively and including theoretical variations in  $\Delta s$  and  $\Delta\phi$  with time, temperature and pressure.

As one final remark, it is noted that the lattice expansion model itself has yet to be verified. The simple concept of competing  $\Delta\phi$  trends tied to the chemisorption-physisorption ratio will also receive due consideration, but will not provide the sensitive sensor which is our ultimate goal.

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