Surface adsorption and bulk diffusion in metallic films sensed by resistivity change

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Adsorption of H_2 and CO on Nb, Co, Ni and Pd films was monitored by changes of the film resistance during the exposure to the gases. Films with thicknesses varying from 6 to 400 nm were deposited onto mica or sapphire substrates. The increase in resistance was measured near room temperature during exposure to 1000 Langmuir of either H_2 or CO. When the gas dosing was discontinued and the chamber was evacuated, the film resistance decreased until it reached its initial value. The change in resistance of very thin, rough Co and relatively thick, smooth Co, Nb and Ni films upon exposure to either H_2 or CO are comparable in magnitude. There is a relationship between this effect and surface roughness. The change in resistance is related to weakly adsorbed states of these molecules close to the surface. On the other hand, the change in resistance of thin Pd films is related to the diffusion of atomic hydrogen into the bulk of the films.

Keywords: Thin films; transition metals; resistivity; hydrogen; carbon monoxide

La adsorción de H_2 y CO por películas delgadas de Nb, Co, Ni y Pd fue estudiada por el cambio de resistividad que experimentaron estas películas cuando fueron expuestas a esos gases. Las películas con grosores que variaron entre 6 a 400 nm fueron depositadas sobre sustratos de mica o safiro. El cambio de resistividad fue medido a temperatura ambiente cuando las películas fueron expuestas a una dosificación de 1000 Langmuir de H_2 o CO. Cuando se cierra el flujo de gas y la cámara de vacío es evacuada, la resistividad de las películas vuelve a su valor inicial. El cambio de resistencia que experimentan película de Co, muy delgadas y rugosas, es de la misma magnitud que el cambio que experimentan películas de Nb, Co o Ni, mucho mas gruesas pero muy lisas, bajo la misma dosificación de H_2 o CO. Existe una relación entre este efecto de cambio de resistividad y la rugosidad superficial. El cambio de resistividad en estas películas está relacionado a estados superficiales de H_2 y CO debilmente ligados. Por otro lado, el cambio de resistencia en películas de Pd expuestas a hidrógeno está relacionado con hidrógeno atómico difundido en el interior de la película.

Descriptores: Películas delgadas; metales de transición; resistividad; hidrógeno; monoxido de carbono

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1. Introduction

There are some issues related to gas adsorption by surfaces that have not been extensively studied yet. One of these issues is the connection between adsorption and its effect on the electrical conductivity of the substrate. In the case of strong adsorption of gaseous molecules by metallic surfaces, it is reasonable to expect a modification of the surface electrical conductivity of the metal. Thus, studying changes in the surface conductivity of the substrate produced by gas adsorption might yield additional information of the adsorption mechanism. Since the surface and bulk contribute to the total electrical conductivity of the substrate, surface conductivity only becomes dominant when the substrate's thickness is reduced to small values. Such is the case of thin films. Consequently, an effect due to adsorption on the surface conductivity would be more readily detectable in a thin film than in a metal foil or single crystal.

On the other hand, the process of hydrogen absorptiondesorption by palladium and palladium alloys is well known. This metal or its alloys are excellent candidates for resistivity studies where the bulk properties of the films should dominate over surface effects when the film is exposed to hydrogen atmospheres. Due to these unique diffusion properties for hydrogen, Pd membranes are used in a variety of hydrocarbon catalytic processes although details of the basic mechanisms are not clearly understood and membrane failures is still a problem [1].

We have measured the hydrogen desorption spectra (TDS) of Pd, Pd alloys [2–4], Ni and Co foils [5] and found great differences between Pd and the other metals. The desorption of hydrogen from Pd implies bulk absorption, whereas in the case of the other metals the hydrogen is confined to the surface.

Shanabarger studied the adsorption of hydrogen on thin Ni [6, 7] and Fe [8] films from the surface resistivity change

of the films when the adsorption of hydrogen occured. Pick *et al.* [9, 10] and Strongin *et al.* [11] performed more careful experiments of H_2 adsorption in Nb films measuring change of resistance of the films. The change in the resistivity of the Nb films upon the adsorption of H_2 was similar to those observed by Shanabarger. Pick and Strongin developed an analytical expression to fit the resistivity data which is quite universal and which can be applied to absorption in the bulk of the film or absorption confined only at the surface of the film (adsorption).

The most plausible explanations of why the resistance of the metallic films changes when H_2 (or gas in general) is adsorbed or absorbed in it is the standard scattering of conduction electrons by impurities theory. In particular for surfaces, the Fuchs-Sondheimer model [12] hypothesizes that the surface adsorbed molecules increase the resistance of the film by increasing the diffusive scattering of specularly reflected conduction electrons from the gas-solid interface. This is assuming that the surface morphology of the film is perfectly planar. In the case of hydrogen absorbed in the bulk, the standard scattering of conduction electrons by impurities theory holds.

A larger resistance change in a Pd film exposed to H_2 is expected since Pd absorbs hydrogen in the bulk. In this case the scattering centers (hydrogen atoms dissolved in the bulk) will be located throughout the film and the resistance change of the film will not be only confined to the surface. The resistance change curve would carry kinematic information of the adsorption and/or diffusion of H in the film.

2. Experimental

Thermal desorption and resistivity were measured for Co, Ni and Nb films exposed to H₂ or CO in a modified AME-TEK (Thermox Instruments Division) system designed for gas analysis. The experimental chamber consists of a 6-way stainless steel cross (base pressure around 1×10^{-9} Torr) mounted on a pumping system, equipped with a sample manipulator, an Ar ion sputtering gun, a quadrupole mass spectrometer, a variable leak valve and a glass viewport. Change of resistivity of the Pd films exposed to H₂ was measured in a glass chamber at pressures between 1–20 Torr.

Samples of Pd and Co films were evaporated on mica substrates using physical vapor deposition (PVD): Pd films of 11, 30 or 54 nm thickness were evaporated onto pieces of mica of approximately $1.0 \times 1.0 \times 0.01$ cm dimension; Co films of 6, 15 or 30 nm thickness were evaporated onto mica. These samples were prepared in ultrahigh vacuum (UHV) and mounted on the manipulator of our testing system. For PVD films the procedure was the following: Once the paint for contacts had dried, the mica was masked with aluminum foil leaving an area of approximately 0.8×0.8 cm exposed where the Pd or Co films were deposited. The films were evaporated with a background pressure in the low 10^{-8} Torr and the film thickness was measured with a quartz thickness monitor within a 10% error.

Samples of 40, 200 and 400 nm films of Nb and 200 nm of Ni and 200 nm Co films ($\approx 0.9 \times 0.3 \text{ cm}^2$ area) sputtered onto 1×1 cm sapphire substrates [(0,0,1) orientation] were also prepared. The thickness of these films was determined from small angle XRD.

Pd and Co ingots and Nb, Co and Ni targets with a purity of 99.999 %, were used for the evaporation of the films.

The flat piece of mica or sapphire was painted at the ends of the face where the metallic film was located with a conductive paint in order to attach electrical contacts for the resistivity measurements. The conductive paint used was Loctite "Quick Grid" — an emulsion of small metal particles in ethyl acetate. Each side of the film where the conductive paint was placed, was spot-welded to a piece of insulated gold wire which was also spot-welded to a pin of a UHV feedthrough on the other end. The electrical feedthrough was connected to a Keithley MicroOhmmeter, model 580 to measure the resistance of the film. More details of this system can be found elsewhere [13].

The Pd films were also characterized by Transmission Electron Microscopy (TEM) using a Philips EM300 system [14]. Electron-transparent Pd films were obtained by thinning the mica substrate layer by layer until only the Pd films remained. Typically, Pd films of 500 Å were used for this characterization.

In order to clean the surface (for the experiments done in ultra high vacuum) the samples were subjected to two cycles of heating up to 450 K followed by Ar ion sputtering. Ar ion sputtering was carried out on a 1×1 cm² area with an ion current of 1 μ A for two minutes which removed less than 1 nm of metal. Assuming the absence of contaminants after this process, the samples were exposed to 1000 L (1L = 10^{-6} Torr×s) of hydrogen or CO at 320 K while the resistivity was measured. For each exposure, the cleaning cycle was repeated prior to the gas exposure.

3. Results and discussion

3.1. Surface resistivity change

The resistivity of the Co, Ni and Nb films increased during exposure to hydrogen or CO (at 320 K) and decreased to approximately the initial value when the gas was removed from the chamber. These changes were quite reproducible and a "saw-tooth" pattern was obtained for cycles of adsorption/desorption on films of different thicknesses.

Figure 1 shows the resistance change of a 40 nm (curve a) and a 400 nm (curve b) Nb films upon exposure to hydrogen. The films are exposed to hydrogen for times between 500 s and 1500 s in the graph. The gas is then turned off and pumped out of the chamber. When the gas is pumped out, the resistance decreases (times between 1500 and 2500 s). Fig. 2 shows the resistance changes of the same 40 nm (curve a) and 400 nm (curve b) Nb films when exposed to CO. In both figures, the maximum resistance change decreases 10 times for the 400 nm film with respect to the 40 nm film since this sur-



FIGURE 1. Resistance changes of Nb films when exposed to H_2 for 1000 s and after removal of the gas. (a) 40 nm; (b) 400 nm.



FIGURE 2. Resistance changes of Nb films exposed to CO for 1000 s and after removal of the gas. (a) 40 nm Nb film; (b) 400 nm Nb film.

surface effect decreases proportionally to the thickness of the films. The resistance change for a given film thickness is almost the same independently of whether the gas is CO or H_2 , indicating that there is no hydrogen diffusion in the film.

Figure 3a shows the resistance changes of 200 nm sputtered deposited (curve a)—and 6 nm—PVD deposited (curve b)—Co films when exposed to CO. One striking feature of this figure is that the resistance increase of a 200 nm—sputtered deposited—Co film under CO is almost twice as large as the resistance increase of the 6 nm—PVD deposited—Co film under the same amount of CO dosage. Nevertheless, we had expected to see a decrease in the resistance proportional to the ratio 6/200, since this surface effect decreases proportionally to the thickness of the film.

Figure 3b shows the resistance changes of 200 nm sputtered deposited—Ni film exposed to 3,600 L (curve a) and 1,000 L (curve b) of CO. The change of resistance of the 200 nm Ni film at 1000 L of CO is about 1/2 the change observed in the 200 nm Co film at the same CO exposure, indicating that CO is more readily adsorbed onto Co than onto Ni.

The resistance change of the film exposed to H_2 or CO can be fitted with an expression developed by Pick, Strongin *et al.* [9]. The analytical expressions which fit the data are the following:



FIGURE 3a. Resistance changes of Co films exposed to CO for 1000 s and after removal of the gas. a) 200 nm—sputtered deposited—Co film; b) 6 nm—PVD deposited—Co film.



FIGURE 3b. Resistance changes of 200 nm -sputtered deposited-Ni films exposed to CO for a) 600 s at 6×10^{-6} Torr and after removal of the gas and b) 1000 s at 1×10^{-6} Torr and after removal of the gas.

For resistance increase,

$$\frac{(1-b)^2\ln(1+y)}{2} - \frac{(1+b)^2\ln(1-y)}{2} - b^2y = at, \quad (1)$$

y is the normalized resistance change due to the surface adsorbed molecules: $(y = \Delta R / \Delta R_{\text{max}})$, t is time, and a and b are parameters obtained from the curve fit.

For resistance decrease,

$$2b\ln\left(\frac{y_o}{y}\right) + b^2(y_o - y) + \frac{1}{y} - \frac{1}{y_o} = at + c.$$
 (2)

In this case, there are two more constants to fit, y_o and c.

Typical data such as the one displayed in Fig. 1, Fig. 2 and Fig. 3 can be directly fitted with Eq. (1) for resistance increase and Eq. (2) for resistance decrease. This was done for resistance increase and the fit is displayed as solid lines for three curves shown in Figs. 2 and 3. In the three cases b = 3and a equal to 0.0005 s⁻¹ for 400 nm of Nb; 0.0026 s⁻¹ for 40 nm of Nb; and 0.0014 s⁻¹ for 6 nm of Co.

Pick *et al.* [9] related the constants a and b with physical parameters involved in the absorption process as follows:

$$b = \left(\frac{2\Gamma s_o}{N_s K}\right)^{1/2},\tag{3}$$

and

$$a = \frac{2\Gamma s_o}{N_s N_l x_{\max}}.$$
(4)

 Γ is the flux of H₂ molecules at a given pressure, impinging 1 cm² of metallic surface per second; s_o is the film sticking coefficient which in our case has a value near to 1; N_s is the number of metal atoms per cm²; N_l is the number of layers in the film; and K is the rate constant for absorption.

The rate constant follows an Arrhenius type of law:

$$K = K_o e^{-2E/RT}.$$
(5)

 K_o is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the temperature. The preexponential K_o has a value around 10^{13} [9, 10].

By combining Eqs. (3), (4) and (5), the following relationship is obtained:

$$\ln(K_o) - 2E/RT = \ln(N_l a x_{\max}) - 2\ln b.$$
 (6)

From Eq. (6), the desorption energy can be obtained using the fitting parameters a and b and it can be compared with TDS results. Values of desorption energy for CO on Co (which produced a resistance change in the film) agreed well with our TDS results on that system [5].

The resistance of metallic films decreases if the film smoothness increases [15, 16]. The "scattering hypothesis" [12] is the most appropiate model to explain these results. Within this model, surface roughness affects the total film resistance and thus adsorbed molecules only increase the fraction of scattering centers on the surface, which in turn cause diffuse scattering of conduction electrons. The effect of adsorbed molecules on film resistance would then be less pronounced for rough films than for smooth films, in agreement with our results.

Low angle XRD scans were taken for the films in specular and off specular arrangement [17]. In the case of Nb, Ni and Co films grown onto sapphire using a sputtering technique, the difference between intensities obtained in specular and off specular arrangement is more than 15 times indicating a very smooth surface. In the case of the Co films grown by PVD, there is no substantial intensity differences, indicating that the surfaces of these films are rough.

The main issue remaining is related to the length scales of the roughness. The adsorption-desorption of hydrogen or CO as sensed by resistivity measurements is possibly affected in a first order by the simple increase in the surface area of the films. This is directly related to the low angle X-ray diffraction measurements that were done to the films. Low angle X-ray diffraction detects roughness at a length scale of 50 nm which is larger than atomic length scales. Other research-



FIGURE 4. Resistance change of Pd films when exposed to different H_2 pressures: 11 nm thick at 2.5 Torr; 30 nm thick at 2 Torr; and 54 nm thick at 4 Torr.

ers [18, 19] had related surface roughness at length scales of $1-10 \ \mu m$ with changes in the resistivity of gas- covered silver films using visible and infrared radiation (wave length between 23 μm and 136 nm). All these results point out that there is definitely a connection between surface roughness at meso-scale and the resistivity increase due to the gas-covered surface.

3.2. Bulk resistivity increase

The films deposited by the PVD technique onto mica substrates are homogeneous, polycrystalline and free of defects as determined by TEM inspection [20].

The resistivity of the Pd film increased during exposure to H_2 and decreased to approximately the initial value when the H_2 was removed from the controlled atmosphere chamber. These changes were quite reproducible and a "saw-tooth" pattern was obtained for a cycle of absorption/desorption for films of different thicknesses. This resistance change as a function of time is displayed in Fig. 4 for Pd films of 11, 30 and 54 nm exposed to H_2 pressures of 2.5, 2 and 4 Torr, respectively. We tried to perform the experiments at a constant film temperature near room temperature but this varied between 291 and 307 K.

Pick *et al.* also related the resistivity increase in Nb films to the hydrogen concentration in the film. It can be easily demonstrated that the hydrogen concentration in the film is proportional to the square root of the H₂ pressure [9, 10]. The change in resistance (ΔR) is proportional to the atomic fraction x and this implies that the maximum change in resistance (R_{max}) is also proportional to the maximum atomic fraction of H, x_{max} . In this case y in Eq. (1) and Eq. (2) is the normalized atomic fraction of H in the bulk ($y = x/x_{\text{max}}$),

The resistance change of the Pd films increases until it reaches a saturation value. This saturation value is obtained when no more hydrogen is dissolved in the film. We plotted the relative resistance change at a saturation value as a function of the square root of the H₂ pressure for each Pd film studied. The curves of the relative resistance change as a function of the square root of the H₂ pressure overlapped for all the Pd films and it has a linear dependence on the $P^{1/2}$. A line obeying the following equation fits almost all the data:

$$(\Delta R_{\rm max}/R) \times 100 = 1.9 \times P^{1/2}.$$
 (7)

This is a strong indication that the resistance change in Pd is caused by hydrogen in the bulk (resistance change due to surface adsorption decreases inversely proportional to the film thickness). The data for the three Pd films start to deviate from the linear relationship at a value of 13 Torr due to complete saturation of the films.

The fit of the resistance increase using Eq. (1) was done and it is displayed as solid lines for the three curves shown in Fig. 4. In the three cases b = 1 and a is equal to 0.024 s⁻¹ for 54 nm; 0.043 s⁻¹ for 30 nm; and 0.056 s⁻¹ for 11 nm. We can calculate the activation energy for absorption using Eq. (6). From this calculation we obtained 8.9 Kcal/mole for the absorption results on the 54 nm Pd film and 8.8 Kcal/mole for the 11 nm film, in excellent agreement with our thermal desorption measurements of hydrogen from Pd foils [2].

A useful relationship for Pd made- H_2 sensors can be derived from the dependence of hydrogen bulk concentration and the resistivity increase of Pd films.

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- 1. J.N. Armor, Chemtech 22 (1992) 557.
- A.L. Cabrera, E. Morales, and J.N. Armor, J. Mater. Res. 10 (1995) 779.
- A.L. Cabrera, E. Morales, J. Hasen, and I. K. Schuller, *Cat. Lett.* 30 (1995) 11.
- A.L. Cabrera, E. Morales, J. Hasen, and I.K. Schuller, Appl. Phys. Lett. 66 (1995) 1216.
- A.L. Cabrera, W. Garrido, and U.G. Volkmann, *Cat. Lett.* 25 (1994) 115.
- 6. M.R. Shanabarger, Solid State Commun. 14 (1974) 1015.
- 7. M.R. Shanabarger, Surf. Sci. 44 (1974) 297.
- 8. M.R. Shanabarger, Surf. Sci. 52 (1975) 689.
- M.A. Pick, J.W. Davenport, M. Strongin, and G.J. Dienes, *Phys. Rev. Lett.* 43 (1979) 286.
- 10. M.A. Pick, Phys. Rev. B 24 (1981) 4287.

- M. Strongin, M. El-Batanouny, and M.A. Pick, *Phys. Rev. B* 22 (1980) 3126.
- G. Hohler, ed. "Surface Physics", Springer Tracts in Modern Physics, No 77, (Springer-Verlag, Berlin, 1975).
- A.L. Cabrera, W. Garrido-Molina, and U.G. Volkmann, Surf. Rev. Lett. 2 (1995) 159.
- 14. E.G. Silva, *Materials Characterization*, (Elsevier Science Publishing Co., Inc., 1993), Vol. 31, p. 83.
- G., Wedler, *Thin Metal Films and Gas Chemisorption*; editd by P. Wissmann, (Elsevier, Amsterdam, 1987), Sect. 5.3, p. 63.
- 16. E.Z. Luo et al., Phys. Rev. B 49 (1994) 4858.
- 17. A.L. Cabrera et al., Phy. Rev. B 55 (1997) 13999.
- C. Holzapfel, W. Akemann, D. Schumacher, and A. Otto, *Surf. Sci.* 227 (1990) 123.
- M. Hein and D. Schumacher, J. Phys. D: Appl. Phys. 28 (1995) 1937.
- 20. A.L. Cabrera and R. Aguayo-Soto, Cat. Lett. 45 (1997) 79.