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Resistance change of cobalt and niobium films when exposed to hydrogen and carbon monoxide

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The resistance of thin cobalt and niobium films was monitored during 1000 s exposures to hydrogen or carbon monoxide at a fixed pressure (10^{-6} torr) and also during their removal. Upon an adsorption-desorption cycle the resistivity changed in a ''sawtooth'' fashion, similar to the changes previously observed in niobium foils. The resistivity increase by the adsorbed gas seems to be directly related to weakly adsorbed states on the surface. The magnitude of the resistivity changes due to gas adsorption is related to the surface roughness of the film. [S0163-1829(97)02219-4]

I. INTRODUCTION

A strong surface adsorption of gaseous molecules is expected to modify the surface electrical conductivity. Since both the surface and bulk contribute to the total electrical conductivity of a solid, an effect due to surface adsorption is more readily detectable in a thin film. In particular, transition metals are excellent candidates for such studies. Most transition metals are good catalysts for the production of hydrocarbons from the reaction of H_2 with CO.[1,2] An important intermediate step for these reactions is the adsorption and dissociation of both molecular H_2 and CO on the surface. In general, two hydrogen chemisorption states (β_1 and β_2), and molecular and dissociated CO states are observed on the surface of transition metals.

Nickel, cobalt, and iron adsorb hydrogen on the surface with almost no diffusion into the bulk.[3–10] The adsorption of hydrogen and CO on polycrystalline Ni and Co surfaces[8–10] and single crystal Ni with different surface orientations[3,11,12] has been extensively studied.

Shanabarger studied the adsorption of hydrogen on thin Ni (Refs. 13 and 14) and Fe (Ref. 15) films by monitoring their resistance upon the adsorption of hydrogen. The low activation energies for desorption observed in these studies implies that this effect depends on the β_1 state. The fact that the resistance of the film is sensitive to this adsorption state and not to the higher energy one (β_2) implies that this effect is not related to an electron transfer mechanism.

Niobium allows some diffusion of hydrogen atoms[16] into subsurface sites (0.0028 atomic fraction). In this case, resistance changes have also been observed upon the absorption of H.[16,17] The inhibition or enhancement of hydrogen absorption by metallic overlayers has also been observed in this type of experiments.[18–20] Pd, on the other hand, is the only metal which absorbs hydrogen into the bulk in large quantities:[21] two H atoms for every four Pd atoms in the lattice (0.50 atomic fraction). Several theoretical models have been developed to explain the large bulk diffusion of hydrogen in Pd and its absence in Nb and Ni.[22–24]

Other studies have claimed that resistance increases due to surface adsorption of gases such as oxygen molecules on silver films.[25,26] Moreover, ultraviolet photoemission spectroscopy measurements on the O/Ag and O_2/Ag have shown that a π orbital of the adsorbed molecules is located above the Fermi level of the silver film where conduction electrons can be additionally scattered.[27]

Several explanations have been advanced to explain changes in film resistance with adsorbed gas. The Suhrmann model[28] claims that the molecular orbitals of a molecule located on the surface overlap with the conduction bands. The Sachtler model[28] hypothesizes an effective decrease in the thickness of the metal film when the molecules are adsorbed on the surface. A model based on the Fuchs-Sondheimer theory[28] hypothesizes that the surface adsorbed molecules increase the resistance of the film because they increase the diffuse scattering of electrons reflected from the surface. This assumes that the surface morphology of the film is perfectly planar. A refinement of this theory, known as ''the scattering hypothesis,''[28] is a more general case. In this model, surface roughness increases diffuse scattering, effectively making the relative effect of the adsorbed molecules on the resistivity smaller.

In this paper, we study the effect of H_2 or CO adsorption on the resistance of Co and Nb films. The resistance change in a 40 nm Nb film exposed to 1000 L of either hydrogen or CO is twice that for a 6 nm Co film exposed to the same dosage of CO. The film resistance increases monotonically with hydrogen or CO exposure and the absolute change after 1000 s of exposure decreases with increasing film thickness. These results imply that the difference in uptake is a direct result of the surface morphology since the adsorption kinetics in Nb is not much different from those in Co.

II. EXPERIMENT

Thermal desorption and resistivity were measured for Co and Nb films exposed to H_2 and CO in a modified AMETEK (Thermox Instruments Division) system designed for gas analysis. This consists of a six-way stainless steel cross (base pressure 10^{-9} torr) mounted on a vacuum system equipped with a sample manipulator, an Ar ion sputtering gun, a quadrupole mass spectrometer, a variable leak valve, and a glass viewport.

Gas evolution and resistivity measurements were performed on 40, 200, and 400 nm films of Nb (1.1×0.3 cm^2 area) sputtered onto sapphire substrates. The same type of experiments were performed on 6, 15, or 30 nm films of Co (0.9×1.2 cm^2 area) evaporated in ultrahigh vacuum (UHV) on mica. The Co and Nb sources used for the films were 99.999% pure. Elemental surface composition was monitored with Auger electron spectroscopy or x-ray photoelectron spectroscopy using a hemispherical analyzer (Physical Electronics, System 5100). Spectra in the 15 to 1000 eV energy range show typical surface C and O without any other impurity.

The crystal structure of the films was characterized with high and low angle x-ray diffraction (XRD) using a rotating anode x-ray diffractometer. Low angle XRD, performed in a medium-resolution configuration[29] using Cu K_α radiation ($\lambda = 0.15418$ nm), was also used to measure the thickness of some of the films. The thicknesses of the nominally 15 nm thick Co and 40 nm thick Nb films were 15.4 nm and 41.4 nm, respectively, thus confirming that the film thicknesses estimated from the quartz thickness monitor used during deposition were correct to within 5%.

Electrical contacts were attached to the films with a conductive emulsion of small metal particles in ethyl acetate (Loctite ''Quick Grid''). Two insulated gold wires were spot welded to the film, at the location of the conductive paint on one side and connected to pins of a UHV feedthrough on the other side. The electrical resistance of this configuration was measured with a Keithley MicroOhmmeter (model 580).

In order to clean the surface, the samples were subjected to two cycles of heating to 450 K followed by Ar ion sputtering. Ar ion sputtering was carried out on a 1×1 cm^2 area with an ion current of 1 μA for two minutes which removes less than 1 nm of metal. Assuming the absence of contaminants after this process, the samples were exposed to 1000 L (1 L = 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.

III. RESULTS AND DISCUSSION

The resistivity of the Co and Nb films increased during exposure to hydrogen of 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 ''sawtooth'' 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 film upon exposure to hydrogen. Between 0 s and 500 s the samples are in an UHV environment, and the data for these times represents the background measurement of the instrument. The films are exposed to hydrogen from 500 s up to 1500 s and then the gas is pumped out of the chamber. When the gas is pumped out, the resistance decreases (between 1500 and 2500 s).

Figure 2(a) shows the resistance changes of the same 40 nm (curve *a*) and 400 nm (curve *c*) Nb films and the resis-

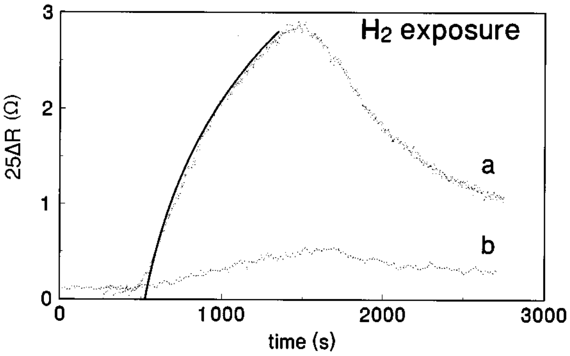

FIG. 1. Resistance changes of Nb films when exposed to H_2 (500–1500 s) and after removal of the gas. Curve *a*, 40 nm; curve *b*, 400 nm. Solid line for curve *b* corresponds to fits to Eq. (3.1).

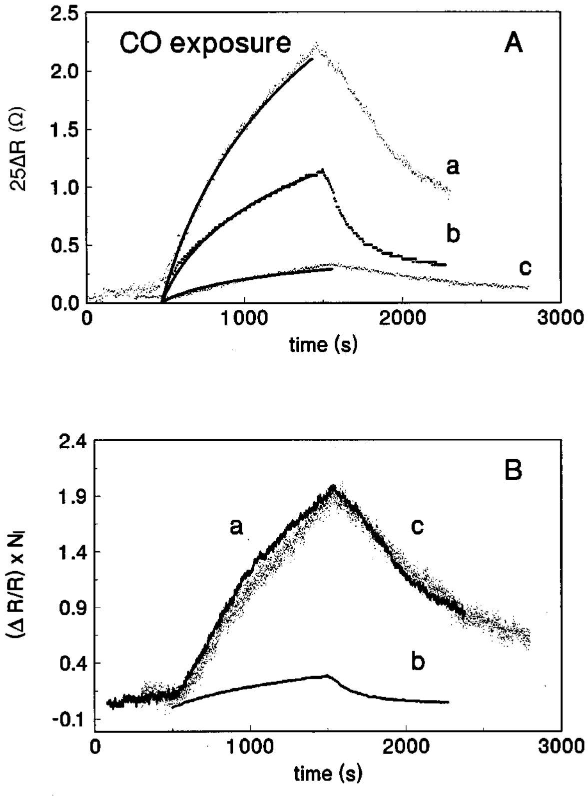

FIG. 2. (a) Resistance changes of Nb and Co films exposed to CO (500–1500 s) and after the removal of the gas. Curve *a*, 40 nm Nb film; curve *b*, 10 nm Co film; curve *c*, 400 nm Nb film. Solid lines for all the curves correspond to curve fitting using Eq. (3.1). (b) Normalized resistance change multiplied by thickness of film (N_l) in a number of layers. Curves *a*, *b*, and *c* correspond to the same samples as (a).

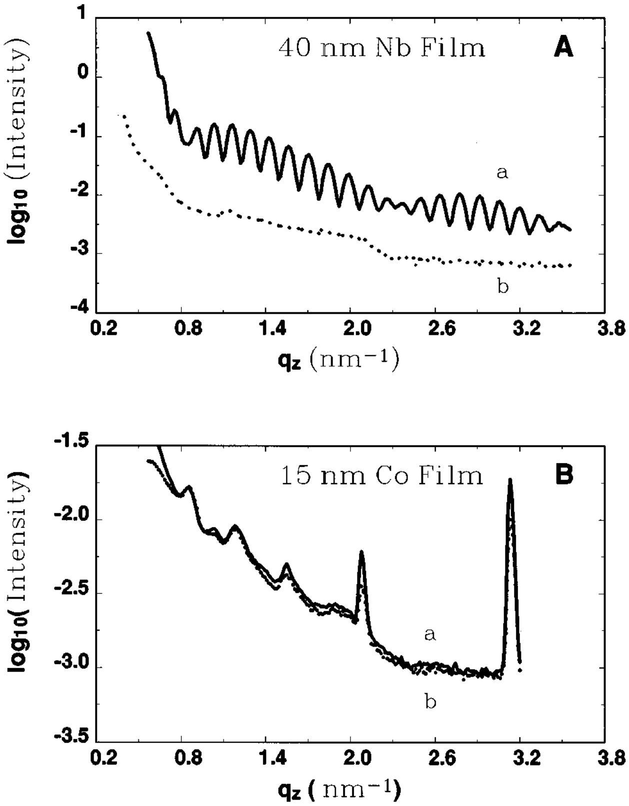

FIG. 3. Longitudinal ($\theta-2\theta$) x-ray reflectivity scans of the (a) 40 nm Nb and (b) 15 nm Co sample. Curve *a* represents the specular reflectivity and curve *b* the diffuse near-specular reflectivity. Note the low specular intensity of the Co sample with respect to the diffuse background.

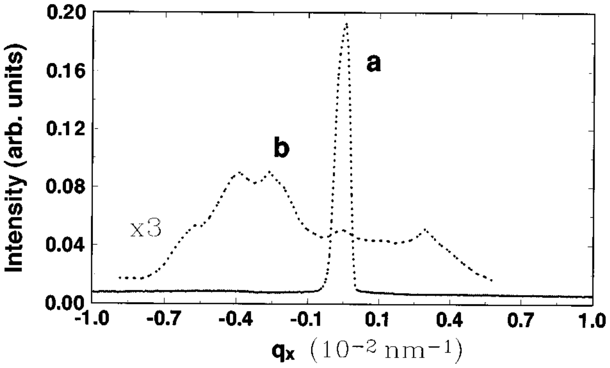

FIG. 4. Transverse scans ("rocking curves") for the Nb (curve *a*) and Co (curve *b*) samples. q_{zo}, as defined in the text, is 0.8535 nm^{-1} for Co and 0.9104 nm^{-1} for Nb. Note the low specular intensity of the Co sample with respect to the diffuse background.

tance change of 6 nm Co film (curve *b*) when exposed to CO. Again, before 500 s the samples are in an UHV, between 500 s and 1500 s the samples are exposed to CO, and after 1500 s the gas is pumped out.

Representative x-ray reflectivity patterns obtained from the Co and Nb films used in the adsorption experiments are displayed in Fig. 3. The x-ray intensities were normalized to the incident x-ray beam. Figure 3 shows longitudinal scans ($\theta-2\theta$) as a function of q_z, where q_z is the momentum transfer wave vector, both of the specular and near-specular diffuse intensities. The specular scans were obtained by aligning the surface so that the incidence angle α of the incoming radiation was identical to the angle of the detector β with respect to the surface ($\alpha=\beta$). The diffuse near-specular data were measured with $\alpha=\beta+0.1°$. The difference between these two intensities represents the *true* specular reflectivity, and is a measure of the surface height fluctuations due to the surface roughness.[30] If the *true* specular reflectivity is large, the surface height fluctuations are low.

In Fig. 3(a), the specular intensity of the Nb sample is much greater than the near-specular diffuse intensity throughout the entire q_z range. Conversely, the specular and near-specular diffuse intensities of the Co sample [Fig. 3(b)] are virtually identical over the entire range. Hence, the *true* specular reflectivity of the Co sample is almost zero (to within the experimental accuracy). This is a clear indication that the surface height fluctuations are much larger in the Co sample than in the Nb samples.

Note that in Fig. 3(a) the peaks in the 40 nm Nb sample scan represent the interference between the top and bottom surfaces of the film ("finite-size" peaks). These peaks are not visible in the scan which corresponds to the 400 nm Nb film because of the finite resolution of the diffractometer. For the Co sample [Fig. 3(b)], peaks appearing for $q_z<2.6$ nm^{-1} are "finite-size" peaks, while the sharp peak which appears at $q_z>2.6$ nm^{-1} is a diffraction peak due to the mica.

A further indication of the difference in surface morphology between the Nb and Co films are the transverse scans ("rocking curves") shown in Fig. 4. In these scans the position of the detector remains fixed while the sample is rotated so that $\alpha+\beta=2\theta$, where 2θ is the detector angle with respect to the incoming beam (which is a fixed). Transverse scans probe the lateral length scales of the roughness, since q_z is almost constant ($q_z\approx q_{z0}=4\pi\sin\theta/\lambda$) while q_x changes significantly [$q_x=q_{z0}\sin(\alpha-\beta)$]. The peaks away from $q_x=0$ for the Co sample, also known as "Yoneda wings,"[31] represent diffuse scattering from sections of the surface that are at the critical angle of reflection with respect to the incoming beam. A comparison of the Nb (curve *a*) and Co (curve *b*) transverse scans indicates that the specular intensity at $q_x=0$ with respect to the diffuse intensity at $q_x\neq 0$ of the Nb sample is much larger than that of the Co sample. The presence of a large diffuse intensity and "Yoneda wings" is generally considered a strong indication of large amounts of surface height fluctuations.[30,32] This is further evidence that the surface of the Co sample is much rougher than the surface of the Nb sample.

A quantitative analysis of x-ray reflectivity generally requires extensive numerical modeling. Quantitative analyses of low-angle x-ray reflectivity have been used to determine the surface and interface structure of various types of thin films,[33–35] liquid crystal polymer superlattices,[36] semiconductor superlattices,[37] and metallic superlattices.[38,39]

These analyses have shown that the reflectivity can be sensitive to the surface morphology at a lateral scale ranging from a few nm to several thousand nm. Also, note that the lateral coherence of the beam, approximately 50 nm,[40] which determines the lateral length scales over which the x-rays probe the surface, becomes on the order of thousands of a nm

TABLE I. Changes in the resistance of Co films of different thicknesses exposed to 1000 L of carbon monoxide at 335 K.

N_l (nm)	R (Ω)	ΔR (Ω)	$\Delta R/R$ ($\times 100$)
06	4.10	0.040	0.98
15	2.05	0.010	0.49
30	0.82	0.002	0.24

when projected on the surface at very low angles of incidence (measured with respect to the sample surface).

Qualitatively, the absence of ''true'' specular intensity in the Co sample's longitudinal scans, coupled with the large diffuse scattering intensity in the transverse scans, are strong indications that the Co films' surface is much rougher (i.e., has significantly larger height fluctuations) than the Nb films at the length scales probed by the x rays. Note that this lack of ''true'' specular intensity makes an accurate quantitative analysis of the Co sample almost impossible.

The resistance increase of the 6 nm Co films after 1000 L of CO exposure is approximately $40\times 10^{-3}\Omega$ (initial resistance is 4.1 Ω). This corresponds to a resistivity change of 0.98%. Results for the resistance changes of various Co films exposed to CO and various Nb films exposed to H_2 and CO are displayed in Tables I and II, respectively. A comparison of the relative resistance changes $\Delta R/R$ between the 6 nm Co film (0.98%) and the 40 nm Nb film (0.78%) indicates that the Nb film resistance reacts more readily during the adsorption of these gases if $\Delta R/R$ is normalized to the film thickness. Figure 2(b) shows $N_l \Delta R/R$, where N_l is the film thickness in number of atomic layers. Clearly, the data for the two Nb samples scale almost perfectly with the thickness, indicating that the surface characteristics of these films are similar. However, the data for the Co sample do not coincide with the Nb data, meaning that the parameters dominating the surface contribution to resistivity must be significantly different between Co and Nb samples.

Lauterbach *et al.*[41] have demonstrated, using Fourier transform infrared spectroscopy, that the CO desorption peak located at 378 K corresponds to *molecular* CO adsorption. The desorption energy for molecular CO was calculated from the thermal desorption spectroscopy (TDS) experiments and corresponds to about -4 Kcal/mol.[10] Since at 320 K (room temperature) the resistivity change is sensitive to the CO pressure and heating to higher temperatures is required to remove dissociated CO from the surface, we must assume that a molecular-adsorbed CO state is responsible for the resistance change.

Two phenomena could be responsible for the large differences between Co and Nb: (i) differences in adsorption kinetics or (ii) differences in the surface morphology. Although at this stage we cannot unequivocally rule out large differences in adsorption kinetics, this is not expected since sticking coefficients for adsorption of CO and H_2 in most transition metals are similar to within 10%.[42] The second possibility, that differences are due to surface morphology, is likely because of the x-ray reflectivity measurements presented above.

TABLE III. Curve fitting for Fig. 1 and Fig. 2 using Eq. (3.1) for the Nb and Co films resistance increase when exposed to hydrogen or carbon monoxide at 335 K. The parameter b is around 3 for all the curves. The parameter a^* was calculated from Eq. (3.2) assuming $s_0/x_{\max}=0.25$.

N_l		Carbon monoxide		Hydrogen	
(nm)	Metal	a	a^*	a	a^*
006	Co	0.0014	0.0225		
040	Nb	0.0026	0.0093	0.0044	0.0093
400	Nb	0.0008	0.0009		

The resistance changes of Nb films due to H_2 adsorption is related to the saturation of the β_1 state since normally this is a weakly adsorbed state. The changes in the resistance of the Co and Nb films upon hydrogen or CO adsorption are similar to those observed in Nb foils when exposed to hydrogen.[16,18] Interestingly, it has been claimed that Nb absorbs some hydrogen, but definitively no CO into the bulk, while Co does not absorb hydrogen or CO.[41] The resistance increase can be fit to the analytical expression developed by Pick,[16]

$$\frac{1}{2}(1-b)^2\ln(1+y)-\frac{1}{2}(1+b)^2\ln(1-y)-b^2y=at, \tag{3.1}$$

where y is the normalized resistance change ($y=\Delta R/\Delta R_{\max}$), t is time, and a and b are fitting parameters. The resistance increase for Nb and Co shown in Fig. 1 (hydrogen exposure) and Fig. 2 (CO exposure) is reasonably well fit by Eq. (3.1). These fits are displayed in both figures as solid lines. The parameters a and b obtained for the fit are listed in Table III.

The parameter ln(a) is related to the solution energy required for the gas to dissolve into the bulk and ln(b) to the surface chemisorption energy. In order to obtain accurate values of the desorption energy, $\Delta R_{\max}$ must be related to the absolute amount of gas dissolved in the bulk determined from an independent measurement. In our case, we have obtained relative values for a and b since we have not measured the amount of hydrogen dissolved in Nb under our experimental conditions.

TABLE II. Changes in the resistance of Nb films of different thicknesses when exposed to 1000 L of carbon monoxide or hydrogen at 335 K.

		Carbon monoxide		Hydrogen	
N_l (nm)	R (Ω)	ΔR (Ω)	$\Delta R/R$ ($\times 100$)	ΔR (Ω)	$\Delta R/R$ ($\times 100$)
40	11.5	0.090	0.78	0.110	0.96
200	6.5	0.030	0.46	0.030	0.46
400	1.6	0.003	0.19	0.004	0.25

According to Ref. 18, a is related to the flux of molecules (Γ) impinging upon the film surface, the initial sticking coefficient (s_0), the number of surface atoms (N_s) of the film, the thickness (N_l) of the film, and the maximum atomic fraction of gas dissolved ($x_{\max}$):

$$a = 2\Gamma s_0 / N_s N_l x_{\max}. \tag{3.2}$$

For our conditions, $\Gamma = 1.35\times 10^{15}$ (molecules/cm^2 s), since we keep the pressure and the temperature constant. Because the Nb lattice spacing is 0.164 nm and that of Co is 0.203 nm, there are about 30 layers in 6 nm of Co and 243 layers in 40 nm of Nb. Finally, assuming that $N_s = 1\times 10^{15}$ (atoms/cm^2) and $s_0 / x_{\max} = 0.25$ for both cases, we can calculate a theoretical value for a. This is denoted as a^* and also listed in Table III. Since we do not know the value of s_0 or $x_{\max}$, we chose a value of 0.25 for their ratio in order to see how a^* changes with thickness. The value chosen is such that a^* agrees with the value of a for the 400 nm Nb film.

The parameter b is given by the following equation:

$$b = (\beta/\nu) x_{\max}, \tag{3.3}$$

where β is the diffusion constant for gas entering the film and ν is the diffusion constant for gas leaving the film.

In our case, the fraction β/ν must be small since $1/x_{\max}$ should be very large (especially for CO because neither Nb nor Co absorb CO) so that the product of these two quantities is equal to 3, as found from a fit to Eq. (3.1). Assuming that the initial sticking coefficient s_0 for the adsorption of CO is similar for Co and Nb, the a parameter for the 6 nm Co film should be 2.4 times larger than for the 40 nm Nb film, based purely on kinematic effects, neglecting surface morphology. From Table III, we find the opposite result: a for Nb is about 2 times larger than for Co. To compensate for this effect, we must assume that the number of Co surface atoms exposed to the gas is 5 times larger than for the Nb surface. This supports our interpretation that the change in resistance due to surface adsorption is determined by the surface morphology.

Other possible factors which could affect the resistance changes can be ruled out. The polycrystalline nature of the Co films, which would expose grains with different surface crystallographic orientations, would not affect the CO nor hydrogen adsorption because the same adsorption states are observed for (110), (111), and (100) orientations in most transition metals.[9,10] Furthermore, for an fcc or hcp structure, the (110) or (100) surfaces have a jagged morphology, thus creating sites for gas adsorption. The large surface density of these sites makes the contribution of grain boundaries negligible. Therefore, the contribution of grain boundaries to the total resistance change of the film is also negligible.

In the event that some H atoms were to diffuse through the grain boundaries to the bulk of the film, the resistance change due to the resulting absorption would be much larger than what we observe, since this would contribute to the bulk resistance. This would also cause the resistance change to increase in proportion to the film thickness, since the number of scattering centers would be proportional to the volume of the film. Furthermore, neither Co nor Nb form hydrides under our experimental conditions.

In our case, the resistance change decreases as the film becomes thicker, indicating that this is a surface effect. In any case, CO diffusion through grain boundaries is highly unlikely for any metal due to the large size of the molecule. Moreover, the resistance change for Nb due to H_2 or CO adsorption are similar in magnitude, as is evident from Fig. 1 and Fig. 2(a), thus ruling out H diffusion through grain boundaries for these films. Hence, we conclude that the dominant factor which determines the magnitude of the resistance change is the surface morphology.

Previous research has claimed that the changes in resistance of a film are enhanced if the film smoothness increases.[26] Our results show that the resistance change in a 40 nm Nb film is comparable to the change observed on a 6 nm Co film exposed to the same quantity of gas. In view of these arguments, we conclude that the 40 nm Nb film is smoother in such a way that at least 5 times less surface area is exposed to the gas.

The ‘‘scattering hypothesis’’[22] is a convenient model to explain our results. Within this model, surface roughness affects the total film resistance and therefore 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 be less pronounced for rough films than for smooth films, in agreement with our results.

An important issue is related to the lateral length scales of the roughness. The adsorption-desorption of hydrogen or CO, as sensed by resistivity measurements, is possibly affected to the first order by the simple increase in the surface area of the films. This is clearly demonstrated by the x-ray reflectivity measurements, which detect the roughness at length scales ranging from a few nm to thousands of nm. The short, atomic length scale roughness is difficult to determine quantitatively for a surface of arbitrary roughness. In some limiting cases, such as flat surfaces with atomic scale steps, scanning microscopy can give excellent atomic resolution. However, in general the length scale of the roughness is determined by a convolution of the tip shape with the surface morphology, and a quantitative determination of the surface requires extensive numerical modeling.[43] Therefore, within the present framework we are unable to quantitatively determine the lateral length scale of the roughness, although we can qualitatively conclude that the Nb samples are smoother than the Co samples. In any case, the present results provide direct evidence for the connection between surface roughness and resistivity change due to the adsorption of gases in metals.

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