

Adsorbate-induced changes in the infrared reflectance and resistivity of metals

K. C. Lin and R. G. Tobin*

*Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University,
East Lansing, Michigan 48824-1116*

P. Dumas

*Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Centre Universitaire Paris-Sud,
F-91405 Orsay Cedex, France
and Laboratoire de Spectrochimie Infrarouge et Raman, CNRS, F94320 Thiais, France*

C. J. Hirschmugl

Department of Applied Physics, Yale University, New Haven, Connecticut 06520

G. P. Williams

National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

(Received 19 October 1992)

We present an experimental test of a predicted relationship between adsorbate-induced changes in the infrared reflectance and dc resistivity of a metal. We have measured the absolute change in reflectance for O and CO on Cu(100) and for CO on Ni(100) over the frequency range 300–2000 cm^{-1} and compared it with published resistivity changes for the corresponding thin-film systems. For the two adsorbates on Cu the results are consistent with a simple model based on scattering of conduction electrons by the adsorbate. For CO on Ni, however, the reflectance change is much smaller than predicted.

There has been considerable recent interest in adsorbate-induced changes in the broadband IR reflectance of metals, stimulated by the observations of Reutt, Chabal, and Christman¹ and Riffe, Hanssen, and Sievers² for H on W(100) and Mo(100), and especially by the measurements for CO on Cu(100) by Hirschmugl *et al.*³ These reflectance changes are too large and of the wrong sign to be explained simply by the dielectric properties of the adsorbate;⁴ they must be caused by adsorbate-induced changes in the electronic properties of the metal. For W and Mo, the reflectance as a function of frequency shows a definite minimum, which led to an interpretation in terms of an adsorbate-induced surface state. For CO on Cu(100), however, the spectral shape is largely structureless except for an asymmetric antiabsorption resonance assigned to the dipole-forbidden hindered rotation of CO.³

Persson has argued that the broadband reflectance change and the antiabsorption feature, as well as damping of the hindered rotation and the adsorbate-induced change in the resistivity of thin films, all rise from diffuse elastic scattering of conduction electrons by the adsorbate.^{5–7} We show below, however, that the relationship between reflectance and resistivity does not depend on the other, more speculative aspects of the model. We present an experimental test of this relationship by comparing our own reflectance measurements for CO on Cu(100), O on Cu(100), and CO on Ni(100), over a broad spectral range from 300 to 2000 cm^{-1} , with published resistivity data for similar thin-film systems. For CO and O on Cu, we find that the predicted relationship between reflectance and resistivity is confirmed, within the accuracy of the resistivity data. For CO on Ni, however, we find that the reflectance change is much smaller than expected.

The reflectance experiments were performed using the U4IR far-infrared beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. Details of the optics have been presented elsewhere.³ The light was *p* polarized and incident at an angle of 85° to the surface normal; these conditions are nearly optimal for the observation of reflectance changes due either to adsorbate vibrations or to changes in surface electronic properties.⁸ We used a Ge:Cu photoconductive detector sensitive to frequencies above 300 cm^{-1} . The Cu crystal was cleaned using Ne-ion bombardment at 500 K followed by annealing at 750 K, and the Ni crystal by a combination of ion bombardment at 600 K, oxygen treatments, and annealing to 1100 K. No surface impurity showed an Auger peak larger than 0.3% of the Cu 920-eV peak or 1.0% of the Ni 100-eV peak. For O on Cu(100), the coverage was determined from the oxygen Auger peak height, assuming a saturation coverage of 0.50 monolayer (ML) at room temperature.⁹ For CO on Cu(100) and Ni(100), the coverage was determined by temperature-programmed desorption and low-energy electron diffraction. The sample temperatures were 300 K for O on Cu(100) and CO on Ni(100), and 90 K for CO on Cu(100).

Synchrotron radiation is ideal for the absolute measurement of reflectance changes because the intensity is not subject to thermal fluctuations, but strictly proportional to the current in the stored electron beam.¹⁰ Before analysis, all spectra are normalized to the measured beam current. Figure 1(a) shows the fractional reflectance change $\Delta R_p/R_p$ for two successive spectra of a clean surface; the deviations from zero indicate the level of systematic error arising from such sources as uncertainty in the current and beam drift in the storage ring. Taking these uncertainties into account, we can determine

$\Delta R_p/R_p$ to an absolute accuracy of $\pm 0.2\%$.

Spectra (b)–(d) of Fig. 1 show $\Delta R_p/R_p$ for CO and O on Cu(100) and CO on Ni(100) over the frequency range from 300 to 2000 cm^{-1} . The spectral resolution was 6 cm^{-1} for O on Cu(100) and CO on Ni(100) and 16 cm^{-1} for CO on Cu(100); the data above 750 cm^{-1} have been smoothed to a resolution of 23 cm^{-1} . The noise at the higher frequencies and the absence of data in certain regions in spectra 1(a), 1(c), and 1(d) are due to the low transmittance of the polyethylene windows, which were selected to optimize sensitivity below 750 cm^{-1} . Cesium iodide windows were used for spectrum 1(b). The data for CO on Ni(100) are consistent with zero reflectance change (the fact that $\Delta R_p/R_p$ does not extrapolate to zero at zero frequency suggests that the apparent change of -0.2% is due to systematic error). For 0.4 monolayer (ML) CO on Cu(100), $\Delta R_p/R_p$ approaches zero at low frequencies and reaches a constant value of $-1.1 \pm 0.2\%$ above 1500 cm^{-1} . (This is consistent with a value of $-1.9 \pm 0.1\%$ recently measured at an incident angle of 87° by Borguet and Dai.¹¹) For 0.25 ML O on Cu(100), the reflectance reaches a minimum of $-1.1 \pm 0.2\%$ near 1500 cm^{-1} , and increases slightly at higher frequencies.

Persson attributes the reflectance change for CO on Cu(100) to diffuse scattering of conduction electrons by the adsorbate, and suggests that the same mechanism applies to a broad range of adsorption systems.⁵ [Scattering was also invoked² to explain surface absorption on W(100), but was subsequently rejected on the basis of the frequency dependence of the reflectance.¹] It has been known for many years that adsorbates increase the dc resistivity ρ of thin metal films,^{12–14} and there have been

several earlier attempts to relate both optical and resistivity measurements to scattering.^{15–17} We derive here a simple relationship between the IR reflectance and the dc resistivity, for free-electron metals, using the ideas of Ref. 5. Our derivation makes no reference to Persson's proposed relationship⁵ between the resistivity and the damping time of the adsorbate's hindered translation, the validity of which is in question.¹⁸ We emphasize that the relationship between resistivity and reflectance is very general; its only connection to the proposed models^{5,6} of frictional damping and antiabsorption resonances is that they all invoke electron scattering. While its refutation would call all the models into question, its confirmation can neither confirm nor negate these ancillary theories.

The calculation of surface effects on reflectance requires nonlocal corrections to the classical Fresnel formulas.^{19,20} The fractional change in the reflectance of p -polarized light due to a change in surface properties can be calculated using Feibelman's d -parameter formalism:¹⁹

$$\Delta R_p/R_p = -(4\omega/c)[\text{Im}(d_{\parallel})]/\cos\theta, \quad (1)$$

provided that $|\epsilon| \gg (1/\cos^2\theta) \gg 1$, with ϵ the complex (local) dielectric function of the metal, θ the angle of incidence, ω the frequency of the light, and

$$d_{\parallel} = \left[\int z(\partial\sigma_{\parallel}/\partial z) dz \right] / \int (\partial\sigma_{\parallel}/\partial z) dz. \quad (2)$$

Here σ_{\parallel} is the complex conductivity parallel to the surface for a uniform electric field, and z is the direction normal to the surface. (Because of strong refraction by the metal, the E field inside the metal is nearly parallel to the surface, even for p -polarized light at near-grazing incidence.⁸) We assume⁵ that $\text{Im}(d_{\perp})$ is negligible compared to $\text{Im}(d_{\parallel})$. The problem of finding the reflectance change therefore reduces to that of calculating $\sigma_{\parallel}(z)$.

Deep inside the metal, the conductivity simply has its bulk value σ_B . Near the surface, it is modified by the presence of adsorbates. These changes affect the electron current to a depth on the order of the electron elastic mean free path $l_B = v_F\tau_B$ (v_F is the Fermi velocity and τ_B the bulk scattering time). Persson⁵ proposes a slab model, in which the conductivity has a constant value $\sigma_s(\omega) = \sigma_B(\omega) + \Delta\sigma(\omega)$ from the surface to a depth l_B , and the bulk conductivity σ_B throughout the rest of the solid. When d_{\parallel} is calculated from this model, using Eq. (2), it follows that

$$\Delta R_p/R_p = [(4\omega l_B/c)/\cos\theta] \text{Im}[\Delta\sigma(\omega)/\sigma_B(\omega)]. \quad (3)$$

The conductivity of a film of thickness l_B in this model is simply σ_s , so if the adsorbate-induced change in conductivity of such a film is known, the reflectance change for the same adsorbate on a bulk crystal can be calculated.

It is appropriate to use a local description of the metal's dielectric response, provided that $\delta \gg v_F/\omega$, where δ is the classical skin depth;^{5,6} that is, the electric field should not vary appreciably over the distance traveled by an electron during one cycle of the electric field. For both Cu and Ni in the frequency range studied, the local response is well described^{21,22} by the Drude model,²² in which the bulk conductivity is given by

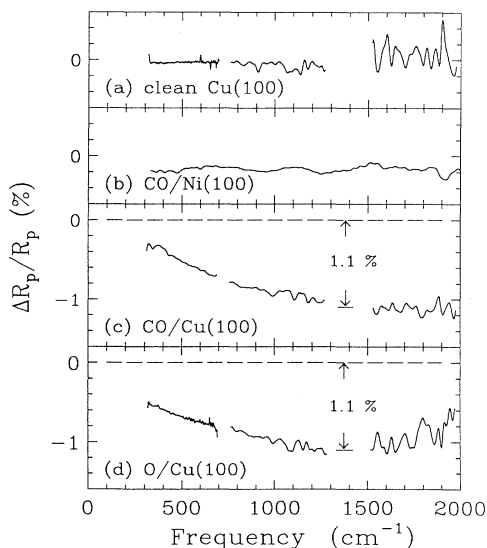


FIG. 1. Adsorbate-induced reflectance change $\Delta R_p/R_p$ from 300 to 2000 cm^{-1} . The gaps in spectra (a), (c), and (d) and the noise at high frequencies are due to absorption in the polyethylene windows. Cesium iodide windows were used for spectrum (b). The vertical scale is the same in all spectra. (a) Cu(100) with no adsorbate, indicating the level of systematic error. (b) 0.4 ML CO on Ni(100) at 300 K. (c) 0.4 ML CO on Cu(100) at 90 K. (d) 0.25 ML O on Cu(100) at 300 K.

$$\sigma_B(\omega) = ne^2\tau_B/m(1 - i\omega\tau_B), \quad (4)$$

where n is the conduction-electron density and m is the electron mass. The adsorbate can in principle affect both n and τ near the surface. We can expand $\Delta\sigma$ to first order in the changes Δn and $\Delta\tau$ in the electron density and scattering time, respectively:

$$\Delta\sigma(\omega)/\sigma_B(\omega) = (\Delta n/n_B) + [\Delta\tau/\tau_B(1 - i\omega\tau_B)]. \quad (5)$$

At zero frequency, both terms enter equally, but only the term in $\Delta\tau$ has an imaginary part that can give rise to a reflectance change through Eq. (3). (A second-order term in $\Delta n\Delta\tau$ has been used to model absorption by a surface state.^{1,2}) More detailed treatments^{16,17,22} lead to essentially the same conclusion.

If we assume^{5,12-14} that scattering dominates ($\Delta n/n_B \ll \Delta\tau/\tau_B$), then $\Delta\sigma(\omega)$ can be predicted from the change in the dc resistivity $\rho = 1/\sigma(\omega=0)$ of a film of thickness l_B . For $\omega \gg 1/\tau_B$, we find that

$$\text{Im}[\Delta\sigma(\omega)/\sigma_B(\omega)] = -(1/\omega\tau_B)[\Delta\rho(l_B)/\rho_B]. \quad (6)$$

In fact, we can use the dc resistivity change for a film of arbitrary thickness t , since it is well established experimentally^{12,14} that $\Delta\rho(t) \propto 1/t$. The reflectance change can therefore be written

$$\frac{\Delta R_p}{R_p} = -\frac{4l_B}{c\tau_B \cos\theta} \frac{\Delta\rho(l_B)}{\rho_B} = -\frac{4}{c\rho_B\tau_B \cos\theta} [t\Delta\rho(t)]. \quad (7)$$

Only the term $t\Delta\rho$ refers to the thin-film sample; all of the quantities in the prefactor relate to the bulk crystal. The reflectance change is predicted to be independent of frequency and proportional to $t\Delta\rho$. A microscopic scattering calculation by Watanabe and Hiratuka¹⁶ also found ΔR_p proportional to $\Delta\rho$.

For simplicity, we have derived this result assuming a frequency-independent scattering time τ_B , but the same equation is obtained if separate optical (τ_{op}) and dc (τ_{dc}) times²² are used, provided that the adsorbate contribution to the scattering rate is frequency independent. It is then the dc scattering time τ_{dc} that appears in the denominator. But $\rho_B\tau_{\text{dc}} = m/ne^2$ is a constant that depends only on the density of conduction electrons in the metal, so we can rewrite Eq. (7):

$$\Delta R_p/R_p = -(4ne^2/mc)(1/\cos\theta)[t\Delta\rho(t)]. \quad (8)$$

This is similar to, but more general than Eq. (40) of Ref. 5. It can also be obtained by combining Eqs. (41) and (49) of Ref. 5, but the present derivation avoids any assumption about the damping of adsorbate vibrations.

We attempt here to test Eq. (8), and by extension the scattering hypothesis, by comparing our IR reflectances with published data on thin-film resistivity changes. A similar comparison, for a single adsorption system, was used in Ref. 5 to lend support to the models proposed there. It would of course be preferable to make simultaneous reflectance and resistivity measurements on well-characterized films deposited *in situ*, but we were not equipped to attempt this difficult measurement. In Table I, we present the best available literature values for the resistivity change $t\Delta\rho$ (see below), our measured

TABLE I. Adsorbate-induced changes $\Delta R_p/R_p$ in the reflectance of p -polarized light at the adsorbate coverage n_a indicated, measured experimentally (see Fig. 1) and calculated from Eq. (8) using the indicated values of $t\Delta\rho$ for thin films of thickness t , the electron density n given in Table II, and an angle of incidence $\theta = 85^\circ$. See the text for discussion of the uncertainties in $t\Delta\rho$.

System	n_a (10^{14} cm $^{-2}$)	$(t\Delta\rho)$ (10^{-12} Ω cm 2)	$(\Delta R_p/R_p)_{\text{calc}}$ (%)	$(\Delta R_p/R_p)_{\text{exp}}$ (%)
CO/Cu(100)	6.1	0.60 ^a	-2.2	-1.1 \pm 0.2 -1.1 \pm 0.1 ^b
O/Cu(100)	3.8	0.42 ^c 0.70 ^d	-1.5 -2.6	-1.1 \pm 0.2
CO/Ni(100)	6.4	1.47 ^e	-5.8	-0.2 \pm 0.2

^aSee text.

^bReference 11, corrected for the difference in incident angles.

^cReference 13.

^dReference 23.

^eReference 24.

reflectance change $\Delta R_p/R_p$ at the reflectance minimum, and the reflectance change predicted from Eq. (8), using the values of n listed in Table II.

For O on Cu and CO on Ni, explicit plots of $t\Delta\rho$ versus coverage n_a are available in the literature.^{13,23,24} For CO on Cu, the shape of the coverage dependence $\Delta\rho(n_a)$ is quite reproducible,^{12,15,17} while $t\Delta\rho$ at saturation varies considerably. Wissmann^{27,28} reports an average saturation value of $t\Delta\rho$ (for ~ 50 measurements) of 1.5×10^{-12} Ω cm 2 for films annealed at 60°C , while a series of films annealed at room temperature gave values ranging from 1.1 to 2.6×10^{-12} Ω cm 2 .¹⁵ The effect of annealing temperatures higher than 60°C is unknown, as the films develop cracks.²⁸ To arrive at the value of $t\Delta\rho$ listed in Table I, we have scaled the coverage-dependence curves by Wissmann's average saturation value. Variable sample preparation and uncertainties about thickness and surface structure make all the values of $t\Delta\rho$ reliable only within about a factor 2, as the listed values for O on Cu suggest. Uncertainty also arises from the crystallographic orientation of the surfaces; the films are polycrystalline, but are believed to be predominantly of [111] orientation,¹² while (100) crystals were used for the reflectance measurements. This difference in orientation could affect the strength of electron scattering by the adsorbates.

For the two adsorbates on Cu, both $t\Delta\rho$ and $\Delta R_p/R_p$ are the same within experimental error. These results must be regarded as consistent with the model, even

TABLE II. Bulk material parameters for Cu and Ni. Values for n and v_F are calculated assuming one conduction electron per atom (Refs. 25 and 26). The (optical) scattering time τ_B and skin depth δ are taken from Drude parameters given by Ordal *et al.* (Ref. 21); the (optical) electron mean free path is given by $l_B = v_F\tau_B$. Frequencies in s $^{-1}$ have been divided by $2\pi c$ to convert to cm $^{-1}$.

Metal	n (10^{22} cm $^{-3}$)	τ_B^{-1} (cm $^{-1}$)	v_F/δ (cm $^{-1}$)	l_B (\AA)	δ (\AA)
Cu	8.5	73	310	1140	270
Ni	9.2	350	210	240	400

though the measured reflectance change is roughly a factor 2 smaller than predicted. A discrepancy of this size could be due to the simplicity of the model or to uncertainty in $t\Delta\rho$.

For CO on Ni, however, the predicted $\Delta R_p/R_p$ is nearly a factor 30 greater than the observed value. Uncertainty in n , inadequacy of the slab model, and deviations from the Drude approximation are not likely to account for such a large discrepancy—particularly since the agreement is much better for Cu. The disagreement cannot be assigned to a failure of the approximations leading to Eq. (8), even though the derivation requires $\omega \gg \tau_B^{-1}$ and v_F/δ , conditions that are only marginally met in our experiment. At 1000 cm^{-1} , $\omega\delta/v_F \approx 3$ for Cu, and $\omega\tau_B \approx 3$ for Ni (see Table II). The fractional correction to Eq. (8) due to these effects, however, is at most only $\sim 10\%$ [see Eq. (5) and Ref. 7]; these errors are much smaller than the uncertainty in $t\Delta\rho$, and are roughly the same for Cu and Ni. For Ni, unlike Cu, $l_B < \delta$; according to Ref. 5, this would render the d -parameter formalism invalid. But the formalism in fact requires only $|l_E| \ll \delta$, where $l_E^{-1} = (\omega + i/\tau_B)/v_F$.²⁹ For Ni above 1000 cm^{-1} , $l_E \approx v_F/\omega$, so this requirement simply reduces to the locality condition $\omega \gg v_F/\delta$ discussed above. To a good approximation, then, Eq. (8) should apply to both metals for frequencies above 1000 cm^{-1} .

It is possible that the reported $t\Delta\rho$ for CO on Ni is overestimated, for example, because the film was of nonuniform thickness; there are apparently no more recent experiments with which to compare. The discrepancy between theory and experiment is so large, however, that it suggests that for this system either scattering is *not* the dominant cause of the change in resistivity or the theory relating reflectance and resistivity is seriously incomplete. Changes in n have been invoked to explain thin-film resistivity changes due to surfaces, defects, and

adsorbates,^{12,30} and oxygen incorporated at grain boundaries in thin Cu films has been shown³⁰ to reduce n ; such a mechanism could in principle account for the small reflectance change. It seems premature, however, to speculate extensively on the origin of the discrepancy until more experimental data are available.

We have reported new measurements of changes in the broadband IR reflectance for CO and O on Cu(100) and CO on Ni(100), and compared them with the changes predicted from published thin-film resistivity measurements, using a simple model based on the scattering of conduction electrons by the adsorbates. For the adsorbates on Cu, the results are consistent with the model, but a large and unexplained discrepancy was found for CO on Ni. Uncertainties in the resistivity data, and doubts about the comparability of the thin-film and single-crystal surfaces, however, prevent a definitive and quantitative test. There is a clear need for more experimental work. Reflectance and resistivity measurements should be performed simultaneously on well-characterized samples, such as epitaxial films.

We thank Tamara Bush for assistance with the Ni data. It is a pleasure to thank B. N. J. Persson, W. L. Schaich, P. Wissmann, D. Schumacher, and E. Borguet for their insightful comments and criticisms and for providing results prior to publication. Research at the Brookhaven National Laboratory was performed under the auspices of the U.S. Department of Energy, Contract No. DE-AC02-76CH00016. C.J.H. was sponsored through Brookhaven Educational Programs Office. G.P.W. and P.D. thank the NSF and CNRS (France) for International Collaborative Award No. INT-9016771. K.C.L. and R.G.T. gratefully acknowledge support from the NSF under Grants Nos. DMR-8815616 and DMR-9201077.

*Author to whom correspondence should be addressed.

¹J. E. Reutt *et al.*, Phys. Rev. B **38**, 3112 (1988).

²D. M. Riffe *et al.*, Phys. Rev. B **34**, 692 (1986).

³C. J. Hirschmugl *et al.*, Phys. Rev. Lett. **65**, 480 (1990).

⁴R. G. Tobin, Phys. Rev. B **45**, 12 110 (1992).

⁵B. N. J. Persson, Phys. Rev. B **44**, 3277 (1991).

⁶B. N. J. Persson and A. I. Volokitin, Chem. Phys. Lett. **185**, 292 (1991).

⁷B. N. J. Persson, Chem. Phys. Lett. **197**, 7 (1992).

⁸Y. J. Chabal, Surf. Sci. Rep. **8**, 211 (1988).

⁹M. Wuttig *et al.*, Surf. Sci. **213**, 103 (1989).

¹⁰W. D. Duncan and G. P. Williams, Appl. Opt. **22**, 2914 (1983).

¹¹E. Borguet and H. L. Dai (unpublished).

¹²P. Wissmann, in *Surface Physics*, edited by G. Hohler, Springer Tracts in Modern Physics (Springer, New York, 1975).

¹³D. Dayal *et al.*, in *Thin Solid Films and Gas Chemisorption*, edited by P. Wissmann (Elsevier, Amsterdam, 1987).

¹⁴D. Schumacher, *Surface Scattering Experiments with Conduction Electrons*, Springer Tracts in Modern Physics (Springer, New York, 1993).

¹⁵U. Merkt and P. Wissmann, Z. Phys. Chem. Neue Folge **135**,

227 (1983).

¹⁶M. Watanabe and A. Hiratuka, Surf. Sci. **86**, 398 (1979).

¹⁷M. Watanabe and P. Wissmann, Surf. Sci. **138**, 95 (1984).

¹⁸R. G. Tobin (unpublished).

¹⁹P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).

²⁰W. L. Schaich and W. Chen, Phys. Rev. B **39**, 10 714 (1989), and references therein.

²¹M. A. Ordal *et al.*, Appl. Opt. **24**, 4492 (1985).

²²F. Abeles, in *Optical Properties of Solids*, edited by F. Abeles (North-Holland, Amsterdam, 1972), p. 93.

²³H. Buck *et al.*, in *Nichtmetalle in Metallen*, edited by D. Hirschfeld (DGM-Informationsgesellschaft, Wiesbaden, 1988), p. 219.

²⁴G. Wedler *et al.*, Z. Naturforschung **26a**, 1452 (1971).

²⁵N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976), p. 5.

²⁶W. A. Reed and E. Fawcett, J. Appl. Phys. **35**, 754 (1964).

²⁷P. Wissmann, Thin Solid Films **13**, 189 (1972).

²⁸P. Wissmann (private communication).

²⁹W. L. Schaich (private communication).

³⁰J. Vancea and H. Hoffmann, Thin Solid Films **92**, 219 (1982).