Study of Oxide Interlayers Formed
Reactively at a Silver-Electrolyte Boundary

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ABSTRACT

The differential reflectance of reactively oxidized versus unoxidized silver foils in aqueous potassium hydroxide has been measured in the 1.5 to 5 eV energy range. From these results the imaginary part of the dielectric constant of the oxide can be determined directly in the free-electron region of silver, and the zero-frequency interband contribution to the dielectric function of the oxide-covered metal can be estimated. The scattering contribution to the reflectance from the oxide surface nonuniformities is discussed.

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An often repeated approach to the study of the dielectric properties of a metal such as silver is to determine its complex dielectric function by use of reflectance or a form of ellipsometry from a very clean surface. Less systematic attention seems to have been given to examining optical behavior under just the opposite conditions; namely in the case in which the surface of the metal is purposely oxidized in a regulated way to examine the resulting changes on an otherwise uncontaminated surface. This approach is useful not only in elucidating the changes occurring to the optical properties of the metal, but also in examining related effects taking place during oxidation.

In this paper we describe differential reflectance measurements¹ made on matched pairs of thick freshly evaporated silver films immersed both in clean electrolyte (0.1 M KOH in water) and subsequently in air. Procedures similar to those used in studies of chemisorbed species at vacuum-solid² or liquid-solid interfaces³ or at semiconductor-oxide interfaces⁴ were used to measure the differential reflectance between oxidized and unoxidized foils.⁵ A liquid capacitive cell was constructed consisting of a platinum plate, a platinum ring used as a liquid plasma probe, and the silver film to be studied. The platinum plate contained a hole through which light was passed for normal incidence reflectance measurement on the silver. Controlled amounts of oxide adlayer could be added or subtracted from the metal foil by application of cell voltages such that open-circuit probe-film potentials of 0 to ~ 0.25 V were obtained. Beyond approximately this potential range, rapid oxidation of silver occurs leading to large reflectance changes.

A normalized differential reflectance spectrum typical of those observed is illustrated by curve A in Fig. 1. This curve shows the differential spectrum due to the oxide obtained under the condition when a voltage bias remains

applied. The observed reflectance changes develop in a matter of a few minutes after the cell voltage is turned on. The quantity $\Delta R/R$ then becomes approximately stationary during the minutes taken to record a given spectrum and is repetitive within this time scale. This quasi-equilibrated value of $\Delta R/R$ is an increasing function of the cell voltage at any given wavelength. Moreover, the size of the reflectance signal is approximately proportional to the integrated current which has passed through the cell. The monotonic rise of the spectral curve over the photon energy range in the free-electron region of the silver below the interband onset at ~ 3.8 eV will be examined below. An exception to this monotonic behavior is seen at the resonant dip labelled P, which is the surface plasmon resonance at the clean silver-liquid interface. The surface plasmon at the metal-liquid interface in the presence of the oxide is strongly damped in these measurements.

Reflectance curve B shows the residual signal remaining after the cell voltage has been removed, and curve C shows the same residue in air. The shift in the resonant surface plasmon dip P in this case can be explained by the approximate condition⁶ $\epsilon_{mR} = -n^2$, where ϵ_{mR} is the real part of the metal dielectric function. The refractive index n is that of the liquid in cases A and B and that of air in case C.

In Fig. 2 we have determined the imaginary part of the dielectric function of the interlayer ϵ_{aI} from the expression⁷

$$\frac{\Delta R}{R} = 4n \left(\frac{\omega}{c} \right) l \operatorname{Im} \left(\frac{\epsilon_a - n^2}{n^2 - \epsilon_m} \right) \quad (1)$$

For an interlayer with a rough surface the thickness l (assumed $\ll \lambda = 2\pi c/\omega$) may be reinterpreted as an average thickness.⁸ Below the Ag metal interband onset, $|\epsilon_{mR}| \gg \epsilon_{mI}$. Thus, Eq. (1) can be rewritten as

$$\epsilon_{aI}^t = \frac{c}{4\pi n\omega} \frac{\Delta R}{R} (n^2 - \epsilon_{mR}). \quad (2)$$

Using measured values for the real part of the metal dielectric function ϵ_{mR} ,⁹ we determine the quantity ϵ_{aI}^t for energies below the surface plasma resonance of silver. Using transmission and reflectance measurements on Cu_2O ,¹⁰ which is isomorphic to Ag_2O , and absorption measurements on low-pressure oxygen-plasma deposited Ag_2O and AgO ,¹¹ we estimate $\epsilon_{aI}^t \sim 7$. For case A in Fig. 2 this would give $t \sim 16 \text{ \AA}$ and yields a residual layer thickness in cases B or C of perhaps $\sim 4 \text{ \AA}$. Values for the average thickness can be determined for thicker layers in air by interferometric step-height measurements or in the liquid by examining the integrated cell current. The values thus obtained are approximately consistent with the present analysis. However, we emphasize that since the interlayers formed are not microscopically smooth but consist of distributions of nodules on the order of a micrometer in size, these latter measurements are subject to some uncertainty.

Because of the form of the reflectance for photon energies below the Ag surface plasmon energy, we may also study the properties of the silver underlayer directly using the differential reflectance measurements in curve A. Setting $\epsilon_{mR} = \epsilon_0 - \omega_p^2/\omega^2$, we may write Eq. (2) as

$$\frac{\omega}{\omega_p} \left(\frac{\Delta R}{R} \right)^{-1} = -\beta + \alpha \left(\frac{\omega_p}{\omega} \right)^2 \quad (3)$$

where $\alpha = c/4\pi n\omega_p^2 \epsilon_{aI}$ and $\beta = (\epsilon_0 - n^2)\alpha$. As shown for the oxide data of Fig. 3, this form fits the observed spectrum well, except for some resonant dips due to transitions in the oxide which modify ϵ_{aI} . The ratio of the intercept to slope in this curve yields $\epsilon_0 - n^2 = 2.75$ so that using $n = 1.35$ gives

$\epsilon_0 = 4.5$. In obtaining this curve we have used the unscreened plasma frequency¹² giving $\hbar\omega_p \approx 9.09$ eV as obtained from the metal data by Johnson and Christy.⁹ In the corresponding silver case the value obtained for ϵ_0 is 3.5. The zero-frequency d-band to Fermi surface contribution to the metal dielectric function is just $\epsilon_0 - 1$. The value of ϵ_0 obtained for the oxide-covered metal is higher than that of the metal because of the slight increase of ϵ_{aI} with frequency and also because in the region where ϵ_{aI} is most constant, the interband contribution to ϵ_{mR} is already felt resulting in a deviation from the Drude free-electron picture. This deviation is seen for ϵ_{mR} for the metal curve in Fig. 3 (arrow).

Significant changes are observed in the oxide differential reflectance in the spectra of Fig. 1 taken in liquid with and without an applied interfacial potential and in air. We tentatively believe these changes to be due primarily to scattering properties due to changes in surface layer roughness caused by oxide molecule structure or to possible compositional oxide phase modifications. Oxide electric-field effects in the liquid seem less likely to be highly contributory because most of the observed reflectance changes are not instantaneous with applied voltage changes.

In order to treat the scattering mechanism, we have carried out calculations using the same approximations as those leading to Eqs. (1) and (2) using an extension of a classical method described by Celli, Marvin, and Toigo.¹³ This determines s- and p-wave differential light-scattering rates from a weakly corrugated thin adlayer. In the limit that the size parameter of surface oxide nonuniformities or the transverse Gaussian correlation length $a \gg \lambda/2\pi n$, and in the limit of small rms oxide roughness ζ_0 , the integrated s- and p-wave scattering contributions become equal. The

scattering contribution to the reflectivity obtains a simple form which is

$$\Delta R_{\text{scat}} = 4\pi^3 \left(\frac{\omega}{c}\right)^3 \epsilon_0^2 a \frac{|\epsilon_a - n^2|^2}{(n^2 - \epsilon_{mR})^2} D\left(\frac{n\omega a}{c}\right) \quad (4)$$

when $|\epsilon_{mR}| \gg \epsilon_{mI}$. The tabulated function $D(x)$ is Dawson's integral.¹⁴

Inserting estimates for the various experimental quantities, we find that this contribution can yield a sizable share to the total differential reflectance. If we plausibly suppose that removing the cell voltage in case B leads to back reactions and oxide shedding tending to eliminate nodules smaller in size, then the resulting increased roughness could explain the enhanced ultraviolet reflectance changes in this case as compared to A. This tentative conclusion needs confirmation through scattering measurements. In the case of the air interface C the appearance of weak peaks in $\Delta R/R$ in the region near 2 eV may indicate the presence of some compositional interlayer changes in air in comparison to liquid. The discussion given here will be taken up in more detail elsewhere.

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Due to the conditions of formation the interlayer is thought to be predominantly Ag_2O ; however, the oxide composition is not determined. Fortunately our present analysis is rather insensitive to the nature of this oxide phase mixture because of the similarity of the optical properties of the most likely constituents in the frequency range of interest.
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FIGURE CAPTIONS

Fig. 1. Differential reflectance $\Delta R/R$ for slightly oxidized compared to unoxidized silver versus photon energy and wavelength at an Ag - 0.1 M KOH boundary. Shown are an equilibrated spectrum under an applied cell voltage (A), a spectrum of residual oxide (B) remaining at the metal-liquid interface after removal of the cell voltage, and (C) the same residual spectrum of the oxide in air. The surface plasmon resonance labelled P shifts in energy in this latter instance.

Fig. 2. Imaginary part of the oxide dielectric function ϵ_{AI} times the average thickness of the interlayer in cases A and B of Fig. 1 for photon energies in the near red and visible below the surface plasma resonance. Estimates of layer thickness are $\sim 16 \text{ \AA}$ in case A and $\sim 4 \text{ \AA}$ in case B (see text).

Fig. 3. Drude model fit of the quantity $\omega/\omega_p (\Delta R/R)^{-1}$ of a thin oxide on silver and of the real part of the metal silver dielectric function versus $(\omega_p/\omega)^2$. In the metal case ω_p is determined as $1.385 \times 10^{16} \text{ sec}^{-1}$ ($\lambda_p = 1360 \text{ \AA}$). The arrow shows the deviation of the free particle fit from the experimental data due to the Ag d-band onset.

Fig. 1

Fig. 2

Fig. 3