STUDY OF INHOMOGENEOUS SOLID ADLAYERS
AT ELECTROLYTE-SOLID INTERFACES
USING DIFFERENTIAL REFLECTANCE SPECTROSCOPY

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S. O. Sari
University of Arizona
Tucson, Arizona 85721

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ABSTRACT

Differential reflectance spectroscopy has been used to study interactions at liquid-solid and air-solid interfaces. This work is aimed toward examining a number of properties of adsorbed solid and molecular interlayers formed at such boundaries. Differential optical techniques have not previously been used to a large degree to investigate details of interfacial properties. However, in conjunction with x-ray and electron analysis these approaches are important for examining both electronic structure and adsorption-adhesion mechanics of surface coverings even if these are only a few atomic diameters in thickness. Such layers are induced in our experiments by electronic circuitry devised to add or subtract controlled amounts of adlayer through reactions at electrolyte-solid interfaces.

The purpose of the study is to supply new information of a basic nature concerning interfacial properties. This can be important since crystal phases of some materials exist only in thin surface coverings. Thus, a connection of this work may well be important to new thin-layer technology. Moreover, an important relation seems well established to problems in solar energy. It is known, for example, that interfacial layers modify gas evolution at some electrolyte-oxide boundaries and thus their study is closely relevant to improvement of some new fuel production schemes.

1. INTRODUCTION

This progress report describes some work carried out over the past half-year on a number of problems associated with interlayer properties at liquid-solid interfaces and air-solid interfaces. Some extensions to this work are also described. The approach used has been to produce very thin material layers at an electrolyte-solid boundary which are then examined optically. These interlayers are, of course, simply corrosion products. They can be examined both as they are formed in the liquid or later in air after production. This latter possibility allows us to proceed to some low-temperature spectroscopy which is essential for precise determination of adlayer electronic structure. A comparison may thus be made to band-structure calculations as they become available.

In our present work interlayers on silver have been formed utilizing the electrolytic reaction of hydroxyl ions on the metal surface yielding the reaction products of silver oxide and water in the electronic charge exchange. These procedures will be discussed in more detail below. However, we find generally that care must be exercised in ensuring a clean silver boundary in order to yield relatively uniform coverings. This is similar to procedures followed in related experiments at solid-vacuum interfaces,^{1,2} where cleanliness is essential. Under such conditions, however, the oxides formed are found to be inhomogeneous; that is, they have rough surfaces. Thus, as we will describe, some precautions not usually considered are necessary in analyzing our results.

In the case of the metal silver, a good deal of work has been done to determine optical constants on surfaces thought to be clean.^{3,4}

Moreover, an extended literature exists on oxidized surfaces in connection with studies of surface plasmon resonances.^{5,6,7} However, the point of view in some of these studies has quite properly been to de-emphasize the effect of the unknown oxide layer covering. However, here we proceed to intentionally oxidize clean surfaces to more closely examine previously ignored effects. Thus, we can provide an answer to questions concerning changes in metallic optical properties through intentionally adding a native surface oxide. At the outset a tentative conclusion concerning surface plasmons is the same as that of previous investigators^{5,8}; namely, that if the metal oxide added to the metal surface is absorptive, not only is the surface plasmon in the metal damped but also the shifted mode due to the oxide will be considerably broadened and thus be unobservable. This conclusion seems to be experimentally supportable though a more careful examination of small effects is desirable to understand small irregularities which appear in some of our spectra.

The adjoining problem of determining the dielectric properties of the surface covering on silver has formed a central aspect of this work. This procedure can be extended to other metals. To our knowledge, little systematic effort has thus far been given by previous workers to the problems we address. In the case of silver, the surface oxide is a semiconductor with an optically determined energy gap believed to be approximately 1.8 eV as will be discussed below. The oxide is expected to behave much like cuprous oxide for which more is known both experimentally⁹ and theoretically¹⁰ with regard to its optical and electronic structure. Thus, an indirect exciton series similar to that in Cu_2O may be apparent in our

adlayers. However, in order to determine this, it would be essential to obtain the low temperature behavior of the lines believed to form states of this hydrogenic exciton.

II. BACKGROUND AND RESULTS OF PRESENT WORK ON INTERLAYERS AT A SILVER-LIQUID INTERFACE

In the investigation completed prior to beginning differential reflectance experiments, the current-voltage behavior of a number of transition-metal oxides was examined in both acid and basic liquid solutions. It was found that oxides of foils of titanium and tungsten showed sizable enhancements of photoelectrolytic response to oxygen evolution.^{12,13} However, from the practical point of view, the necessity of using external voltage biases in order to observe enhanced oxygen evolution rates seems to limit the feasibility of such cells. In attempting to circumvent this difficulty one may consider fabricating series photoelectric-electrolytic cells¹⁴ or optimizing the choice of materials, such as by use of those with high electron affinity.¹⁵ Concurrently, one may ask to examine problems associated with surface gas formation, such as the question of competing interlayer formation. Reaction channels leading to such interlayers may be energetically more favorable than gas reactions in which case the solid rather than water is corroded. The reverse effect is desired in photoelectrolysis. Our motivation in the current approach has been influenced by such considerations, though it is now more obvious that the interface problem is a somewhat more multifaceted one. The metal-electrolyte boundary is chosen as a system which is, at least in principle, relatively uncomplicated for investigation. Moreover, this is a problem relatively well understood optically. Thus, we now proceed to examine some of our recent results.

The differential reflectance experiments carried out to date have used a new differential spectrometer constructed to accommodate dual silver-in-

liquid cells in such a way that one metal surface may be slightly oxidized in comparison to the other. A mechanically chopped light beam then alternately samples the dual surfaces in order to determine the differential reflectance. Figure 1 shows our particular optical arrangement in which asymmetries in reflecting components other than the surfaces under investigation will conveniently cancel.¹⁶ Synchronous detection and a signal averaging method allow us to directly measure the differential reflectance normalized by the average, $\Delta R/R$. This scheme yields baselines flat to less than 0.5% with carefully chosen samples over our present 1.5 to 5 eV spectral range. The sensitivity limit of this scheme is $\Delta R/R$ of approximately 0.5 to 1×10^{-3} for experiments in liquid. This limit is in agreement with those quoted for similar experiments at vacuum interfaces. We believe, however, that in the case of a liquid interface, this lower level may be set by physical fluctuations rather than by instrumental considerations. As observed at vacuum interfaces,¹ the presence of monolayers leads to reflectance changes that are a fraction of a percent. In some cases, spontaneous changes may occur which are fractions of this amount.

In the experiments analyzed below, we consider reflectance changes somewhat larger than this lower limit. These are a fraction of a percent to a few percent. The silver surfaces oxidized to yield these results appear "normal" when examined visually, showing no apparent change over unoxidized metal. More strongly oxidized surface films appear to have an azure blue haze.

The silver surfaces used consist of foils approximately 3000 Å thick. They are vacuum-evaporated onto cleaned glass microscope slides from tungsten boats containing metal having less than 10^{-5} parts of contaminant.

Fig. 1. Optical configuration in new differential reflectance spectrometer showing light exiting from monochromator slit, S, return reflected by middle mirror, M, and split by vibrational chopper, CH, to dual cells, C. Detection is at the photomultiplier, P.

Wire contacts are shock soldered to an edge of fresh films ready for use while mechanically shielding the surface to be optically exposed. Matched pairs of foils are obtained by pre-examining all films upon which experiments are to be performed. The electrolyte used in all experiments is pure KOH (0.1 M) in distilled water and thus contains approximately $6 \times 10^{19} \text{ cm}^{-3}$ OH^- ions. Cleanliness of both silver and electrolyte is necessary to insure macroscopically uniform oxide coverings although, as we will discuss, the layers formed consist of close-spaced small surface nodules of perhaps 10 μm to 20 μm in average size. Uniform wetting of the metal by clean electrolyte seems often to be an adequate indicator that relatively uniform oxide films can be produced.

To oxidize the metal a three electrode combination is used. This consists of the silver film to be studied, biased positively, a thin-wire platinum ring, and a platinum plate containing a hole through which light is passed. The thin-wire ring serves as a conventional plasma probe and allows a silver-electrolyte potential to be established for any given cell current. In order to yield reflectance changes caused primarily by oxide formation, voltage differences of 0.2 to 0.35 volts are applied. In this range the phase Ag_2O is expected to appear on silver.¹⁷ Within the voltage range quoted, reflectance changes of 0.2 to 0.3% can be observed for voltage changes less than 10^{-3} V .

By measuring the total charge transfer q at the interface, an estimate of the amount of reaction product formed can be obtained. The contributions

to q are

$$q = q_c + q_{\text{reac}} + q' \quad (1)$$

where q_c measures the contribution due to formation of charged screening layers due to ions in the liquid and of dipolar layers due to polar molecules in the liquid. These are capacitive effects which may be closely estimated in the potential screening limit ($V > kT$). The quantity q_{reac} is the total charge transfer due to reaction chemistry and q' measures whatever residual charge transfer occurs in the liquid through hopping conduction or elastic charge exchange reactions. Normally, $q' = 0$. The contribution of q_c is also normally smaller than q_{reac} . If the net charge transfer is considered, this latter quantity can be written as $q_{\text{reac}} = \int dt i$. Here i must be taken as the net current and includes both that due to forming the interlayer and also that due to back reactions which act to remove some of it. In the case of silver, assuming at Cu_2O structure, a reaction surface area of $2 \times 2 \text{ cm}^2$, and a known lattice constant of $4.71 \text{ \AA}$ yields approximately $1 \text{ mA} \cdot \text{sec}$ of charge transfer per average unit cell layer of oxide formed.

The differential reflectance contribution of a layer of thickness much less than a wavelength at an interface has been examined by a number of workers from alternative points of view.^{18,19,20} We have also examined this problem using a scattering formalism in which the adlayer is treated as a perturbation on the reflectance of an unperturbed boundary. These calculations yield the first order result at normal incidence that

$$\frac{\Delta R}{R} = \frac{8\pi nd}{\lambda} \operatorname{Im} \left(\frac{\epsilon^{(2)} - n^2}{n^2 - \epsilon^{(3)}} \right) \quad (2)$$

Here λ is the vacuum wavelength, d is the thickness of the interlayer, and n^2 , $\epsilon^{(2)}$, and $\epsilon^{(3)}$ are respectively the dielectric functions of the liquid, interlayer, and substrate. None of these calculations includes the effect of surface roughness. However, when roughness is included, the equation above remains approximately valid if the thickness d is reinterpreted as an average thickness. Thus, it will be used in the discussion of our present data. The effect of roughness will be considered in the following section.

Differential spectra obtained in the oxidation process are shown in Fig. 2. The three reflectance curves in the figure were taken at correspondingly increasing oxidation voltages at 0.2 V, 0.25 V, and 0.27 V, while these voltages remained applied. A monotonic growth of interlayer as a function of voltage is observed. This growth takes place within a few minutes after a voltage increase. Thereafter the oxide growth slows considerably so that the spectrum is nearly stable over the time (a few minutes) taken to obtain it. For spectra whose detailed shape dependence is important to our analysis, oxidation is carried out at a low voltage. After a given frequency scan, the spectrum can be repeated to confirm that it remains nearly stationary. The general monotonic rise of the differential reflectance curves versus photon energy is characteristic of most of the spectra examined. This rise continues in the free-electron gas region of silver below the plasma frequency until the interband threshold of the metal is reached. There is, however, a resonant dip in the spectrum near 3.30 eV due to the surface

Fig. 2. Differential reflectance versus photon energy for a very thin oxide adlayer formed on silver at an electrolyte-metal interface. Increased coverage is obtained at increased oxidation potentials.

plasmon at the silver-electrolyte interface. It is known to be the surface plasmon, since this peak can be made to shift energy by exchange of liquids.⁵ The observed resonance is not the surface plasmon mode in the oxide, however, but is simply that due to the silver metal in the unoxidized cell. A surface plasma resonance in the oxide is not generally identifiable as on the metal. It has been conjectured that it may be strongly damped by single-particle or other excitations as suggested by earlier oxide studies.^{7,8} A detailed examination of the surface plasmon behavior as thin oxide coverings are formed does not show a continuous frequency shift of this mode as is simply predicted and has been observed with magnesium fluoride coatings.⁵

In Fig. 3 we show another spectrum of differential reflectance. This is nearly the same as the previous spectrum with the exception that the differential reflectance due to the plasma resonance now is negative. The reason for this is that the surface plasmon resonance in the reference silver foil is considerably stronger (perhaps, due to increased surface roughness) than in the silver foil to be oxidized. Thus, for very thin oxide over-coverings a negative signal will be obtained. Features observed in the same spectrum near 1.8 eV (6900 Å) may be due to excitonic states in the interlayer, since they occur at the same energy as states observed in an earlier study by Gross.¹¹ However, caution should be emphasized in this initial interpretation until further experimental information has been obtained.

In order to analyze this spectrum we note that the imaginary part of the dielectric function in silver is small, that is, $|\epsilon_R^{(3)}| \gg \epsilon_I^{(3)}$. If

Fig. 3. Single differential reflectance curve of an adlayer on metallic silver at the metal-liquid interface. The silver surface plasmon resonance appears as the strong dip near 3.44 eV (3600 Å).

we now assume that the imaginary part of the adlayer dielectric function $\epsilon_I^{(2)} \gg \epsilon_I^{(3)}$ we may rewrite Eq. (2) as

$$\epsilon_{2I}d = \frac{\lambda}{8\pi n} \frac{\Delta R}{R} (n^2 - \epsilon_{3R}). \quad (3)$$

Thus, our optical measurement yields the product of the average layer thickness and the imaginary part of its dielectric function. The result above holds in the spectral region just above the absorption onset of the interlayer to that just below the surface plasma region and can be used to estimate the quantity $\epsilon_{2I}d$ directly. We have carried this out using measured values of ϵ_{3R} for metallic silver⁴ giving the result shown in Fig. 4. An optical gap of the oxide under the assumption that the peak near 1.8 eV is an exciton yields an energy gap of 1.85 eV. Above the free electron region in the interband region the form of $\epsilon^{(3)}$ contains both real and imaginary parts and thus another procedure, such as Kramers-Krönig inversion, is needed to extract the adlayer dielectric function. We should note that the absorption given is that of the oxide in the liquid under an applied voltage. In air and under no applied bias, results are similar, as noted below.

In order to determine ϵ_{2I} , the thickness must be measured independently. We have estimated the thickness of some films using interferometric step height measurements. Moreover, some confirmation of this approach can be obtained by measuring the total net charge transfer during deposition as remarked earlier. Unfortunately, both of these methods suffer from uncertainty, since the oxide layers formed are not smooth and since the estimate

Fig. 4. Absorptive part of the adlayer dielectric function times the average layer thickness obtained from the data of Fig. 3 using measured optical constants of pure silver. The peak near the absorption onset near 1.8 eV may be an exciton band (see text). Absorption data are not obtained in the surface plasmon region beyond approximately 3.1 eV.

depends on the shape of irregularities which are formed on the metal surface. However, within this limitation all measurements appear to be approximately consistent. If we re-examine Fig. 4 we see that in the plateau region $\epsilon_{2I}d$ is approximately $75 \text{ \AA}$. Since ϵ_{2I} is also unknown it is perhaps convenient to estimate this quantity to see if the value of d obtained by this method is again consistent with the measurements described above. We may approximately do this by comparing Ag_2O to its isomorphic counterpart Cu_2O for which more is known, since crystals of this latter semiconductor are more readily available. Since silver is a heavier atom than copper there is expected to be a general downshift in energy of most of the states when comparing the first oxide to the second. Using transmission and reflectance data on wafers of Cu_2O ⁹ we may estimate $n \approx 3$ and $K \approx 2$ for Ag_2O , which would give $\epsilon_{2I} \approx 10$. Thus $d \approx 8 \text{ \AA}$. From estimates of fractional coverage and thickness of nodules formed this seems to be in accord with thickness and current measurements.

The relative lack of features of the oxide from 2 to about 3 eV suggests that the present oxide layer measurements can also be used to extract information concerning the silver metal underlayer directly. To see this we proceed first to reconsider the optical constants of the pure metal. The data of Johnson and Christy⁴ for the real part of ϵ are replotted in Fig. 5 as a function of $(\omega_p/\omega)^2$. Since ϵ_R may be written as

$$\epsilon_R = \epsilon_0 - (\omega_p/\omega)^2 \quad (4)$$

we may determine the intercept ϵ_0 as -3.5 and the slope as $\hbar\omega_p \approx 9.1 \text{ eV}$ ($\lambda = 1360 \text{ \AA}$). This gives the unscreened plasma frequency. The ordinary zero-frequency d-band contribution to ϵ_R is just $\epsilon_0 - 1 = 2.5$, which is in approximate agreement with earlier estimates of this number.²¹ However, we

Fig. 5. Real part of the dielectric function ϵ_1 of metallic silver showing fit to the free-electron Drude model. The deviation in the measured points from the linear extrapolation for $(\omega_p/\omega)^2 \leq 15$ is due to interband d to s-p Fermi surface transitions in the metal.

notice a deviation of the measurements of ϵ_R from Eq. (4) for energies higher than about 2.5 eV. This means that the interband onset is felt quite far into the free-electron region.

If we now rewrite Eq. (3) using Eq. (4), we can obtain the form

$$(\omega_p/\omega) (\Delta R/R)^{-1} = -B + A (\omega_p/\omega)^2 \quad (5)$$

where $A = c/4n\omega_p d\epsilon_{21}$ and $B = (\epsilon_0 - n^2)A$. Here ω_p is again taken as the unscreened plasma frequency as determined from metallic silver data. Thus, the ratio of the intercept to the slope of the form above may be used to determine ϵ_0 from our oxide measurements. The plot given in Fig. 6 yields $A = 0.4$ and $B = 1.1$. Thus $\epsilon_0 - n^2 = 2.75$ so $\epsilon_0 = 2.75 + 1.82 = 4.75$. This number is an over-estimate. The reason is that the low energy tail of the interband contribution modifies our fit, much as observed in the free metal case. Moreover, the oxide is only nearly uniformly absorbing in the energy region where the interband contribution is already high. As an added point, the deviations from linearity in the slope of Fig. 6 may be seen to be due to optical structure in the adlayer.

The earlier remark of the similarity of layers formed under application of a potential and those "residual" layers left after removal of the potential may be examined in Fig. 7. This residual is probably due to the fact that the oxidation reaction forming the initial oxide interlayer is not entirely reversible. If this process were completely irreversible, the observed effect could also be due to small surface nodules which become detached from the metal after removal of the applied voltage. Other effects

Fig. 6. Spectral fit of the differential reflectance of an oxide-covered metal surface to the Drude model. The intercept yields the interband contribution to the metal reflectivity, but the result given is an over-estimate (see text). Dips in the experimental curve are due to adlayer electronic structure giving resonant dips.

Fig. 7. Differential reflectance versus photon energy for an adlayer showing residual layer reflectance in the liquid. The air residue is similar.

in either the liquid adjoining the oxide or in the adlayer itself could also be contributory causes. These possibilities have yet to be investigated. In any case, about a quarter of the original signal is observed in the residue. The determination of the properties of this residue forms part of the work now in progress.

III. PROPOSED EXTENSIONS INCLUDING LIGHT-SCATTERING FROM INTERFACES

A number of avenues can be followed which we believe will lead to fruitful results. In working with silver and silver oxide, it is necessary to examine changes which may occur in the interlayer over times long compared to the period of initial formation. This may include phase changes in the interfacial solid which would be expected to lead to modifications in its optical structure. Moreover, in examining the liquid-metal boundary, some effort is desirable to determine whether residual interlayer components in the liquid are formed simultaneously with electrolytic action. Low-temperature optical experiments on the residue oxide will be carried out to obtain more detailed information on the band-structure related electronic states of these very thin reaction products. The hydrogenic exciton series, which may appear just above the fundamental gap, forms an important problem for further investigation. It is believed that information obtained from study of resolved lines, if they truly exist, could yield information about symmetry of the oxide surface nodules, structural properties of the oxide semiconductor, charge screening in the layer, and related properties. In addition, extensions to adlayers on other materials, such as other noble metals, would form an important addition to this work. These activities would be expected to carry this work through well into the second year of the effort under way.

We also wish to emphasize the conjugate problem presently under consideration of complementing our reflectance experiments with light

scattering measurements. This aspect was emphasized in some initial laser experiments in previous work and now merits continuation using multi-line lasers in a new experimental configuration.

Some conceptual motivation for this portion of this work should be given. It is well known that a uniform and smooth surface simply reflects light with no scattering. This is ensured due to translational invariance along the plane of the surface, or alternatively, by noting that there is no way to couple momentum from the incident light beam to a direction parallel to the surface to give scattering. However, for a surface consisting of corrugations there is a contribution to the direct backward light-scattering amplitude (reflection coefficient) due to both absorption and to scattering of light from the boundary irregularities. In this more general sense we may write the total differential reflectance $\Delta R/R$ as the sum of the contribution given previously by Eq. (2) plus a new contribution due to the scattering. This second contribution is the scattering component due to roughness and can be written as

$$\left(\frac{\Delta R}{R}\right)_s = \frac{1}{R} \int d\Omega \left(\frac{dp^s}{d\Omega} + \frac{dp^p}{d\Omega} \right). \quad (6)$$

In the previously given analysis this contribution to the differential reflectance has been assumed small, but it would be desirable to examine this effect in greater detail. The best means of achieving this result would be to examine the differential scattered power at several laser frequencies as a function of angle. A comparison to the backward scattered intensity could then be made using Eq. (6). Both the s-wave and p-wave scattering

components have been derived using the Rayleigh-Fano method^{22,23} and for a very thin adlayer may be written as

$$\frac{dp^S}{d\Omega} = \frac{n^4}{\pi^2} \left(\frac{\omega}{c}\right)^4 g\left(\frac{n\omega}{c} \sin\theta\right) \cos^2\theta \sin^2\phi \frac{|\epsilon(2) - n^2|^2}{(n^2 - \epsilon_R(3))^2} \quad (7)$$

$$\begin{aligned} \frac{dp^P}{d\Omega} = & \frac{n^4}{\pi^2} \left(\frac{\omega}{c}\right)^4 g\left(\frac{n\omega}{c} \sin\theta\right) \cos^2\theta \sin^2\phi \left(\frac{n^2 \sin^2\theta - \epsilon_R(3)}{n^2 \sin^2\theta - \epsilon_R(3) \cos^2\theta} \right) \\ & \cdot \frac{|\epsilon(2) - n^2|^2}{(n^2 - \epsilon_R(3))^2} \end{aligned}$$

where $g(\vec{G}) \equiv \int d\vec{p} e^{i\vec{G} \cdot \vec{p}} \langle\langle \zeta(\vec{R}) \zeta(\vec{R} + \vec{p}) \rangle\rangle$ is the Fourier transform of the roughness correlation function. The function $\zeta(\vec{R})$ measures the surface topography. These expressions represent a generalization of earlier work,^{23,24} which has not been concerned with interlayer effects.

Thus a scattering experiment forms a useful adjunct to the reflectance measurements already in progress in yielding information on the surface correlations introduced above. As an example, we anticipate that as the oxide clusters on the silver nucleate, the time evolution of the distribution of scattered light from the surface would change markedly. Hence, observation of this effect would provide additional valuable information on the mechanics of the time evolution of the interlayers studied.

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