Electromodulation of the Optical Properties of Gold

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When a strong electric field is applied to the surface of a thin gold-film electrode in contact with aqueous electrolyte, we observe a change in the attenuated total reflection (ATR) spectrum of as much as 7%. The change was measured as a function of photon energy, angle of incidence, polarization, and electric field modulation frequency. It is shown that this effect is due to changes in the optical properties of the gold and not to changes in the electrolyte. The peak in this derivative ATR spectrum is at 2.5 eV, where the optical properties of gold are changing most rapidly with frequency. The effect is quantitatively explained by a shift in the optical constants of gold due to the change in electron concentration.

I. INTRODUCTION

In the last few years, modulation techniques have been employed in which the optical properties of solids have been perturbed periodically by the application of a strong electric field. The resulting change in reflectance or transmittance can then be observed by phase-sensitive detection techniques. These electroeffects have been observed in many semiconductors[1] with consequent rich spectral detail. It is of great interest to know if similar effects exist to a measurable extent in metals.

Feinleib[2] observed a change in near-normal reflectance from gold contained in salt water. The gold formed one electrode of a cell across which a modulating voltage was applied, and the resulting change in reflectance was recorded as a function of photon energy. The source of the effect was unclear, but one suggested explanation[2,3] was that it was due to modulation of the refractive index of the solution contracting the gold. It has been shown[4] that this cannot be the case, but that modulation of the optical properties of a thin surface layer of the gold can account for Feinleib's observations.

From free-electron theory the plasma frequency in a metal is given by[5]

$$\omega_p = (4\pi n e^2/m)^{1/2}, \qquad (1)$$

where n is electron concentration, e is electron charge, and m is the mass. The contribution to the dielectric constant made by the free electrons at a frequency ω is given by[5]

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau}, \qquad (2)$$

and at frequencies of concern in this paper (about 1 eV and greater) a change in ω_p by a certain amount simply shifts the entire $\epsilon(\omega)$ curve by a corresponding fractional amount along its frequency axis. Therefore, if the free-electron concentration is modulated, the plasma frequency ω_p of the metal and its optical constants will also be modulated. In fact, the Fermi energy itself will be modulated, and this will affect interband transitions involving the conduction band. But it is expected that the bound electrons will be essentially unaffected. If the contribution to the dielectric constant from interband transitions is either constant with free-electron concentration in the frequency region of interest, or varies in a way similar to the contribution of the free electrons, the optical constants of the metal will simply be shifted on the frequency axis by the same fraction that ω_p is shifted. Based on this simple model some numerical calculations made by us indicated that the change in reflectance near 2.5 eV of bulk gold or a thin gold film can be measured readily if n in the first 50 Å is changed by as little as 1%, or if an equivalent number of electrons is removed or added with rather arbitrary distribution in the first 100 Å or so of the surface region.

The simple model discussed above in which the optical spectra are simply "shifted" may be especially applicable to gold, silver, copper, and the alkali metals. But it is expected that any metal can have its optical properties electromodulated.

Here we investigate experimentally the case of a thin gold film. The results are remarkably consistent with this simple theory. They show beyond doubt that the optical constants of the metal itself change with applied electric field. They also introduce a new method of observing derivative spectra. Since the beam approaches the semitransparent gold film from the back side at angles beyond critical from an optically dense phase, perhaps the experimental method should be called electro-ATR (ATR is the accepted abbreviation for "attenuated total reflection").

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[1] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).
[2] J. Feinleib, Phys. Rev. Letters 16, 1200 (1966).
[3] Reference 1, p. 697.
[4] Arnold Prostak and Wilford N. Hansen, Phys. Rev. 160, 600 (1967).
[5] Charles Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., pp. 227 ff.

II. EXPERIMENTAL

A. Experimental Setup

The gold-film electrode used was prepared by evaporating gold onto a glass plate to a thickness of about 50 Å. It was obtained from Liberty Mirror Div., Libbey-Owens-Ford Glass Co., Brackenridge, Pa., by special order, and the glass was first coated with a very thin layer of material to bond the gold to the glass and to give a uniform spreading of the gold. The electrical conductivity and optical constants of the resulting thin gold film were similar to those of bulk gold.

The gold was in contact with aqueous 0.1 M Na_2SO_4 solution in an electrochemical cell and was observed spectroscopically by internal reflection from the glass side. When only a single angle of incidence was desired, the setup described by Hansen, Kuwana, and Osteryoung[6] was used, except that the counter electrode had a separate compartment. This allows for multiple reflections in a very simple way with consequent gain in sensitivity. In the present case, we used five reflections at 72° internal angle of incidence. For measurements as a function of angle of incidence, a somewhat smaller cell was used with its glass plate optically contacting the sample face of the variable-angle reflection unit described by Hansen.[7] Each gave sufficient sensitivity for accurate measurements. Conventional phase-sensitive detection techniques were not used. Reflectance measurements were made with a Cary 14-R spectrophotometer equipped with polarizers. A standard absorbance slidewire [absorbance is $\log_{10}(I°/I)$, where $I°$ and I are the two light intensities being compared, and a standard slidewire reads 0–2.0 absorbance] was used with multiple reflections, and an expanded slidewire (0–0.2 absorbance) was used when one reflection only was involved.

Standard electrochemical techniques were used. A standard reference electrode (saturated calomel electrode, abbreviated SCE) was placed near the gold and the potential of the gold was modulated as desired, using a potentiostat. In the case of rapid modulation of the potential, the chopper motor of the spectrophotometer was stopped, and the output of the phototube was displayed on a dual-trace oscilloscope along with the gold potential. Any phase shift and/or intensity variations with modulation frequency were easily observed using this technique.

B. Observed Field Effect

When the potential of the gold-film electrode was cycled within a potential range that avoided Faradaic effects, the reflectance was found to vary with the applied potential in a reproducible way. The top curve of Fig. 1 shows the magnitude of the effect as a function of photon energy for 72° angle of incidence and a
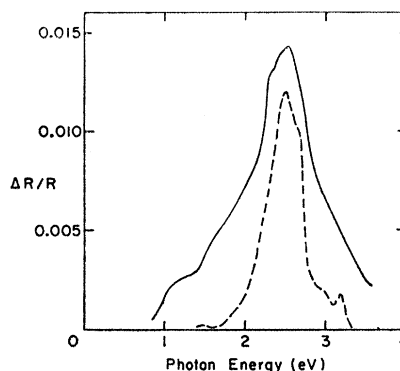

FIG. 1. Observed (——) and calculated (– – –) electric field induced changes in the attenuated total reflection (ATR) spectrum of a gold film, for perpendicular polarization at 72° internal angle of incidence. The potential sweep was from 0.035 to 0.72 V versus SCE for the observed curve. The calculated change assumed a shift of 0.1 eV in photon energy for a 5-Å surface layer of the gold using bulk optical constants.

potential change similar to that shown in Fig. 2. The bottom curve is calculated assuming bulk optical constants, for a rough comparison. The "observed" curves of Fig. 3 show the effect as a function of internal angle of incidence and polarization. The absorbance increases as the gold film is made anodic, and is strictly linear with charge passed, in the potential range used.

It will be noted that the shapes of the internal reflectance curves of Fig. 1 are similar to that of the reflectance curve observed by Feinleib[2] for gold, which we showed to be due to a field effect in the metal.[4] For perpendicular polarization and angles close to critical (cf. Fig. 3), the reflectance change is about 25 times as large as that observed by Feinleib. This is because of the greater sensitivity of the internal reflection method and because we controlled the potential of our gold with a three-electrode system. In fact, the observed reflectance change under these conditions is larger than that caused by the generation of a highly absorbing dye at the interface.[8] If it were desired
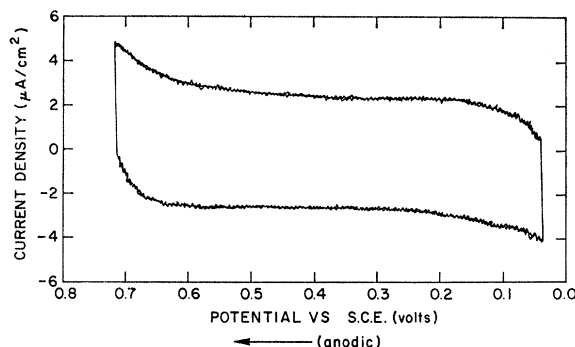

FIG. 2. Voltametric electrochemical curve for thin-film gold electrode in 0.1 M Na_2SO_4 solution. Potential sweep is linear and reversed at end points. Curve is traversed counterclockwise every 25 sec.

[6] Wilford N. Hansen, Theodore Kuwana, and R. A. Osteryoung, Anal. Chem. 38, 1810 (1966).

[7] Wilford N. Hansen, Anal. Chem. 37, 1142 (1965).

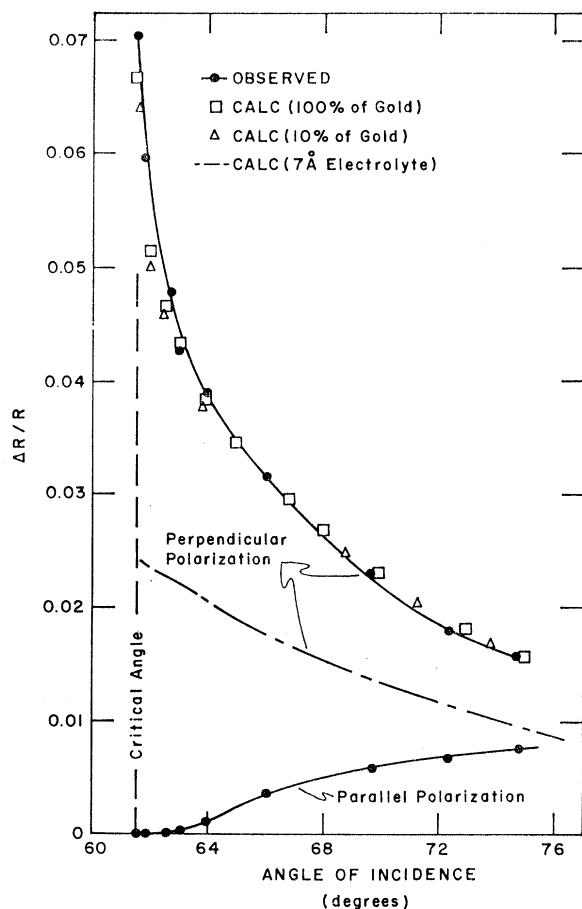[8] Arnold Prostak, Harry B. Mark, Jr., and Wilford N. Hansen, J. Phys. Chem. (to be published).

FIG. 3. Observed and calculated field effect as a function of angle of incidence and polarization at a wavelength of 4800 Å (2.582 eV). For the observed values the potential sweep is from 0.34 to 0.94 V versus SCE. The shift in optical constants for the calculated curves was determined by Eq. (1) and corresponds to a fractional eV shift of 0.0030, or a shift of 0.0076 eV for 100% of gold. For a 10% surface layer the shift is 0.076 eV.

to observe an absorbing species in the solution, however, the lower curve of Fig. 3 shows that one should work close to the critical angle and use parallel polarization. These are the conditions for maximum sensitivity in this type of measurement anyway, so it offers no problem.

The electroeffect is due solely to changes in the fraction of light absorbed by the gold film since there is no other absorbing species present, and there is no refracted beam. The key question is whether the change in light absorption is due to changes in the optical properties of the gold film or to changes in its surroundings. The results presented below show that the gold itself changes.

C. Proof of Optical Changes in Gold

The potential of the gold-film electrode was controlled relative to a calomel reference electrode, and cycled with triangular wave form of about 0.7 V peak

to peak. A typical voltametric curve is shown in Fig. 2. In 1 cycle the curve is traversed counterclockwise and can be repeated many times with no change. A simple calculation comparing the charge involved in 1 cycle with that required to charge the double layer at a typical gold electrode shows that essentially all of the charge can be accounted for by double-layer charging. If of the 30 μC involved in a cycle, 5 μC were Faradaic, it would account for only about 1% of a monomolecular layer on the electrode. In addition, the smooth nature of the voltametric curve in the selected potential region strongly suggests that no important non-Faradaic reactions are occurring, such as the electroadsorption of organic molecules which might be present in the electrolyte as impurities.

Further indication that the electroeffect is not due to impurities in the electrolyte is offered by its constancy, since effects due to impurities should be fickle. Our observations were made using Na_2SO_4, K_2SO_4, and $NaNO_3$ solutions of various concentrations. A reduction of concentration by 100-fold decreased the effect by about 30%, but otherwise all solutions gave similar results. Changing the source of distilled water also made no change.

We built a small cell with an electrical time constant of about 60 μsec. We then cycled the potential at up to 1.2 kHz, observing the changing cell potential and the optical effect on a dual-trace oscilloscope, and found the optical effect to follow the potential without change in phase or magnitude. It is unlikely that electro-adsorption could behave in this fashion.

Optical calculations were made assuming various models. Using equations valid for a general stratified medium[9] we calculated the effect of changing the refractive index of a thin layer of electrolyte near the gold. Such a change might be caused by Faradaic reactions at the interface, by electroadsorption, by changes in double-layer composition, or by changes in optical properties of the double layer due to changes in electric field strength. The change in the dielectric (index changed from 1.34 to 1.6 for a distance from electrode surface of 7 Å) used in the calculation is much more drastic than that expected for any of the above effects. Yet, the result of this calculation for perpendicular polarization, the middle curve of Fig. 3, has neither the right shape nor magnitude. Calculations also show that this model does not give the right shape as a function of wavelength.

On the other hand, we get close agreement with the experimental results of Fig. 3 if we assume that the optical constants of the film change as though the spectrum of gold were shifted by 0.0076 eV. [This is the amount of shift predicted by Eq. (1).] In Fig. 3 we show the results of a calculation assuming the entire 50-Å-thick film changes and for another which assumes only 5 Å of the film is involved. In the latter case we

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[9] Wilford N. Hansen, J. Opt. Soc. Am. **38**, 380 (1968).

must, of course, assume a larger photon shift (0.076 eV). It is seen that the agreement with observation is very close.

III. THEORY

Making use of Eq. (1) and the simple assumption that the spectra of the optical constants will shift with the plasma frequency but retain their shape as n is changed, we now proceed to calculate the expected change in reflectance and to compare it to the value observed for the voltage cycle shown in Fig. 2. Assuming bulk density, the concentration of free electrons in our gold film is 5.9×10^{22} electrons/cm^3 or 4.7×10^{-3} C/cm^2. In each potential cycle shown in Fig. 2, there is 33 μC/cm^2 added to and taken away from the gold film. This amounts to a fractional change in free-electron concentration of 6.9×10^{-3}. From (1) the fractional shift in plasma frequency will be 3.5×10^{-3}, an anodic potential causing a shift to lower frequencies. If we assume that the entire optical spectrum of gold, in the region of our measurements, shifts by this fraction, we can calculate the resulting change in absorbance if we know the optical constants of gold as a function of wavelength. Using our data[10] for the optical constants of gold to calculate the change in optical constants with photon energy shift, for $\Delta\omega/\omega = 3.5 \times 10^{-3}$ at 4800 Å, we calculate an electroeffect just 1.09 times our observed value.

In the above calculations, it makes no difference whether the electron concentration is assumed to change evenly throughout the film or to form some complicated concentration profile as a function of distance from the interface. This is illustrated by the fact that two of the calculated curves of Fig. 3 are the same. We also see that these comparisons do not tell us what fraction of the gold film is being changed. In these calculations we used the optical constants and thickness determined in our laboratory for the particular gold film used. They differ somewhat from bulk values. In Fig. 1, the dashed curve is the electroreflectance effect calculated as a function of wavelength assuming optical constants of bulk gold taken from the literature and a photon energy shift. The calculated and observed curves agree in their main features. If we had known and used optical constants of the gold film itself at all wavelengths, the agreement may well have been much closer.

It should be noted that the present effect depends on the sign of the charge on the electrode and is observed to be linear with charge. This differs from the case of the Franz-Keldysh effect, where the sign of the field does not enter. The present effect would not have a minimum, therefore, at what electrochemists call the point

of zero charge, i.e., the electrode potential at which the electrode is neutral.

IV. DISCUSSION

It has been shown that the optical properties of gold do indeed change with applied electric field and that this change can be readily observed per internal reflection methods. The magnitude of this electro-effect has been measured as a function of polarization, angle of incidence, and wavelength for a thin gold film. The variation of the effect with photon energy is consistent with calculations assuming a shift in photon energy of the regular gold spectrum as dictated by free-electron theory. To just what depth into the gold the optical changes are effected by the electric field cannot be told from our measurements. In fact, it is not obvious just what to expect. Even though the electric field may penetrate only about one atom layer, since the mean free path of electrons in gold at room temperature is much longer ($\sim$400 Å) than the thickness of our gold film, electrons throughout the film will be reflected frequently from the surface, and their own average properties may be perturbed when the electron concentration changes.

The optical equations used in the calculations of this investigation assume that Maxwell's equations and Ohm's law hold at all points. The latter is open to some question[11] for points inside the gold film. Because of the very high frequencies of visible and uv light and because we found that variation of optical constants with distance into the film is unimportant anyway, we conclude that errors introduced by an assumption of Ohm's law are unimportant in the present case.

It is expected that modulation techniques will greatly add to the usefulness of metal spectra. Once the effect has been measured, it can in turn be used to investigate what is happening at the surface, such as in electrochemistry. In any case, it must be dealt with if internal reflectional measurements involving semitransparent metal electrodes are to be understood.

[10] Wilford N. Hansen, ISA Trans. **4**, 263 (1965).

[11] A. V. Sokolov, *Optical Properties of Metals* (American Elsevier, New York, 1966), p. 172.