

## Electroreflectance in Metals

ARNOLD PROSTAK\* AND WILFORD N. HANSEN

*North American Aviation Science Center, Thousand Oaks, California*

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Calculations have been made which suggest that the prominent maximum in the electroreflectance spectra of metals observed by Feinleib is not due to modulation of the optical constants of the electrolyte, but to modulation of the optical constants of the metal.

IN a recent letter,<sup>1</sup> Feinleib reports obtaining electroreflectance spectra of metals, despite the fact that the applied electric field only penetrates into the metal about 0.5 Å while the electromagnetic field of the light penetrates about 100 Å. Feinleib speculates that at least part of the spectral structure in the electroreflectance can be attributed to the electric field modulation of the optical constants of the electrolyte rather than to any modulation of the optical constants of the metal. This letter will report the results of calculations designed to unravel the influence of these two effects.

The formula derived by Hansen<sup>2</sup> for the optical reflectance from a three-layer structure, which was obtained by an exact solution of Maxwell's equations with appropriate boundary conditions, can be used to calculate the spectral effect of changing the optical constants in a thin layer of electrolyte or in a very thin layer of metal.

Figure 1 shows the calculated fractional reflectance change ( $\Delta R/R$ ) for gold in contact with a 100 Å-thick

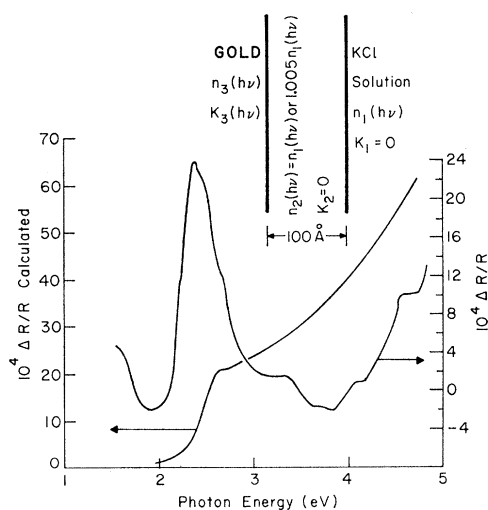


FIG. 1. Calculated fractional normal reflectance change for gold in electrolyte assuming modulation of the optical constants of the electrolyte, compared with the measured electroreflectance of gold reported by Feinleib (see Ref. 1). Shown in the inset is the model assumed in the calculation.

\* National Science Foundation Graduate Fellow. Affiliation: Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104.

<sup>1</sup> J. Feinleib, Phys. Rev. Letters **16**, 1200 (1966).

<sup>2</sup> W. N. Hansen (unpublished); W. N. Hansen, T. Kuwana, and R. A. Osteryoung, Anal. Chem. **38**, 1810 (1966).

layer of transparent electrolyte (representing the Gouy space-charge layer), whose index of refraction  $n$  is assumed to step between  $n$  and  $n+\Delta n$ , such that at each photon energy  $\Delta n/n=0.005$ . This modulated region is in contact with bulk transparent (extinction coefficient,  $k=0$ ) electrolyte of refractive index  $n$ . The optical constants ( $n$  and  $k$ ) of gold were obtained by smoothing the handbook<sup>3</sup> values. The  $n$  of 1 *M* KCl solution was obtained by multiplying handbook values of the  $n$  of water<sup>4</sup> by the factor 1.0074 obtained from measurements on 1 *M* KCl solution.<sup>5</sup> It was determined by further calculations that the shape of this calculated spectrum did not substantially alter for changes of up to at least a factor of 10 in space-charge layer thickness or in  $\Delta n/n$ . Because of discrepancies in the reported<sup>3</sup> optical constants of gold (especially at photon energies above 3.2 eV where the reported constants do not give the measured reflectance), this calculation may not be quantitatively accurate, but it clearly does not show the reported  $\Delta R/R$  peak at 2.35 eV. Additional calculations, which were made using hypothetical optical constants that allowed calculation of the measured reflectance, did not give a substantially different  $\Delta R/R$  spectrum. The thickness of the space-charge layer in the electrolyte was taken to be 100 Å as suggested by Feinleib.<sup>1</sup> However, if 1 *M* KCl solution was used, as is often the case,<sup>6</sup> then the space-charge-layer thickness is better given<sup>7</sup> as 3 Å. In this case, the shape of the  $\Delta R/R$  curve shown in Fig. 1 would be the same, but reduced in ordinate magnitude.

Figure 2 shows the results of calculations made to investigate whether a modulation in the optical constants of gold in a thin surface layer of 0.5 Å thickness due to the applied electric field would be sufficient to cause the reported effect. In the assumed model, the applied electric field uniformly shifts or translates the

<sup>3</sup> *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., p. 6-112; *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill Book Company, Inc., New York, 1929), Vol. V, pp. 249, 252.

<sup>4</sup> *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill Book Company, Inc., New York, 1930), Vol. VII, p. 13.

<sup>5</sup> *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., p. 6-91.

<sup>6</sup> M. Cardona, K. L. Shaklee and F. H. Pollak, Phys. Rev. **154**, 696 (1967).

<sup>7</sup> P. Delahay, *Double Layer and Electrode Kinetics* (John Wiley & Sons, Inc., New York, 1965), p. 44.

optical constants of the gold to lower photon energies.<sup>8</sup> For each photon energy, a 0.5 Å-thick surface layer of gold was assumed to have its optical constants step between those of the bulk gold and those appropriate to gold for a photon energy 0.1 eV different from that used for the bulk gold. In this calculation, the electrolyte was assumed to be homogeneous with no modulation of its optical constants. A large peak at 2.5 eV was obtained that resembles the derivative of the reflectance curve and is similar to the reported large peak at 2.35 eV (shown in Fig. 1). The calculated peak height is of the same order of magnitude as the peak height observed by Feinleib. This calculated  $\Delta R/R$  is proportional to the assumed thickness of the gold layer having changed optical constants, at least in the range of 0.5 to 2 Å, and is approximately proportional to the assumed shift in photon energy of the optical constants, if the shift is less than a few tenths of an electron volt.

It should also be pointed out that, in a KCl electrolyte, some metals, including gold and silver, may form metal chloride compounds, as a function of applied potential. Formation of these compounds would be expected to affect the reflectance. Calculations have been made to simulate a chemically formed film on the gold, for which films of material of refractive index varying between 1.8 and 2.4, extinction coefficient varying between 0 and 0.012, and thickness varying between 1 and 10 Å were sandwiched between the gold and the electrolyte. For all these calculations, the resulting  $\Delta R/R$  curve had no major peak in the visible region. Because the electrochemical apparatus used<sup>1</sup> was not reported to have had a nonpolarizable reference electrode placed close to the test metal, the electrochemical potential of the test metal is undefined, and so whether or not metal chlorides were formed in the experiments described<sup>1</sup> cannot be determined from the information given.

It appears from the calculations reported here that electric field modulation of the optical constants of the electrolyte will not produce the reported<sup>1</sup> peak in the

<sup>8</sup> T. S. Moss, *J. Appl. Phys. Suppl.* **32**, 2136 (1961); R. Williams, *Phys. Rev.* **126**, 442 (1962); B. O. Seraphin, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), pp. 165-170.

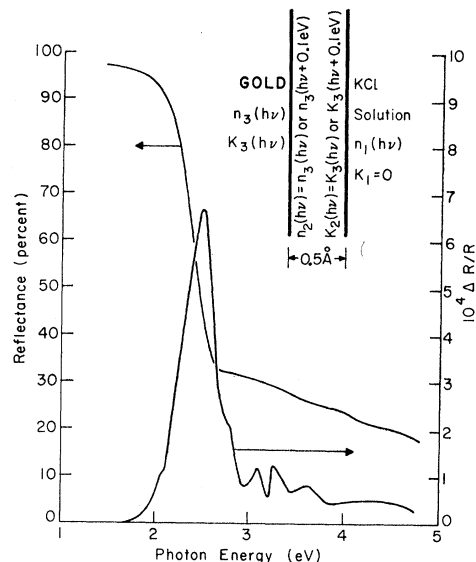


Fig. 2. Calculated fractional normal reflectance change for gold in electrolyte assuming modulation of the optical constants of the metal. Shown in the inset is the model assumed in the calculation. Also shown is the normal reflectance calculated for gold using the same optical constants.

electroreflectance of gold, at least not for a simple model of this modulation. On the other hand, modulation of the optical constants of the metal will produce a peak at approximately the reported photon energy, even if the modulation of the optical constants of the metal extends only 0.5 Å into the metal.

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