by some means such as copper plating),

$$J_c(t) = 10M(2t/3)$$
 A/cm.

According to these results the critical surface current of foils of a given material should vary at a given field and temperature as $t^{-1/2}$.

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ELECTROREFLECTANCE IN METALS

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Longitudinal electric field modulation of reflectivity has proven to be a powerful tool for investigating electronic band structure in semiconductors.^{1,2} In metals, the penetration of the low-frequency (<100-Hz) electric field was thought to be insufficient to produce an observable change in reflectivity. Nevertheless, we have observed electric field modulation of the reflectivity at a metal-electrolyte interface in several metals.

According to recent theories,^{1,3} electroreflectance depends on the influence of the low-frequency field on the energy bands, which causes an oscillating singularity at critical points.³ The relative change in the reflectivity at these singular-point energies should therefore depend on the magnitude of the electric field inside the solid within the penetration depth of the light. Using an electrolyte method, $4,^2$ it is possible to obtain large fields at the sample surface with small applied voltages because a dipole layer is formed in the electrolyte at the interface. The penetration of the low-frequency field into the material is limited by the screening of the free carriers. The Thomas-Fermi screening length for a static charge in an electron gas is given as $\lambda^2 = \mathcal{E}_F / 6\pi n e^2$, where *n* is the carrier density, and $\mathcal{E}_{\mathbf{F}}$ is the Fermi energy. In semiconductors the screening length for the nearly static field can be of the order of the wavelength of the light, but in good conductors the screening occurs within atomic dimensions of the surface, leaving a field-free region in the bulk of the metal. In copper, for example,

the screening length $\lambda \approx 0.5 \times 10^{-8}$ cm ≈ 0.5 Å. The electric field should therefore have little effect on the band structure at the depth that is probed by the light which is of the order of 100 Å. Despite these considerations, in the metals examined to date, silver, gold, copper, and the metallic-oxide sodium tungsten bronze,⁵ peaks in the electroreflectivity spectra have been observed which are closely correlated with structure in the reflectivity of each metal. The relative change in reflectivity at the strong peaks was about 0.5% which is comparable with the electroreflectance structure observed in semiconductors.²

The experimental arrangement is similar to the electrolyte technique used for studying semiconductors.² The metal sample is placed in a fused-quartz cell at the entrance slit of a single-pass Perkin-Elmer prism monochromator and is illuminated by a 1600-W xenon arc source. A 35-Hz modulating voltage of about 2 V peak to peak is applied between the sample and a platinum electrode which are immersed in the KCl-water electrolyte. No dc bias voltage was required. The detectors used are photomultiplier tubes with responses from about 1.3 to 6.0 eV. Most of the structure in the electroreflectance is observable with moderate resolution, using slit widths of 100 μ and a CaF₂ prism for the ultraviolet or a glass prism for the visible spectrum. The photomultiplier output detected at the 1000-Hz chopper frequency is kept constant over the spectral range by a servo control

of the photomultiplier-tube voltage. The signal recorded after phase-sensitive detection at 35 Hz is thus proportional to $\Delta R/R$.

The electroreflectivity for two different samples of pure silver, and the absolute reflectivity for one of the samples, are shown in Fig. 1. The distinctive features are a negative peak which occurs at the steep plasma edge and a sharp rise to a narrow peak in the region where the metal has low reflectivity. The plasma edge and relectivity minimum occur at 3.9 eV instead of the calculated free-electron value because of an interband transition thought to be the $L_{32} - L_{2'}$ band at the Fermi surface with this energy.⁶ The positive peak in electroreflectance, $\Delta R/R$, occurs near this energy but may be caused by the small value of R rather than by the critical point in the band structure. The smaller peak near 3.0 eV appears to be real, and may be related to a similar peak seen when a magnetic field is applied.⁷ Another prominent interband peak is expected around 5 eV, but measurements have not as yet been made in this region. However, the decrease beginning at 4.6 eV may represent the onset of this transition, in analogy with the negative peak observed in gold at 3.8 eV.

The data for gold are displayed in Fig. 2. Again there is a dip near the less well-defined plasma edge of gold, and this is followed by the peak at 2.35 eV. The reflectivity minimum here is identified with a similar $L_{32} \rightarrow L_{2'}$ band transition as in silver.⁶ A negative peak at 3.8 eV is clearly resolved in the electroreflectance spectrum, but is only vaguely seen in the



FIG. 1. Electroreflectance of silver for two samples: (1) high-purity polished sample, (2) high-purity polished commercial sheet silver. Curve (3) is the reflectivity measured for sample (1) in air.

reflectivity. This structure in the reflectivity has been attributed⁶ to a transition $X_5 \rightarrow X_4'$. The broadening of the 2.35-eV peak in the electroreflectance has also been observed in the imaginary part of the dielectric constant for the bound electrons as derived from reflectivity data.⁶ While there is an apparent reproducible correlation between structure in the electroreflectance and structure in the reflectivity, the correspondence to critical points in the band structure of the metal must be determined by further experiments and theory.

At least part of the structure in the electroreflectance at the metal-electrolyte interface 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. In terms of the complex dielectric constants, $\mathcal{E}_{M, E} = D_{M, E}$ $\times \exp(i\theta_{M, E})$, for the metal and electrolyte, respectively, the reflectivity from the interface is

$$R = \left| \frac{\mathcal{E}_{M}^{1/2} - \mathcal{E}_{E}^{1/2}}{\mathcal{E}_{M}^{1/2} + \mathcal{E}_{E}^{1/2}} \right|^{2}.$$

The region modulated by the electric field in the electrolyte depends on the concentration of ions, the diffusion length of the ions, and nature of the dipole layer. Generally, the region in which a concentration gradient exists is ~100 Å. Thus, in this region $D_{\rm E}$, which has a relatively flat spectrum, will be modulated by the electric field and will modulate R. The relation for R is symmetric in $D_{\rm M}$ and $D_{\rm E}$, hence a change in R caused by $D_{\rm E}$ is related



FIG. 2. Electroreflectance of a thick gold film evaporated on an optical flat. The reflectivity of an identically prepared sample is also shown.

to the change in R caused by D_M by

$$\frac{D_{\mathbf{M}}}{R} \frac{\partial R}{\partial D_{\mathbf{M}}} = -\frac{D_{\mathbf{E}}}{R} \frac{\partial R}{\partial D_{\mathbf{E}}}$$

and

$$\frac{1}{R} \frac{\partial R}{\partial \theta_{\mathbf{M}}} = -\frac{1}{R} \frac{\partial R}{\partial \theta_{\mathbf{E}}}.$$

In this model, the observed $\Delta R/R$ is

$$\frac{1}{R}\frac{\Delta R}{\Delta F} = \frac{1}{R}\frac{\partial R}{\partial D_{\rm E}}\frac{\Delta D_{\rm E}}{\Delta F} + \frac{1}{R}\frac{\partial R}{\partial \theta_{\rm E}}\frac{\Delta \theta_{\rm E}}{\Delta F},$$

where F is the electric field. Subsituting, we have

$$\frac{1}{R} \frac{\Delta R}{\Delta F} = -\frac{1}{R} \frac{\partial R}{\partial D_{\mathbf{M}}} \frac{D_{\mathbf{M}}}{D_{\mathbf{E}}} \frac{\Delta D_{\mathbf{E}}}{\Delta F} - \frac{1}{R} \frac{\partial R}{\partial \theta_{\mathbf{M}}} \frac{\Delta \theta_{\mathbf{E}}}{\Delta F}$$

If we assume that $\Delta D_E / \Delta F$ and $\Delta \theta_E / \Delta F$ are essentially constant over the transparent region of the electrolyte, then the observed frequency dependence of $\Delta R/R$ is caused only by changes in the optical constants of the metal. In this model, therefore, the electrolyte acts as a sensitive probe for the reflectivity of the metal. Our first results show that this model can account for the positive peak at the plasma edge. Other mechanisms, such as a small modulation of the Fermi level or an induced piezoreflectance, may also be involved and are being considered in detail. Studies of the mechanism of electroreflectance at metal-electrolyte interfaces may aid in obtaining a quantitative understanding of line shapes and magnitudes of the electroreflectance observed in semiconductors.²

I gratefully acknowledge the encouragement received from the helpful discussions of this work with G. Wright, J. G. Mavroides, and W. Scouler. I would like to thank B. Feldman for helping with the measurements and construction of the apparatus, and R. L. Carman for furnishing some samples. I especially appreciate the contributions of G. Dresselhaus who pointed out the simple relation between the optical constants of the metal and the modulation in the electrolyte.

*Operated with support from the U. S. Air Force. ¹B. O. Seraphin and R. B. Hess, Phys. Rev. Letters <u>14</u>, 138 (1965); B. O. Seraphin and N. Bottka, Phys. Rev. Letters <u>15</u>, 104 (1965); B. O. Seraphin, Phys. Rev. <u>140</u>, A1716 (1965); B. O. Seraphin, R. B. Hess, and N. Bottka, J. Appl. Phys. <u>36</u>, 2242 (1965).

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EXPERIMENTAL ENERGY-MOMENTUM RELATIONSHIP DETERMINATION USING SCHOTTKY BARRIERS

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The relation between electron energy and complex wave vector, over a portion of the forbidden energy gap in GaAs, has been deduced from experimental voltage-(tunnel) current characteristics of GaAs Schottky-barrier rectifiers.

The effect of nonparabolic energy bands in a potential barrier on the tunneling electrons has been previously considered.^{1,2} Stratton² has shown that it would lead to an increase of the tunnel current if the barrier height is an appreciable fraction of the forbidden energy gap of the insulator. More recently Stratton, Lewicke, and Mead³ have proposed a technique to evaluate the band structure in the forbidden gap of an insulator from the study of the voltage-current characteristic of a tunneling metal-insulator-metal sandwich. We have adapt-