to the change in R caused by D_M by

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

and

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

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

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

where F is the electric field. Subsituting, we have

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

If we assume that $\Delta D_\mathrm{E}/\Delta F$ and $\Delta \theta_\mathrm{E}/\Delta F$ 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.

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*Operated with support from the U. S. Air Force.

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EXPERIMENTAL ENERGY-MOMENTUM RELATIONSHIP DETERMINATION USING SCHOTTKY BARRIERS

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(Received 9 May 1966)

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] Stratton[2] 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 Mead[3] 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-

ed their method to the case of a tunneling Schottky barrier and have obtained an experimental determination of part of the energy-(complex) momentum relationship for GaAs.

Stratton, Lewicke, and Mead[3] have shown that the V-I characteristic, resulting from tunneling through an arbitrary potential barrier with arbitrary energy-momentum relationship, can be expressed as

$$J=\frac{2\pi^2 qkTp_{01}^2}{h^3}\frac{\exp(-b_1)}{\sin(\pi c_1 kT)}\times[1-\exp(-c_1V)],\quad c_1kT<1. \tag{1}$$

Here p_{01}, b_1, and c_1 are the leading coefficients of the Taylor expansion of the exponent in the transmission coefficient. This expansion was taken with respect to tangential wave vector (about zero wave vector) and electron energy (about the Fermi level). T is the absolute temperature and V the applied bias. It is easy to show that in the case of a Schottky barrier (neglecting the image force for simplicity), b_1 can be expressed as

$$b_1=\frac{1}{\hbar}\left(\frac{2\epsilon}{Nq^2}\right)\int_0^{\psi_B-V}\frac{\bar{p}(\psi)d\psi}{(\psi+\xi)^{1/2}}. \tag{2}$$

Here ϵ is the dielectric constant of the semiconductor, N the impurity concentration, q the electronic charge, ψ_B the metal-semiconductor barrier height, ξ the Fermi level of the semiconductor, and ψ the energy of the tunneling electron, both measured from the bottom of the conduction band of the semiconductor. $\bar{p}(\psi)$ is related to the energy-momentum relationship $p(\psi)$ by

$$\bar{p}^2(\psi)=-p^2(\psi) \tag{3}$$

in the forbidden gap region and is real.

Differentiating Eq. (2), solving for $\bar{p}(\psi)$, and squaring the result yields

$$p^2(\psi_B-V)=-\hbar^2(Nq^2/2\epsilon)(\psi_B+\xi-V)(db_1/dV)^2. \tag{4}$$

Thus the determination of b_1 as a function of the applied bias V will yield the energy-momentun relationship directly. Padovani and Stratton[4] have shown that in the case of parabolic bands, the V-I characteristic of a Schottky barrier is dominated by the term $\exp(-b_1)$ for V sufficiently greater than $1/c_1$, i.e., about 40 meV. We should thus be able to approximate Eq. (4) by

$$p^2(\psi_B-V)=-\hbar^2(Nq^2/2\epsilon)(\psi_B+\xi-V)(d\ln I/dV)^2. \tag{5}$$

To check the validity of this approximation, we computed the voltage-current characteristic given by Eq. (1), assuming for the semiconductor the band structure proposed by Kane[5] for InSb ($\vec{k}\cdot\vec{p}$ approximation) with the parameters appropriate to GaAs. Carrier concentration, barrier height, and Fermi level were chosen to correspond to the diode described below. The energy-momentum relationship was then computed using Eq. (5) and compared with the original one. The result displayed in Fig. 1 shows that the use of Eq. (5) underestimates the value of $(p/\hbar)^2$ by about 4×10^{-4} Å^2 at a fixed energy.

The experimental data were obtained in the following way. A Schottky barrier was made on 2×10^{18}-atom/cm^3 n-type GaAs. Such a high concentration of impurities is necessary to achieve measurable currents (10^{-11} A) at small forward biases (0.01 V) resulting in electrons tunneling at energies well below the bottom of the conduction band. A gold film, 1000 Å thick, was evaporated and cut into 0.01×0.01-inch squares. Chips were subsequently scribed away and mounted in TO-18 packages. The voltage-current characteristic as measured at liquid-nitrogen and liquid-helium temperatures is shown in Fig. 2. Photoelectric measurement yielded the barrier height. Capacitance data gave the carrier concentration and

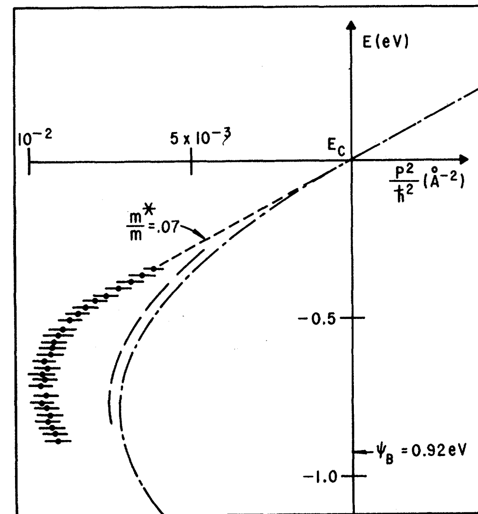

FIG. 1. Experimentally derived values of electron energy E versus wave vector $(p/\hbar)$. Dash-dot line, Kane's band structure; dashed line, approximate result obtained by equating $d(\ln I)/dV$ to db_1/dV. Dots with bars through them, experimental points including error bars.

the position of the Fermi level.

To obtain good accuracy in the evaluation of the term $d(\ln I)/dV$, the voltage across the diode had to be measured within less than 0.1 mV. This was accomplished by the use of a Hewlett-Packard 3440A digital voltmeter equipped with a 3443A high-gain plug-in unit. The derivative was computed by feeding the data to a digital computer programed to make a polynomial fit of the experimental data over a window two decades high in current which was then slid along the whole current range. The resulting E-vs-p^2 relationship is shown in Fig. 1.

Examination of Fig. 1 reveals that, even taking into account the experimental error, our data cannot be explained in terms of Kane's band. This result might be due to the fact that Kane's $\vec{k}\cdot\vec{p}$ calculation was done for InSb where a strong coupling of the conduction- and valence-band states exists as a result of the small value of the energy gap. In the case of GaAs, one might expect to retain the characteristic of the conduction band further in the gap as a result of the large value of the energy gap.

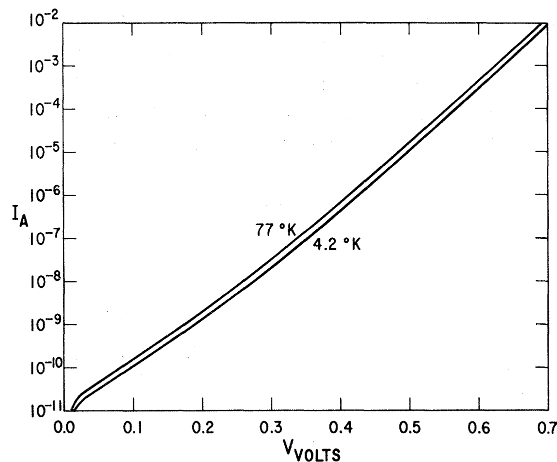

FIG. 2. Voltage-current characteristics for a Au-GaAs diode (2×10^{18} donors per cm^3) at 77 and 4.2°K.

The effect of neglecting the image-force correction leads to values of $(\psi_B - V)$ which are too large for the corresponding deduced value of p^2. This would tend to move the experimental points in Fig. 1 upwards and increase the deviation from Kane's band. Further, at the high doping level employed for our diodes it is possible that tailing of the conduction band into the forbidden energy gap occurs. It is, however, unlikely that this will cause deviations in the forbidden-gap band structure more than a few meV away from the original band edge.

The authors wish to thank G. G. Sumner for the careful preparation of the diodes used in this experiment.

Note added in proof. —Manuel Cardona has informed the authors that the calculation of the energy band structure of germanium and gallium arsenide by the $\vec{k}\cdot\vec{p}$ method[6] has been extended to states in the forbidden gap. The calculations for germanium and silicon lead to a maximum value of $-p^2$ in the $\langle 111 \rangle$ direction which is about 20% greater than the value obtained from Kane's two-band model. This direction corresponds to that of the orientation of our gallium-arsenide diodes and it seems reasonable that at least part of the discrepancy between theory and experiment, shown in Fig. 2, would be removed by a calculation for gallium arsenide (not yet done) which takes into account the interaction of higher-lying bands.

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