Localized states (Tamm levels), having energies distributed in the "forbidden" range between the filled band and the conduction band, may exist at the surface of a semiconductor. A condition of no net charge on the surface atoms may correspond to a partial filling of these states. If the density of surface levels is sufficiently high, there will be an appreciable double layer at the free surface of a semiconductor formed from a net charge from electrons in surface states and a space charge of opposite sign, similar to that at a rectifying junction, extending into the semiconductor. This double layer tends to make the work function independent of the height of the Fermi level in the interior (which in turn depends on impurity content). If contact is made with a metal, the difference in work function between metal and semiconductor is compensated by surface states charge, rather than by a space charge as is ordinarily assumed, so that the space charge layer is independent of the metal. These ideas are used to explain results of Meyerhof and others on the relation between contact potential differences and rectification.

INTRODUCTION

The generally accepted view of the nature of the rectifying contact between a metal and a semiconductor is illustrated in Fig. 1 which applies specifically to an excess semiconductor. Figure 1a shows an energy level diagram of the metal and semiconductor in equilibrium, but with the contact separated. The Fermi level is the same in both the metal and the semiconductor. As shown, the work function of the metal, $x_1$, is greater than the work function of the semiconductor, $x_0$, so that there is a contact difference in potential, $x_1 - x_0$. It is assumed that when the metal and semiconductor are nearly joined, the potential distribution is as shown in Fig. 1b. A double layer is formed such as to give a potential drop, $\phi_0$, from the metal to the interior of the semiconductor equal to the contact potential difference.

This double layer is assumed to consist of a space charge region in the semiconductor, extending to a depth of the order of $10^{-4}$ to $10^{-6}$ cm,
and an induced charge on the metal surface. The space charge gives a rise in electrostatic potential energy at the surface of the semiconductor. Electrons are depleted from the space charge region, giving a layer of high resistivity. If a potential is applied to the junction, most of the drop occurs across this barrier layer. If the potential of the semi-conductor is negative with respect to the metal, the electron energy levels in the semi-conductor are raised, and electrons may flow more easily over the potential hill into the metal. This is the direction of easy flow. On the other hand, if the semi-conductor is positive, the levels are lowered, increasing the height of the hill, and making it more difficult for electrons to travel from the semi-conductor to the metal. This is the direction of high resistance.

According to this view, the equilibrium height of the potential hill, $\varphi_0$, and therefore also the degree of rectification, depend on the work function of the metal. For an excess semi-conductor, the larger the work function of the metal, the larger is the potential rise, and the larger is the reverse resistance of the barrier. If the work function of the metal is less than that of the semi-conductor there is a potential drop instead of a potential rise, and no rectification will occur. For a defect semi-conductor, in which the current is carried by holes, just the reverse is true: low metal work function gives high rectification.

A number of investigations have been carried out which have verified these conclusions in some cases, and in other cases have not. H. Schweickert, as quoted by Schottky, has found a correlation between the resistance of selenium rectifiers in the blocking direction and the work function of the metal. Selenium is a defect conductor, and high reverse resistance was found for low work function metals such as K, Na, Li, Ba, and low reverse resistance was found for such high work function metals as Ag, Au, Ni. The metal electrodes were put on by evaporation.

W. H. Brattain, working in this laboratory, has found a good correlation between degree of rectification and work function for metal contacts evaporated on cuprous oxide (a defect conductor) and on both N- and P-type silicon. Metals used, listed in order of decreasing degree of rectification, were Al, Ag, and Pt on cuprous oxide; Pt, Be, Ag, Mg, and Al on N-type silicon; and Mg, Cd, Ag, and Pt on P-type silicon. He found that when contact is made to the semi-conductor by a metal junction in air, the rectification is practically independent of the work function of the metal used. Results somewhat similar to those of Schweickert have been obtained by J. N. Shive who studied the rectification characteristics of a number of contacts made by evaporation of various metals on selenium. Metal contacts, listed in order of decreasing degree of rectification, are Be, Zn, Pb, and Au.

A. V. Joffe has studied contact potential differences and the resistances of the contacts formed from a large number of different semiconductors and metals. Most gave very poor rectification characteristics. While there was some qualitative correlation of contact potential differences with contact resistance, quantitative agreement with theories of Schottky and Davydov was poor.

W. Schottky, Physik Zeits. 41, 570 (1940).
Unpublished work done at the Bell Telephone Laboratories in 1940 under the general direction of J. A. Becker. The author is indebted to Drs. Brattain and Shive for permission to quote their results.

The designations N- and P-type refer to the direction of rectification. An N-type is an excess semi-conductor, and the direction of easy flow occurs when the semi-conductor is negative relative to the metal. A P-type semi-conductor is a charge conductor, and the direction of easy flow is opposite. In both cases, the direction of easy flow is that in which the carrier moves from the semiconductor to the metal.