THE TUNNEL EFFECT IN SULFIDE RECTIFIERS

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Abstract

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The theory of the tunnel effect ($^{1-4}$) has so far received no experimental confirmation. This is partly explained by the fact that the operation of ordinary technical rectifiers—such as selenium, cuprous, germanium, and silicon rectifiers—is based on other processes. The phenomena occurring in sulfide rectifiers ($^{5-6}$), and associated with the overcoming by electrons of a thin potential barrier in the near-electrode layer, are of interest for testing the theory of the tunnel effect.

The basic propositions and conclusions of the theory of the tunnel effect that are, to one degree or another, accessible to experimental verification are as follows:

1. The contact is a gap of thickness approximately 10^{-7} cm. The gap may either be empty or be filled with a dielectric medium. Owing to the presence of the gap, a potential barrier arises whose thickness is equal to the thickness of the gap, and whose height is $0.5 \div 4$ eV.
2. Current passes more readily from a metal into a hole semiconductor than in the reverse direction.
3. Rectification decreases with increasing barrier thickness; thick barriers are opaque to electrons.
4. Rectification decreases with increasing concentration of current carriers in the semiconductor.
5. The resistance of a contact between two metals in the presence of a gap should differ only slightly for different current directions; moreover, the dependence of the current I on the voltage at the contact V is determined by formula (1):

$$I = \alpha V + \beta V^2, \qquad (1)$$

where α and β are constants. This same dependence of current on voltage should occur in the case of contact between a metal and a semiconductor with good conductivity (^{2}).

6. With increasing temperature, rectification decreases and, finally, changes sign.

Fig. 1

Figure 1: Fig. 1

It is assumed that the applied voltage is less than the height of the potential barrier; otherwise the conclusions of the theory cease to be valid.

The phenomena that will be described below occur at the contact of an aluminum (or magnesium) plate with a pellet of monovalent cuprous sulfide. The thickness of the pellet was $3 \div 4$ mm, and its area 0.5 cm^2.

Pure monovalent cuprous sulfide β-Cu_2S had the following properties: specific gravity 5.52 g/cm^3, and, calculated from X-ray structural data, 6.1 g/cm^3; specific resistance at room temperature $2.5 \cdot 10^{-3}$ $\Omega \cdot \text{cm}$, and Hall constant $+1.3 \cdot 10^{-22}$ CGSE. The signs of the Hall constant and of the thermoelectric emf correspond to hole conductivity in β-Cu_2S. Ionic conductivity is absent at temperatures below 200°. From these data, by calculation, the values of the concentration $n = 5 \cdot 10^{20}$ cm^{-3} and mobility $\mu = 5$ $\text{cm}^2/\text{V} \cdot \text{sec}$ of the holes were obtained.

During forming of the rectifier the pellet is "welded" to the aluminum plate, with aluminum entering the near-electrode layer of the sulfide,

where its presence is detected by spectral analysis. In this connection, the resistance of the sulfide, which depends strongly on the deficiency of metallic ions (8–9), should increase, and the carrier concentration should decrease. The change in the properties of the sulfide prevents exact quantitative calculations from being carried out; only a qualitative comparison of the experimental results with the predictions of the theory of the tunnel effect can be made.

The processes occurring in a sulfide element depend substantially on the voltage applied to it. If the latter exceeds 0.7 V, then the near-electrode layer becomes saturated with aluminum (or magnesium), and, probably, conditions arise for an electron-hole transition. The dynamic characteristics resemble the characteristics of other technical rectifiers, for example selenium ones. The capacitance of the rectifier, when a blocking voltage of 6 V is applied to it, is $0.04\,\mu\text{F}$. If the dielectric constant of the layer having increased resistance is taken to be 10, then its thickness is approximately 10^{-5} cm.

Fig. 1

When the voltage is decreased below 0.5 V, the aluminum in the near-electrode layer in an unstable state apparently partly diffuses into the thickness of the tablet, and partly separates out in the form of metallic grains and dendrites, which penetrate into the sulfide to a depth of several hundred angstroms. The change in the composition of the near-electrode layer when the voltage is changed is confirmed by the change in the resistance of the rectifier as a function of time. After the voltage is decreased, the resistance falls for several minutes and then reaches an equilibrium value; when the voltage is increased, the resistance rises. When the voltage is below 0.5 V, the near-electrode layer of sulfide has sufficiently good conductivity and is separated from the aluminum by a thin oxide film 20-30 Å thick. Consequently, the conditions considered by the theory of the tunnel effect arise. Below, a comparison is given of the experimental results with the above-noted propositions of the theory.

1. Figure 1 shows the dynamic current-voltage characteristic of a rectifier with an aluminum electrode at a temperature of 22°, taken from the screen of a cathode-ray oscilloscope. The effective voltage on the rectifier was 0.4 V; a current $I_{\text{eff}} = 0.2$ A flowed through it. The coordinate axes were drawn on the basis of an approximate calculation. The arrows indicate the direction of change of the current. The voltage is considered positive when the plus is applied to the sulfide, and the current when it flows from the sulfide into the aluminum. The loop-shaped form of the characteristic shows that the capacitive current is large. The capacitance of the rectifier, calculated from dynamic current-voltage characteristics taken at different voltages, does not depend on the voltage in the interval from 0 to 0.4 V and is approximately equal to 0.005 F. At the same voltages, the capacitance measured on an alternating-current bridge at a frequency of 50 Hz is equal to 0.007 F. Such a value of the capacitance is obtained if one assumes that the thickness of the oxide layer is 20 Å, its dielectric constant is 10, and the surface of the layer is 2000 cm^2 per unit area of the rectifier washer. The large magnitude of the layer surface is not surprising if one takes into account that the surface of the dendrites may be large.

Assuming that the potential barrier has the shape of a triangle with a height equal to 0.7 eV, one can bring into agreement the values calculated on the basis of the pred—

positions concerning the existence of the tunnel effect and the measured values of the current.

2. The current passes more readily from aluminum or magnesium into the sulfide.

3. The tunnel effect appears only in the case where thin insulating layers are present. For example, if aluminum is covered with a stable oxide layer approximately $5 \cdot 10^{-5}$ cm thick, then the current passes more readily from the sulfide into the aluminum. In Fig. 2 the dependence of the rectified current on voltage is presented for this case. It is seen that the characteristic differs from that which is obtained in the presence of a thin layer (see Fig. 2). Rectification in the case of a thick layer is connected with the entry of aluminum into the sulfide. If this does not occur, then the current-voltage characteristic is symmetric with respect to the zero value of the voltage, as is the case for niobium coated with a thick oxide layer.

Fig. 2

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

4. If tantalum is used instead of aluminum, its surface having been preliminarily cleaned of oxides and impurities, then metal ions do not enter the sulfide. With a loose contact between the sulfide and the tantalum, a gap is formed, probably several angstroms thick. The dependence of current on voltage, in general, obeys equation (1), with the ratio β/α being approximately 100 times smaller than in the case of aluminum, when the latter, on passing into the sulfide, contributes to a decrease in the concentration of holes. Consequently, with an increase in the concentration of carriers the rectification decreases. Since the thickness of the empty gap changes from experiment to experiment, the magnitude of the current also changes. In experiments with tantalum electrodes it varied by a factor of 2–3 at the same voltage values.

Fig. 3

5. In Fig. 2 the rectified I_v and effective I_eff currents of a sulfide element with an aluminum electrode are shown as functions of the effective voltage at a temperature of 22°. Characteristics of approximately the same form are obtained in the case of a magnesium electrode, as was known earlier, although the nature of the phenomenon had not been clarified ($^{6-7}$). The rectified current at voltages up to 0.4 V increases with voltage according to a quadratic law, and the effective current according to a linear law. At voltages above 0.5 V the rectification has the opposite sign and is associated with other processes.

6. In Fig. 2 the dependence of the rectified current on voltage is presented at different temperatures for an element with a magnesium electrode. With increasing temperature the rectification decreases, and at temperatures above 200° changes sign. An element with an aluminum electrode changes the direction of rectification at tempera-

higher than 100°. In the case of a tantalum electrode, the rectification changes sign at a temperature of about 60°.

Of interest is the dynamic current-voltage characteristic of a rectifier with a tantalum electrode, preliminarily electrolytically coated with an oxide layer, Fig. 3. The characteristic was taken from an oscilloscope screen at an rms voltage across the rectifier of 0.6 V and a temperature of 22°. When a positive voltage is applied to the tantalum electrode, the current increases along a stepped curve and then decreases smoothly. The nature of this behavior of the current-voltage characteristic has not been clarified. Similar phenomena may be caused by electrons passing over the potential barrier, as was assumed by Mott and Smith (10). The dependence is most clearly expressed for both directions of current in the case of a tantalum electrode. In this connection it is interesting to note that similar phenomena were observed in the study of emission from tantalum and tungsten cathodes (11). Experiment shows that the current produced by electrons passing over the potential barrier, and the capacitive current, are significant.

The experimental material presented qualitatively confirms a number of the main conclusions of the theory of the tunnel effect.

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