Studies on the Selenium Barrier Layer Photoelement. V.[1] Photocurrent, Photopotential and Cell Resistance in Relation to the Intensity of Illumination, and Dependence of the Photocurrent and the Photopotential on the Temperature.*

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Introduction. Until now mechanism of a cuprous oxide barrier layer cell has been explained qualitatively by N. F. Mott[2] and one of a selenium barrier layer cell by M. Tomura,[3] but there have been no quantitative studies on the relations of photocurrent, photopotential and cell resistance to the intensity of illumination, and on the dependence of the photocurrent and the photopotential on the temperature. For more detailed studies on the mechanism of cell and the applications of it, the establishment of the quantitative relations of the above quantities is desired.

Mechanism of the Barrier Layer Photoeffect of the Selenium Cell. According to Tomura[3] it is the barrier layer which is formed at the contact between the selenium semiconductor and the translucent metal electrode that plays an important rôle in the barrier layer photoeffect. When both elements are in contact, if the Fermi surface of the metal is higher than the thermodynamic potential of the semiconductor, the electrons in the metal go into the empty impurity centres of the selenium

(1) The preceding reports are in *Proc. Toshiba Lab.*, **18** (1943), **19** (1944).
(2) N.F. Mott, *Proc. Roy. Soc.* (A), **171** (1939), 281.
(3) M. Tomura, *Proc. Toshiba Lab.* **18** (1943), 523.
* Read at the Research Meeting of Electronic Emission, Tokyo (Jan. 1948.)

which is an abnormal semiconductor and consequently the energy level of the selenium in the neighbourhood of the contact becomes like that shown in Fig. 1.

In this way, there occurs a so-called barrier layer of $10^{-5}\sim10^{-6}$ cm. thick in which exists internal field of order of 10^5 v./cm. When the incident light falls through the surface metal electrode on to the barrier layer, photo-electrons are freed owing to the internal photoeffect of selenium. Then they and their holes are accelerated by the internal field through the barrier layer and photocurrent is observed in the external circuit. It is only the photo-electrons and photo-positive-holes (holes of photoelectrons) which are created in the barrier layer that cause the external photocurrent, and the quantum yield is nearly one for the light absorbed in the barrier layer.

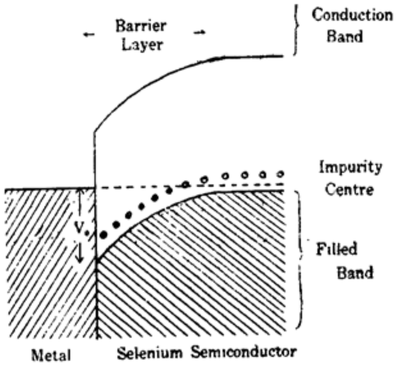

Fig. 1. Potential energy of an electron at the contact between a metal and selenium semiconductor.

On the other hand, when a barrier layer is formed by the contact of a metal with selenium semiconductor, the rectifying action can be detected always, which is explained semiquantitatively by the Mott's theory.(4)

Equivalent Circuit of the Selenium Barrier Layer Photoelement. The above mechanism can be represented by an equivalent circuit which is shown in Fig. 2. Namely, the parallel circuit of the source of the photocurrent Q and the rectifying internal resistance R_i is combined in series with the resistance of electrode metal R_f, the spreading resistance of selenium semiconductor R_s and the external resistance R_e.

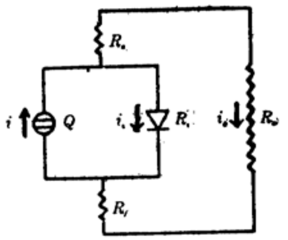

Fig. 2. Equivalent circuit of a selemium barrier layer photoelement.

If photons are absorbed in the cell, photo-electrons and photopositive holes cause the primary photocurrent i in Q by the acceleration of the internal field of the barrier layer, making the external current i_e in the total external resistance $R=R_f+R_s+R_e$. The voltage drop i_eR owing to the flow in the external circuit is impressed upon R_i, so the rectifying current i_i flows through R_i as indicated by an arrow in the figure. This current is a stream of positive holes, being equivalent to the easy flow of the rectification of the cell. As the current i_i cancels a part of the original current i, the remainder forms the external current i_e. Then we have $i-i_i=i_e$.

In this case i is proportional to the intensity of illumination; but i_i and i_e are influenced by R_e and the temperature, because R_i depends on the voltage which is applied on itself and the temperature. This is the

(4) N. F. Mott, *Proc. Roy. Soc.* (A), **171** (1939), 27.

cause of complicated behaviour of the photocurrent, photopotential and cell resistance under different conditions.

Theoretical Calculations. Since the primary photocurrent i is proportional to the intensity of illumination I,

$$i = aI \quad \text{.......................} \quad (1)$$

is obtained. Here a is a constant. From the above section, furthermore, the next relation exists.

$$i = i_i + i_e \quad \text{.......................} \quad (2)$$

Since the selenium photoelement has a barrier of pure contact, we may apply Mott's theory to the barrier of pure contact which has a parabolical internal potential. Then we obtain[5)]

$$\left.\begin{aligned} i_i &= \frac{2\sqrt{V_0}\sqrt{V_0 - V}}{\rho_\infty}\left(e^{\frac{eV}{kT}} - 1\right) \\ \rho_\infty &= \frac{d}{evn_0} \\ n_0 &= 2\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{eV_0}{kT}} \end{aligned}\right\} \quad \text{...........} \quad (3)$$

where V_o is the contact potential difference between the metal and the semiconductor, V the voltage impressed on R_i, e the charge of an electron, k the Boltzmann constant, T the absolute temperature, d the thickness of the barrier layer, v the mobility of a positive hole, m the mass of an electron and h the Planck constant.

For the case of a cuprous oxide backwall cell having a constant internal field in its barrier layer which was treated by Mott, the next formula is to be taken instead of the equation (3).

$$i_i = \frac{V_0 - V}{\rho_\infty}\left(e^{\frac{eV}{kT}} - 1\right) \quad \text{....................} \quad (3')$$

The equations (3) and (3′) hold only in the range of $V < V_o$ and V cannot exceed V_o even if I becomes large. It is the easy flow of the rectifying current that goes into our problem, so the image force effect can be neglected.

From the equations (1), (2) and (3), we obtain

$$\left.\begin{aligned} aI &= i_e + \frac{2\sqrt{V_0}\sqrt{V_0 - V}}{\rho_\infty}\left(e^{\frac{eV}{kT}} - 1\right) \\ V &= i_e R = i_e(R_f + R_s + R_e) \end{aligned}\right\} \quad \text{......} \quad (4)$$

(5) R. Kubo, private communication.

The equation (4) represents the general relations between the photocurrent, photopotential and cell resistance, and their dependence to the intensity of illumination as well as to the temperature.

(a) Photopotential. Photopotential V_p is defined usually as the open potential of the cell, so V_p is given by making $i_e=o$ in (4). Namely,

$$aI = \frac{2\sqrt{V_0}\sqrt{V_0-V_p}}{\rho_\infty}(e^{\frac{eV_p}{kT}}-1) \qquad (5)$$

When $eV_p \ll kT$, or I is small and T is large, we have

$$aI = \frac{2V_0}{\rho_\infty}\frac{eV_p}{kT} \qquad (6)$$

from (5), because the condition $V \ll V_o$ holds. Then V_p is proportional to I.

In the range of $eV_p \gg kT$, (5) becomes

$$aI = \frac{2\sqrt{V_0}\sqrt{V_0-V_p}}{\rho_\infty}e^{\frac{eV_p}{kT}} \qquad (7)$$

so V_p is proportional to log I.

(b) Photocurrent. If we put $V=i_eR=i_e\ (R_f+R_s+R_e)$ into (4), the relations between i_e and I or R are obtained. Especially for the case of $eV \ll kT$,

$$aI = i_e\left(1+\frac{2eV_0R}{\rho_\infty kT}\right)+\cdots$$

namely,

$$i_e = \frac{aI}{1+\frac{2eV_0}{kT}\cdot\frac{R}{\rho_\infty}} \qquad (8)$$

is obtained.

Usually i_e for $R_e=0$ is called the short circuit photocurrent, but since R_f and R_s is finite, we cannot obtain the theoretical short circuit current even though we make use of the Campbell Freeth circuit. R_f and R_s are so small compared to the usual external resistance that the practical short circuit photocurrent i_{es} is obtained as

$$i_{es} = aI \qquad (9)$$

by introducing $V=0$ into (4). This equation is right so long as the condition $V=i_e(R_f+R_s) \approx 0$ holds.

(c). Cell Resistance. So called cell resistance is defined as the ratio of photopotential to the short circuit current at a given intensity of illumination. From (5) and (9),

$$i_{es} = \frac{2\sqrt{V_0}\sqrt{V_0 - V_p}}{\rho_\infty}\left(e^{\frac{eV_p}{kT}} - 1\right) \qquad (10)$$

is obtained. So R_i is given by the next equation.

$$\frac{1}{R_i} = \frac{i_{es}}{V_p} = \frac{2\sqrt{V_0}\sqrt{V_0 - V_p}}{\rho_\infty V_p}\left(e^{\frac{eV_p}{kT}} - 1\right) \qquad (11)$$

The above defined cell resistance is the ratio of two quantities of two different physical states, so it has no real physical meaning. But as (11) shows, it is a formal easy flow resistance of the barrier layer onto which the photopotential V_p is impressed.

(d) Dependence of the Photopotential on the Temperature. If we consider a case of $eV_p \ll kT$, we can derive the next equation from (6).

$$V_p = \frac{aI}{\beta}\frac{e^{\frac{eV_0}{kT}}}{T^{\frac{1}{2}}} \qquad (12)$$

where $$\beta = 4\left(\frac{2\pi mk}{h^2}\right)^{\frac{3}{2}}\frac{e^2 v V_0}{kd}$$

Namely, V_p decreases exponentially with T.

And then, in the region where $e^{\frac{eV_p}{kT}} \gg 1$ and $V_p / V_0 \ll 1$ hold, we can derive

$$V_p = V_0 + \frac{kT}{e}\log\frac{aIe}{\beta kT^{\frac{3}{2}}} \qquad (13)$$

from (5) approximately. This equation means that V_p decreases when T increases, because $\log(aIe/\beta kT^{\frac{3}{2}})$ must be negative from (5), that is to say, T must be larger than a definite value.

(e) Dependence of the Photocurrent on the Temperature. In the same manner as (*d*), we can derive the relations between i_e and T, by introducing $V = i_e R$ into (4) and (8). The result is that i_e decreases when T increases.

At low temperatures we must consider variations of α and v with temperature, and the tunnel effect of positive holes through the barrier layer, making increase of i_i. Thus we cannot gain characteristics of photopotential and photocurrent at low temperatures from (3).

Discussions of the Results. In general the results of the preceding sections can be confirmed by experiments.(6) The equation (3) which we

(6) B. Lange, "Die Photoelemente und ihre Anwendnng", Leipzig (1936).

take as the basis of our calculation is purely theoretical, yet it explains quantitatively the characteristics of the selenium cell, although it fails to explain rigorously the minor details of the experimental results. This fact is attributed to the non-uniform nature of the barrier layer which is found also in the case of the selenium rectifier.

As for the cuprous oxide frontwall cell, since its barrier layer is considered as a pure contact of a metal and a cuprous oxide semiconductor and has a parabolical internal field, the results of the above calculations can be applied just in the same way. But the cuprous oxide backwall cell has a barrier layer of a constant internal field,[4] so we must take up the equation (3′) instead of (3). In this case the results are not very different from the above results.

At very low temperature, as above mentioned, corrections must be added. On the other hand, at higher temperatures than room temperatures, selenide formation takes place in the barrier layer as the author has pointed out,[(7)] so care must be taken in the experiments at the higher temperatures.

Conclusion. By clearing up the relations between the barrier layer photoeffect and rectification of a barrier layer and by applying the Mott's theory of a barrier layer rectifier, the general formula of the relations between the physical quantities of the barrier layer photoelement are derived and their features explained.

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(7) M. Tomura, *Proc. Toshiba Lab.*, **19** (1944), 206.