On the Barrier Layer by the Contact between the Selenium Semiconductor and Metal. II.(1)

On the Selenide Formation in the Barrier Layer.(2)

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Introduction. It is well known that the barrier layer by the contact between the selenium and metal is the cause of retification and barrier layer photoeffect. The author has already explained the formation, rectification and barrier layer photoeffect of pure contact when its barrier layer consists of selenium itself.(3)

The barrier layer of a practical selenium rectifier is not of a pure contact type, but composed of selenide as pointed out by the author.(3) To improve the character of the selenium rectifier, more detailed studies on the structure of the barrier layer are desirable. Here the author will research the formation and structure of the barrier layer of a Cd-Se element.

Description of Experiments. The selenium purified by vacuum distillation is put on a base electrode in melting and it suffers a heat treatment of 4 hours at 200°C. Then cadmium is evaporated on the surface of selenium in vacuum and afterwards the cadmium film is covered with aluminium by the vacuum evaporarion to avoid tarnishing of cadmium at high temperatures.

The area of the element is 15 cm^2.

The element shows an electromotive force between the base electrode and front aluminium electrode, and it increases exponentially with temperature. Thus the current is picked up into the external circuit

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(1) The previous report is in *Proc. Toshiba Lab.*, (*in Japanese*), **19** (1944), 206.

(2) Read at the annual meeting of the Phys. Soc. Jap. in Kyoto, (1948).

(3) M. Tomura, *Proc. Toshiba. Lab.*, (*in Japanese*), **18** (1943) 523, **19** (1944). 206.

and its characteristics are measured. The method of measurement is shown in Fig. 1. The current in the external circuit varies with the external resistance, so the latter is maintained as small as 25 ohms to pick up the former as much as possible. The current flows from the base electrode to the front electrode through the external circuit as shown in the figure in the same direction as the photocurrent of a selenium barrier layer photoelement. At first it amounts to about 100 micro-amperes at 100°C.

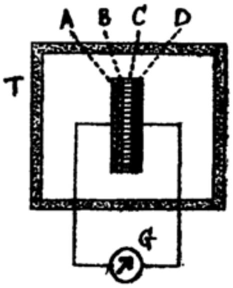


Fig. 1. Measuring apparatus,

A Al electrode.
B Cd film.
C Selenium semiconductor.
D Base electrode.
G Galvanometer.
T Thermostat.

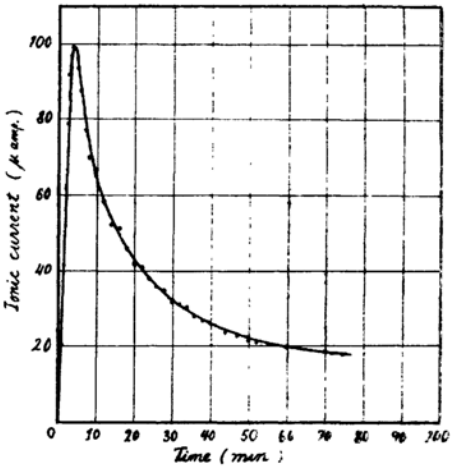


Fig. 2. Relation between the current and time

As the selenium semiconductor and both electrodes, as well as the copper lead wires, are kept at the same temperature, the current cannot be attributed to the so-called thermoelectromotive force by the temperature difference between them.

The relation between the current and time after bringing the element into the thermostat at 100°C is shown in Fig. 2. The initial steep increase of the current may mean the temperature rise of the element by its abrupt inserting into the thermostat, and the temperature of the element may reach 100°C after several minutes. Next, the current decreases with time and tends to zero asymptotically. The lower the temperature, in other words, the smaller the current, the more slowly decreases the current with time. For instance, the current does not decrease practically at room temperatures.

On the other hand, the resistance of the element becomes larger with the flow of current.

Next, the dependence of the current on the temperature is measured. As the current varies with time, cares are taken that the duration necessary to alter the temperature of the element does not influence results. Namely, the element is maintained long enough at the maximum temperature 100°C necessary for the measurement, so that the current reaches to a practically constant value as shown in Fig. 2. And as the current becomes very small exponentially with the temperature decrease, and that makes the variation of current with time small as the above, the currents are measured in the course of the descending of temperature. Thus we can obtain the temperature dependence of the current avoiding the influence of the current decrease with time. Fig. 3. shows these results. The relation between the thermal current j and the absolute temperature T is found to be

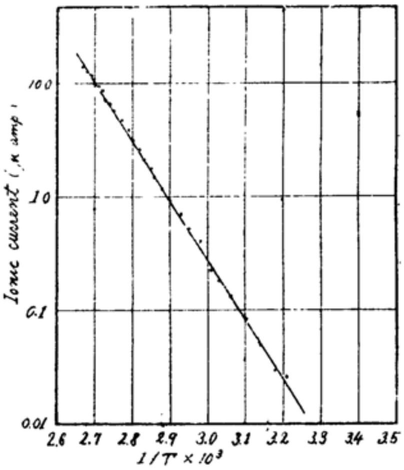


Fig. 3 Dependence of the current on the temperature.

$$j = j_0 e^{-\frac{\alpha}{T}}, \qquad \text{or} \qquad \log j = \log j_0 - \frac{\alpha}{T},$$

where j_0 and α are constants.

The static characteristics of rectification before and after the heat treatment are given in Fig. 4. The results show that the resistance of

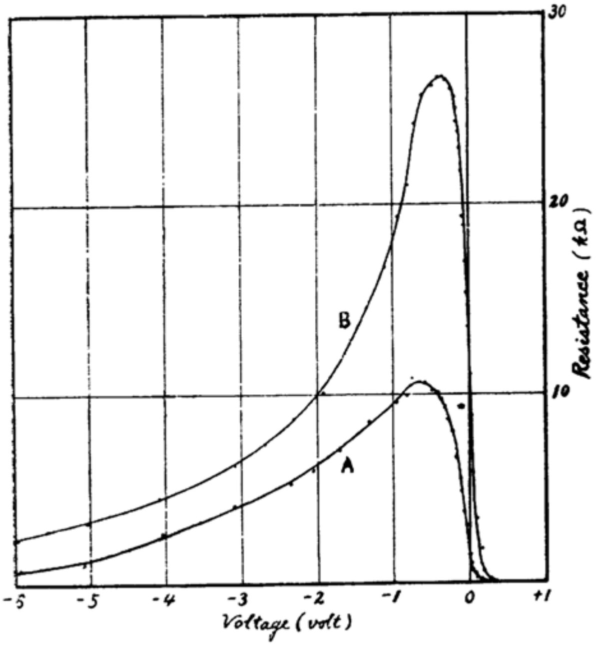


Fig. 4. Characteristics of rectification before (A) and after (B) the heat treatment of 100 min. at 100°C.

rectification of the element becomes very large by the heat treatment and furthermore the characteristics of rectification change by that treatment.

On the other hand, samples are made which have thin cadmium films of $10\sim50\ \mathrm{m}\mu$ thick deposited by the vacuum evaporation on the selenium semiconductors. Their surfaces after the heat treatment of 4 hours at 210°C in vacuum are studied by the reflection method of electron diffraction. CdSe layers of the zinc blend type are observed on their surfaces.

Explanations of the Experimental Results. From the verification of the preceding section that the current observed is not attributed to any thermoelectromotive force, the cause of the current flow is none other than the converting process of the free energy difference in the reaction $\mathrm{Cd}+\mathrm{Se}\rightarrow\mathrm{CdSe}$ to the electric energy, in order to keep the first law of thermodyndmics. This assumption is supported by the experimental result obtained by the electron diffraction which shows the existence of CdSe layer on the surface of the sample, in other words, at the contact of the cadmium metal and selenium semiconductor.

From the fact that the current flows in this case, we can conclude that ions move just as in the electrochemical reaction, because an ionic crystal such as CdSe shows an ionic conduction in general by the moving of ions which are derived from lattice defects. Though the ionic conduction of CdSe has not been reported, we can assume as follows: since the ionic radius of Cd^{++} is 0.60 Å, and the one of Se^{--} 1.90 Å, the defect of Frenkel type is expected for CdSe and ionic charges are carried by the moving of cadmium ions through interstitial places of the lattice.

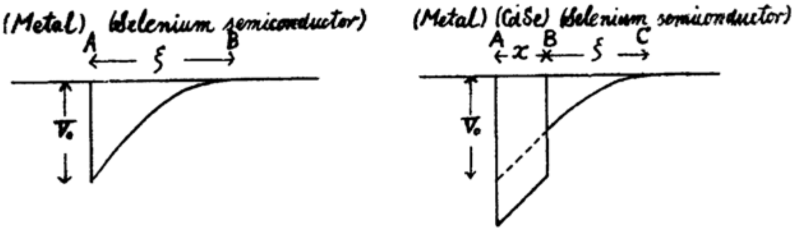
Since there exists an internal field of the order of 10^5 v./cm. at the contact of a Cd-Se element,(3) the cause of the ionic current is that if a CdSe layer is formed by the direct reaction at the interface at first, the internal field acts upon that layer, making the cadmium ions at the interstitial points move to the selenium semiconductor side by the acceleration of the field. As the interstitial cadmium ions must take a distribution of a certain value at a given temperature, they are supplied from the cadmium electrode by the ionization of cadmium atoms into cadmium ions and electrons. The former move through the CdSe layer and the latter through the external circuit towards the selenium side, forming a new layer of CdSe. Thus the ionic current of the metal ion is observed in the external circuit. As will be mentioned afterwards, the mobility and number of the interstitial cadmium ions increase exponentially with temperature, the ionic current has the same nature, satisfying the result of Fig. 3.

The thickness of the CdSe layer becomes large with the flow of ionic current, consequently the field in the CdSe layer decreases and then the current decreases with time as shown in Fig. 2.

The change of the rectification resistance of the barrier layer by the heat treatment shown in Fig. 4. supports certainty of the formation of the CdSe layer. By the transformation the barrier layer from one of pure contact to one of CdSe, the potential barrier at the interface becomes large for positive holes to go over the barrier, making the resistance of rectification large.

And the measurement of the abnormal spectral sensibility of a selenium barrier layer cell which has suffered a heat treatment supports the above explanation from the other side.(4)

Internal Field in the Barrier Layer which has a Selenide Layer. The potential energy of an electron in the neighbourhood of the contact



(a) (b)

Fig. 5. Potential energy of an electron at the interface.

(a) The case of pure contact type.

(b) The case of selenide formation type.

V_0 is the contact potential difference between cadmium and selenium semiconductor.

is shown in Fig. 5. If we take N for the number of empty impurity centres in the unit volume of the selenium semiconductor and they are filled by the electrons from the metal when both elements are in contact, the potential energy of electron V is

$$\frac{d^2V}{d\xi^2} = \frac{4\pi Ne^2}{D}$$

Here e is the electronic charge and D the dielectric constant of selenium semiconductor. Then

$$\frac{dV}{d\xi} = \frac{4\pi Ne^2}{D}\,\xi \quad \text{and} \quad V = \frac{2\pi Ne^2}{D}\,\xi^2$$

are derived by taking ξ as the distance from the point B in Fig. 5 (a). If we put $1/L^2 = 2\pi Ne^2/V_0D$ into the above equations (L the thickness of the barrier layer of pure contact.), we get

$$V = \frac{V_0}{L^2}\xi^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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(4) M. Tomura, This Bulletin, in the press.

and

$$\frac{dV}{d\xi} = \frac{2V_0}{L^2}\xi \text{ ....}(2)$$

where V_0 is the contact potential difference between both elements.

Next we take up the case in which a CdSe layer is growing. We assume that the CdSe layer is an insulator and there is no accumulation of charge at the interface between the CdSe layer and selenium. Thus if we take x as the thickness of the CdSe layer, we obtain

$$D\frac{dV}{d\xi} = D'\frac{dV}{dx} \text{ ....}(3)$$

by the continuity condition of field at the interface. Here D' is the dielectric constant of CdSe. From (2) and (3)

$$\frac{dV}{dx} = \frac{2V_0}{L^2}\frac{D}{D'}\xi \text{ ....}(4)$$

is derived. As the contact potential difference is distributed in the CdSe layer AB as well as in the selenium layer BC as shown in Fig. 5 (b), we get

$$\frac{2V_0\gamma}{L^2}\xi x + \frac{V_0}{L^2}\xi^2 = V_0,$$

namely,

$$\xi^2 + 2\gamma x\xi - L^2 = 0,$$

by considering (2) and (4), where γ is D/D'.

The solutions of the above equation are given by

$$\xi = -\gamma x \pm \sqrt{\gamma^2x^2+L^2},$$

but from the physical standpoint we must pick up the plus sign. Thus the field $F(x)$ in the CbSe layer is

$$F(x) = \frac{dV}{dx} = \frac{2V_0\gamma}{L^2}\{\sqrt{\gamma^2x^2+L^2}-\gamma x\} \text{ ....}(5)$$

$$= \frac{2V_0\gamma}{L^2}x\left\{\sqrt{1+\frac{L^2}{\gamma^2x^2}}-1\right\} \text{ ....}(5')$$

F has its maximum value $2V_0\gamma/L$ at $x = 0$ and tends to zero asymptotically with increase of x. γ may be nearly one, consequently in (5′) if $L^2/\gamma^2x^2 \ll 1$, namely $x \gg L$, we get

$$F(x) = \frac{2V_0}{L^2}x\left\{\left(1+\frac{L^2}{2x^2}-\frac{L^4}{8x^4}+\dots\right)-1\right\} \doteqdot \frac{V_0}{x} \;\dots\dots\dots\dots (6)$$

and in (5) if $\gamma^2x^2 \ll L^2$ or $x \ll L$

$$F(x) = \frac{2V_0}{L^2}(L-x). \;\dots\dots\dots\dots\dots\dots\dots (7)$$

Theoretical Calculation of the Selenide Formation. If n is the number of cadmium ions per unit volume which move through the CdSe layer and u their mean velocity, the ionic current j per unit area is given by

$$j = nu. \;\dots\dots\dots\dots\dots\dots\dots\dots (8)$$

The charge which is brought by the cadmium ions is proportional to the formation of CdSe, that is to say, to the thickness of CdSe, so

$$jdt = \alpha\, dx \dots\dots\dots\dots\dots\dots\dots\dots (9)$$

is given, where α is a constant. The number of lattice defects n is given by

$$n = n_0 e^{-\frac{W}{2kT}} \dots\dots\dots\dots\dots\dots\dots (10)$$

in the case of the Frenkel type(5). W is the energy necessary to form a lattice defect and n_0 a constant. If U is the height of the potential barrier for the travelling of ions through the lattice, u is given by the next equation,(6)

$$u = \beta e^{-\frac{U}{kT}} \sinh\left(\frac{1}{2} ZeFa/kT\right) \dots\dots\dots\dots\dots\dots (11)$$

Here β is a constant, Z the number of electronic charge of the ion, F the field in the crystal and a the distance between the neighbouring lattice sites.

Then from (8), (9), (10) and (11), we obtain

$$j = \alpha\frac{dx}{dt} = Ae^{-\frac{\frac{1}{2}W+U}{kT}} \sinh\left(\frac{1}{2} ZeFa/kT\right) \dots\dots\dots\dots\dots (12)$$

as the equation of growth of the selenide layer.

Here A is a constant. Since Z is 2 for a cadmium ion, a, 2.62 Å. for CdSe of the zinc blend type and kT about 0.03 e.v. at 100°C, the value

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(5) e. g. N. F. Mott and R. W. Gurney, "Electronic Process in Ionic Crystals", Oxford, (1940).

(6) Ibid.

of $\frac{1}{2}ZeFa/kT$ is $10^{-1}\sim 1$, even though we consider the maximum value $2V_0/L$ of F, because V_0 is about $0.5\,v.$ and L, $10^{-5}\sim 10^{-6}$ cm.(3)

Consequently, taking up the first term of the expansion of $\sinh\cdot\left(\frac{1}{2}Ze\,Fa/kT\right)$, we can gain

$$j = a\frac{dx}{dt} = \frac{AeFa}{2kT}\,e^{-\frac{1}{2}\frac{W+U}{kT}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(13)$$

Then the relation between t and x is

$$t = \frac{2akT}{Aea}\,e^{\frac{1}{2}\frac{W+U}{kT}}\int\frac{dx}{F(x)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

In the case of $x \gg L$, from (6) we get

$$t = \frac{2akT}{Aea}\,e^{\frac{1}{2}\frac{W+U}{kT}}\int\frac{dx}{\frac{V_0}{x}}$$

$$= \frac{akT}{Aea\,V_0}\,e^{-\frac{1}{2}\frac{W+U}{kT}}x^2 + C \qquad \ldots\ldots\ldots\ldots\ldots\ldots(15)$$

where C is an integration constant. So we obtain

$$j = a\frac{dx}{dt} = \frac{Aea\,V_0}{2kT}\,e^{-\frac{1}{2}\frac{W+U}{kT}}\cdot\frac{1}{x} \qquad \ldots\ldots\ldots\ldots\ldots(16)$$

And if $x \ll L$, from (7) and (14) we get

$$t = \frac{2akT}{Aae}\,e^{\frac{1}{2}\frac{W+U}{kT}}\int\frac{dx}{\frac{2V_0}{L^2}(L-x)},$$

or

$$t = -\frac{akTL^2}{Aae\,V_0}\,e^{\frac{1}{2}\frac{W+U}{kT}}\cdot\log(L-x) + C'$$

Here C' is an integration constant and given as

$$C' = \frac{2kTL^2}{Aae\,V_0}\,e^{\frac{1}{2}\frac{W+U}{kT}}\cdot\log L,\ \text{because } x = 0 \text{ at } t = 0.$$

Thus we obtain

$$t=\frac{akTL^2}{AaeV_0}e^{\frac{\frac{1}{2}W+U}{kT}}\cdot\log\frac{L}{L-x},\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(17)$$

or

$$x=L\left\{1-\exp\left(-\frac{AaeV_0}{akTL^2}e^{-\frac{\frac{1}{2}W+U}{kT}}\cdot t\right)\right\}\ldots\ldots\ldots\ldots(17')$$

namely,

$$j=a\frac{dx}{dt}=\frac{AaeV_0}{kTL}e^{-\frac{\frac{1}{2}W+U}{kT}}\cdot\exp\left(-\frac{AaeV_0}{akTL^2}e^{-\frac{\frac{1}{2}W+U}{kT}}\cdot t\right)\ldots\ldots(18)$$

In Fig. 6. curves of $q\,(=\int jdt)$ versus t and q^2 versus t are plotted from the experimental data. As q is proportional to x, the curve q^2 versus t is satisfied by (15) except the region in which x is small. The region of the curve q versus t where x is small is satisfied by (17). But owing to the non-steadiness of temperature in the measurement when x or t is small, a rigorous analysis of the experimental curve in this region can not be made.

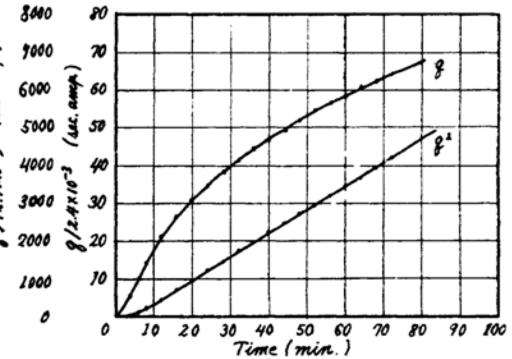

Fig. 6. q versus time and q^2 versus time curves.

As stated above, the curve in Fig. 3 is obtained for the case in which the reaction of selenide formation progresses enough so that the CdSe layer grows thick. Then we can explain that curve by (16) which is derived for the case in which x or the thickness of the CdSe layer is large. (16) shows a linear relation between $\log j$ and $1/T$ at a given x. The activation energy of j is given as 0.98 e.v. from the experimental curve in Fig 3. and corresponds to $1/2W+U$ in (16). This value is allowable as one of a normal ionic conduction. The author has assumed that CdSe has defects of the Frenkel type, but the selection of anothor type of defects does not alter the mechanism of the selenide formation essentially.

From the presumption that the ionic current flows owing to the internal field in the CdSe layer, (12) is substituted by

$$\sigma = \sigma_0 e^{-\frac{E}{kT}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

where σ is the ionic conductivity of CdSe and σ_0 is a constant. Assume the voltage impressed over the CdSe layer is nearly 0.5 v., because the internal field exists almost in the CdSe layer owing to the sufficient reaction in the experiment. Also assume the thickness of the layer $10^{-5} \sim 10^{-6}$ cm ; σ_0 is derived as $10^3 \sim 10^4$ ohm^{-1} cm^{-1}. from the experimental data in Fig. 3. This value is allowable for the moving of ions through an ionic crystal of the Frenkel type. From this magnitude of σ_0, it can be concluded that the reaction takes place at the entire area of the interface and the ions do not move through only cracks of the crystal.

As a cadmium ion transports 2 electronic charges, the thickness of the CdSe layer estimated from the value of q at 60 min. in Fig. 6 is in the order of 10^{-6} cm.;, considering the layer is uniform. This value is also probable for the case of heat treatment of one hour at 100° C.

Conclusion. The author found that a contact element of Cd-Se at elevated temperature had an electromotive force and the current caused by it was ionic, being attributed to the moving of cadmium ion through the CdSe layer accelerated by the internal field in the barrier layer to react with selenium.

Next the internal field in the barrier layer was calculated when the selenide formation took place and the experimental results were explained by the theoretical calculations of the formation of the CdSe layer at the contact.

Lastly, it must be pointed out that the selenide formation has an important rôle in the process of the third heat treatment in making a selenium rectifier.

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