Studies on the Selenium Barrier Layer Photoelement. VI.

Abnormal Spectral Sensibility of a Selenium Barrier Layer Photoelement.

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Introduction. The author has explained the mechanism of the barrier layer photoelement and rectification of the selenium barrier layer cell, by considering its barrier layer which is made at the contact between a metal and selenium semiconductor.(1) According to him, the barrier layer is one in which the distribution of electrons is abnormal and there exists a very large internal field. If the incident light is absorbed in the barrier layer, photoelectrons and their holes which are created by the internal photoeffect of selenium cause a photocurrent in the external circuit owing to the acceleration by the internal field. On the other hand, the existence of the barrier layer gives the action of rectification to the photoelement.

The barrier layer of a normal selenium barrier layer cell is composed of the selenium semiconductor itself. In order to study the structure of the layer and the mechanism of the barrier layer photoeffect and rectification, it is desirable to make a barrier layer which is different chemically from selenium.

Description of Experiments. After the coating of the melted selenium on a metal base electrode, it is converted to a semiconductor by the heat treatment of 4 hours at 200°C and then a thin cadmium film is deposited on it by the cathode sputtering method in the atmosphere of argon. In the next place, after the second heat treatment of 4 hours at 200°C in vacuum, a translucent platinum electrode is put on the element by the cathode sputtering.

The spectral sensibility of the element is measured by a monochrometer over the range of 4000 Å~8000 Å. The result is shown in Fig. 1. It shows a new peak of 7100Å besides the one of a normal cell. The relative height of the new peak with respect to the normal one increases with the thickness of the sputtered cadmium film. The curves 1, 2, 3 in Fig. 1 are spectral distributions of the samples of which the thickness of the cadmium film increases in that order. The thickness of the sputtered film is in the order of 1~10 mμ.

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(1) M. Tomura, *Proc. Toshiba. Lab.*, **18** (1943), 523.

If the heat treatment is omitted after the deposition of the cadmium film, we can observe no new peak of spectral sensibility.

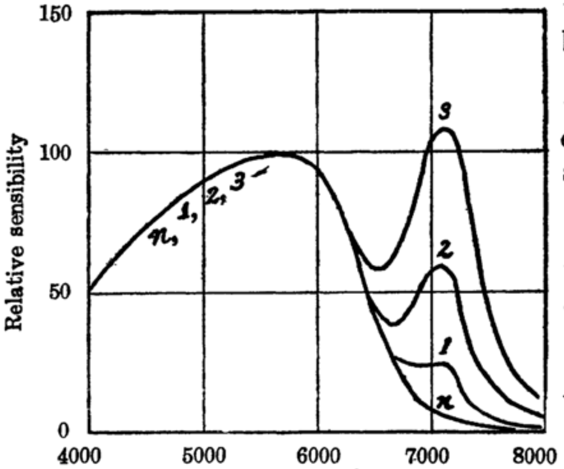

Fig. 1. Spectral sensibility of the cells. The curve n is one of a normal cell.

To have knowledge of the change of the rectification by the heat treatment, another sample is made which has a thick cadmium film evaporated in vacuum on the selenium semiconductor. Its static characteristics of rectification are measured before and after the heat treatment of 1 hour at 100°C. The result is shown in Fig. 2. The resistance of the barrier layer becomes very large by the heat treatment.

On the other hand, to see what substance is created on the selenium by the heat treatment, a direct method of detection utilizing the reflection method of electron diffraction was used for a sample which was made by the heat treatment of 4 hours at 200°C in vacuum. As usual the cadmium film of the order of 10 mμ thick was deposited on the selenium semiconductor by evaporating in vacuum before the heat treatment. The result of the electron diffraction shows the existence of a CdSe layer of the zinc blend type.

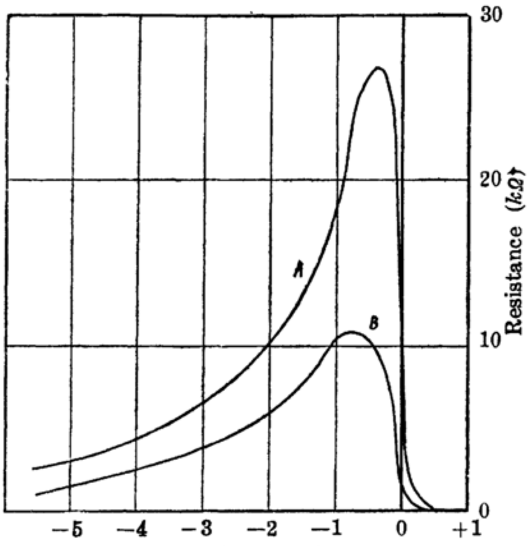

Fig. 2. Characteristics of rectification before (B) and after (A) the heat treatment.

Next, the author measured the spectral transmission of CdSe which was deposited on a glass plate by the vacuum evaporation. This CdSe was made by the wet method, namely, by using the reaction of $Cd^{++} + H_2Se \rightarrow CdSe + 2H^+$. The transmission curve is in Fig. 3.

Discussion of the Experiments. It is clear that the new peak of 7100 Å is caused by the heat treatment. The author has already explained the process of the reaction of cadmium and selenium semiconductor by finding a thermoionic current occurring at a contact of both materials.(2) By the increase of the mobility owing to high temperatures, cadmium ions accelerated by the internal field move through the CdSe layer at the contact and the layer of CdSe grows with the flowing of ionic current in the external circuit. This means just the converting process of the free energy difference in the reaction Cd+Se→CdSe into the electric energy.

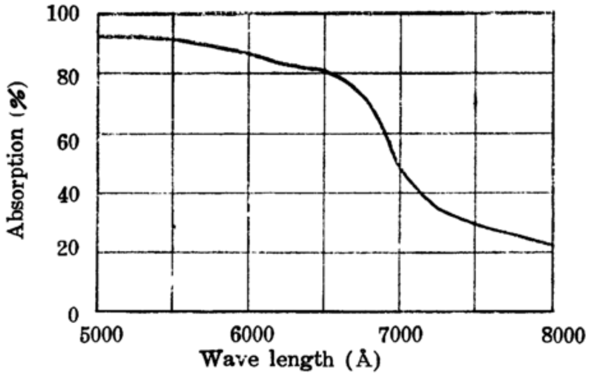

Fig. 3. Absorption spectrum of CdSe film.

The fact that the CdSe layer is found on the selenium by the electron diffraction tells us that the entire layer of the cadmium deposited on the selenium has reacted with the selenium.

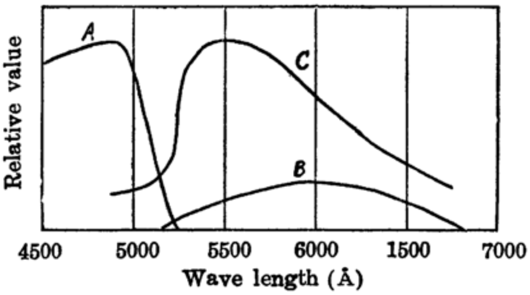

Fig. 4 (b). Spectral absorption (A, B) and photoconductivity (C) of CdS(4).

In this way the barrier layer of the new photoelement is composed of double layers; the CdSe layer and selenium layer over which the internal field extends. If the light is put on the layer, it is first absorbed in the CdSe layer and next in the selenium layer. Then the normal peak of the spectral sensibility is attributed to the internal photoeffect of the selenium and the new peak of 7100 Å to the one of the CdSe layer.

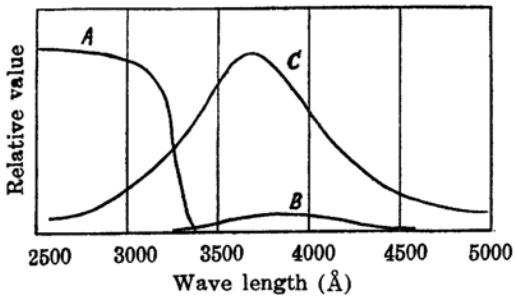

Fig. 4 (a). Spectral absorption (A, B) and photoconductivity (C) of Z_nS(4).

It has been reported that CdSe has the internal

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(2) M. Tomura, this Bulletin, **22** (1949), 82.

photoeffect.(3) From the spectral sensibility of the internal photoeffect and spectral absorption of ZnS and CdS, the following hypothesis to explain the barrier layer photoeffect of CdSe is given.

Fig. 4 shows the spectral absorption and internal photoeffect of ZnS and CdS.(4) The absorption in the visible range corresponds to the transition of electrons from the filled band to the excited states. The tails of the absorption curve, that is 3800Å of ZnS and 6000Å of CdS, correspond to the transition of electrons from the impurity levels to their excited states. The fact that the peak of the sensibility of the internal photoeffect coincides with the peak of the absorption by the impurities means that photoelectrons excited by the absorption of light enter into the conduction band from the excited states by absorbing thermal energy and contribute to the conduction.(5)

From the shape of the long wave end of the spectral absorption curve of CdSe measured by the author, we presume that the characteristic absorption of CdSe extends to the region of the absorption curve by the impurity centre. Consequently the internal photoeffect is expected at the long wave end as well as ZnS and CdS.

As the heat treatment is long enough in duration and high enough in temperature to convert the cadmium film to the CdSe layer; the thicker the cadmium film, the thicker is the CdSe layer formed.

Consequently the light quantity absorbed in the CdSe layer becomes greater relative to the one in the selenium layer when the cadmium film becomes thicker, making the height of the new peak higher with the thickness of the cadmium layer.

As for the rectification, a remarkable change of the resistance after the heat treatment supports the formation of the CdSe layer. By the formation of the CdSe layer, the potential hill to the stream of the positive hole becomes higher at the contact, resulting in the increase of the resistance of the barrier layer.

Conclusions. A selenium barrier layer photoelement which has a new process of heat treatment in its making is formed, having a new peak in its spectral sensibility curve. This peak is attributed to the internal photoeffect of the CdSe layer which is made in the barrier layer by the heat treatment.

From the above discussions, it is concluded that if there are photoconductive substances in the barrier layer of the selenium barrier layer cell where the internal field influences, these substances show their own barrier layer photoeffect when they absorb the light corresponding to the internal photoeffect.

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(3) R. Freirchs, *Phys. Rev.*, **72** (1947), 594.

(4) J. H. Gisolf, *Physica*, **6** (1939), 81; F. A. Kröger, ibid., **7** (1940), 1; B. Gudden and R. W. Pohl, *Z. Physik*, **2** (1920), 181.

(5) F. Seitz, *J. Chem. Phys.*, **6** (1938), 454.