R 344 *Philips Res. Repts* **13**, *265-276, 1958*

PHOTO EFFECTS WITH ANODIC OXIDE LAYERS ON TANTALUM AND ALUMINIUM

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537.312.5

Summary

This article deals with the photoelectric properties of the system Ta/Ta_2O_5/electrolyte during irradiation with ultraviolet light. The electrolyte has also been replaced by a transparent layer of a metal or a semi-conductor. When the system is short-circuited, a photocurrent (i_0) is produced which is proportional to the intensity of irradiation. With a high external resistance a photo e.m.f. V appears which shows considerable inertia as a function of the time t and which can be written as $V = V_{\max}(1 - e^{-kt})$. It appears that k is proportional to the intensity of irradiation. The value of k decreases with increasing thickness (d) of the layer. After correcting for this change of k, which is probably due to absorption, we find that $i_0 d$ = constant. An attempt is made to explain the observed phenomena by assuming that the work function Ta/Ta_2O_5 is smaller than the work function electrolyte/Ta_2O_5.

Résumé

Dans cet article, on décrit les propriétés photoélectriques du système Ta/Ta_2O_5/électrolyte lorsque la couche d'oxyde est soumise à une irradiation ultraviolette. L'électrolyte peut être remplacé par une couche transparente d'un métal ou d'un semi-conducteur. Lorsque le système est court-circuité, il passe un courant photoélectrique (i_0) qui est proportionnel à l'intensité de l'irradiation. Avec une résistance extérieure d'une valeur élevée, il se produit une f.e.m. photoélectrique, qui présente un retard considérable. On peut écrire cette f.e.m. (V) sous la forme $V = V_{\max}(1 - e^{-kt})$, où k est proportionnel à l'intensité de l'irradiation. La valeur de k décroît lorsque l'épaisseur de la couche (d) croît. Après avoir apporté une correction tenant compte de cette décroissance, on trouve $i_0 d$ = constant. On essaie d'expliquer les phénomènes en admettant que le travail de sortie Ta/Ta_2O_5 est plus petit que le travail de sortie électrolyte/Ta_2O_5.

Zusammenfassung

Es werden die photoelektrischen Eigenschaften des Systems Ta/Ta_2O_5/Elektrolyt beschrieben; außerdem wurde der Elektrolyt durch eine durchsichtige Metall- oder Halbleiterschicht ersetzt. Bei Kurzschluß ist der Photostrom i_0 der Beleuchtung proportional. Bei hohem äußeren Widerstand entwickelt sich eine Photo-EMK (V), die eine merkbare Trägheit als Funktion der Zeit (t) aufweist. Man kann diese EMK als $V = V_{\max}(1 - e^{-kt})$ schreiben, worin k der Beleuchtungsintensität proportional ist. Der Wert von k nimmt mit wachsender Dicke der Schicht (d) ab. Wenn man diese Abnahme von k in Rechnung bringt, findet man $i_0 d$ = konstant. Es wird versucht, eine Erklärung der Beobachtungsergebnisse zu geben durch die Annahme, daß die Austrittsarbeit für Elektronen beim Übergang Ta/Ta_2O_5 kleiner ist als beim Übergang Elektrolyt/Ta_2O_5.

1. Introduction

It is well known that several metals, like Ta and Al, can be covered with an oxide layer by electrolytic oxidation. Such a system, e.g. $Ta/Ta_2O_5/$electrolyte, constitutes a rectifier, the direction of easy transmission for electrons being that from Ta to electrolyte. At the same time this system exhibits photoelectric phenomena. Photoconduction and a photovoltaic effect in the ultraviolet with Ta electrodes were first reported by Lifschitz and Reggiani [1]); Rosenthal [2]), Bär [3]) and Walkenhorst [4]) have also investigated similar effects using Ta and Al electrodes. The subject has been re-investigated recently by Young [5]).

In this article we discuss the photocurrent and the photovoltaic effect produced by irradiation with ultraviolet light for the systems $Ta/Ta_2O_5/$electrolyte and $Al/Al_2O_3/$electrolyte. We have also replaced the electrolyte by a thin transparent metal layer or a transparent semi-conducting layer (CuI).

Measurements have been carried out, under constant irradiation, on the dependence of the photocurrent on the applied voltage; the voltage was applied in both the forward (Ta—) and blocking directions (Ta+).

The photovoltage that appears shows a considerable inertia as a function of time and this inertia was studied. We have also measured the photocurrent without any auxiliary voltage as a function of the intensity of irradiation.

Finally we shall draw some conclusions from the measurements and give a provisional picture of what causes the photocurrent and the photovoltaic effect.

2. Apparatus

The set-up was very simple. The Ta or Al plate was oxidized in an electrolyte of borax and boric acid in water. This plate was placed in a horizontal position a few mm under the surface of the electrolyte. A mercury lamp was placed above the surface of the liquid.

The Al_2O_3 layer was sensitive to wavelengths smaller than 2600 Å, the Ta_2O_5 layer to wavelengths smaller than 2850 Å. These values were determined with the aid of filters combined with the known emission of the mercury lamp. The accuracy is about ±100 Å.

The photoeffect will be caused mainly by the 2537 Å line.

Photovoltages were measured with a high-resistance voltmeter having an internal resistance of 10^9 ohms. Photocurrents produced without the application of an auxiliary voltage were measured with a low-resistance meter.

The thickness of the oxide layer on Al as a function of the formation voltage, at small values of the leakage current, was taken 12·7 Å/V [6]). The thickness of the Ta_2O_5 layer was found to be 18·5 Å/V, a result of unpublished measurements.

3. Experimental part

3.1. *The i-V characteristic during irradiation*

(a) The system Ta/Ta_2O_5/electrolyte. Figure 1 shows the dark current i_D and the current during irradiation (i_L) in de forward direction (Ta—) as well as in the blocking direction (Ta+). There is a considerable increase in the current for both polarities.

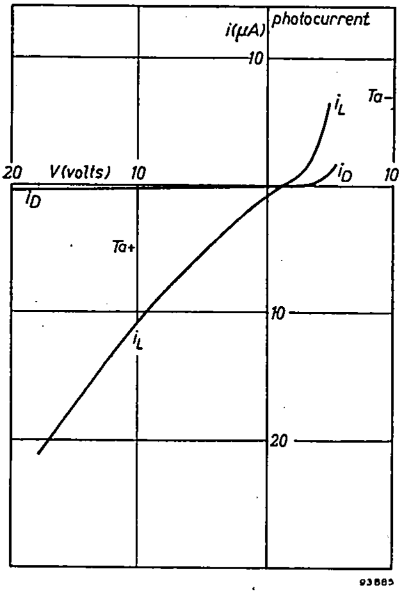

Fig. 1. Photocurrent i_L and dark current i_D against the applied voltage, for the system Ta/Ta_2O_5/electrolyte.

Figure 2 shows a general picture on an enlarged scale of the dark current i_D and the photocurrent i_L in the forward direction as a function of the applied voltage for small values of the latter.

A is the point where no current passes, i.e. where the photocurrent and the forward current have the same value but different signs so that they compensate each other.

B is the point where irradiation does not increase the current.

There is a remarkable likeness to the characteristics of a barrier-layer photocell [7]).

(b) The system Ta/Ta_2O_5/CuI. Figure 3, which is similar to fig. 1, shows the photoelectric current as a function of the applied voltage for a system where the electrolyte is replaced by a CuI layer. It is impossible to compare the photocurrents in the cases (a) and (b), as we do not know the absorption of the CuI layer. The CuI layer was formed on the Ta_2O_5 layer in the following way. Firstly a thin Cu layer was evaporated onto the Ta_2O_5 layer, then the plate was placed in an atmosphere of I_2 vapour, thereby forming the CuI layer.

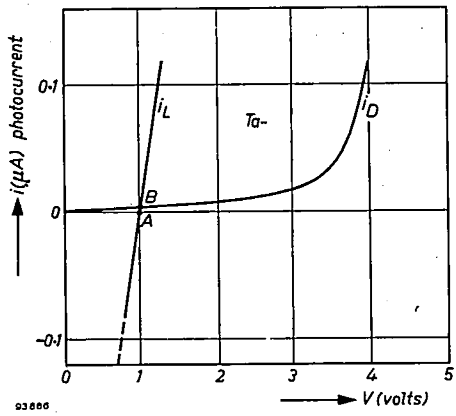

Fig. 2. Photocurrent i_L and dark current i_D against the applied voltage when Ta is the negative electrode (direction of easy transmission). At the voltage corresponding to point A no current is passing; at the voltage corresponding to point B the irradiation has no influence. The system is Ta/Ta_2O_5/electrolyte.

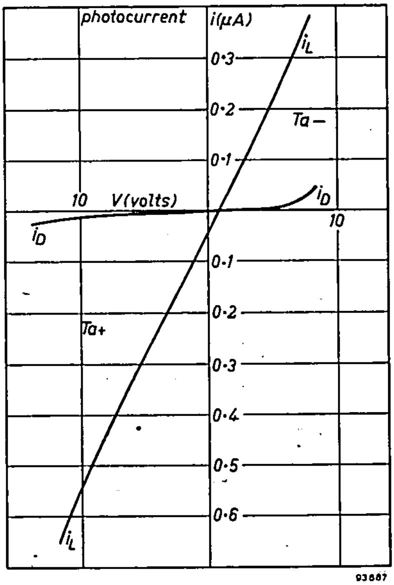

Fig. 3. Photocurrent i_L and dark current i_D against the applied voltage for the system Ta/Ta_2O_5/CuI.

3.2. *The photovoltage*

When the system Ta/Ta_2O_5/electrolyte or Al/Al_2O_3/electrolyte is irradiated with ultraviolet light a photo e.m.f. is built up such that the metal electrode constitutes the negative pole. In our case the resulting forward current is small. This process of the building-up of the photo e.m.f. is slow and the inertia depends on the intensity of the irradiation; this inertia was also found by Young [5]). It was found that $V_{\text{photo}} \doteq V_m(1 - e^{-kt})$ and that V_m is independent of the intensity of the irradiation (fig. 4). Figure 5 shows log $(V_m - V)$ as a linear function of the time for $L = 6$. In fig. 4 the intensity of irradiation L is given in arbitrary units. If we determine the value of k for the successive intensities of irradiation and plot the value of k against L we find that k is proportional to L. Figure 6*a* gives k as a function of L for the system Al/Al_2O_3/electrolyte and fig. 6*b* does the same for Ta/Ta_2O_5/electrolyte. We see that for Ta_2O_5 k is about 40 times as large as for Al_2O_3. This means that for Ta_2O_5 the maximum photovoltage V_m is far more rapidly reached than for Al_2O_3.

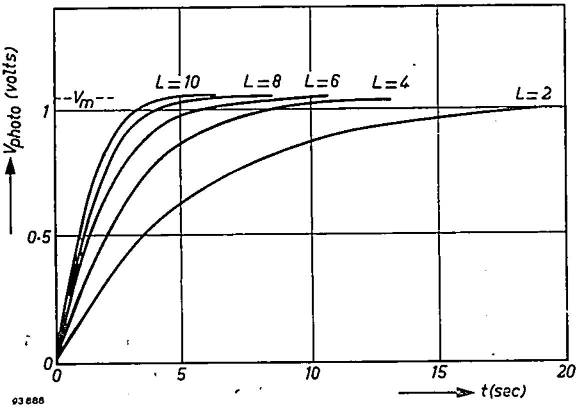

Fig. 4. The photovoltage for the system Ta/Ta_2O_5/electrolyte as a function of the time, during irradiation with a constant intensity, given for different values of the intensity. The curve can be written as $V = V_m(1 - e^{-kt})$.

In addition we found that for the system $Ta/Ta_2O_5/Cu$ the value of k is about 30 times smaller at —200 °C than at room temperature. Here a thin transparent layer of Cu was evaporated on the Ta_2O_5 layer.

3.3. *The photocurrent*

When the photocurrent was measured without an auxiliary voltage it was found to be proportional to the intensity of irradiation. In this case care was taken to keep the resistance in the circuit very low, so that no voltage could be developed over the photoelectric system.

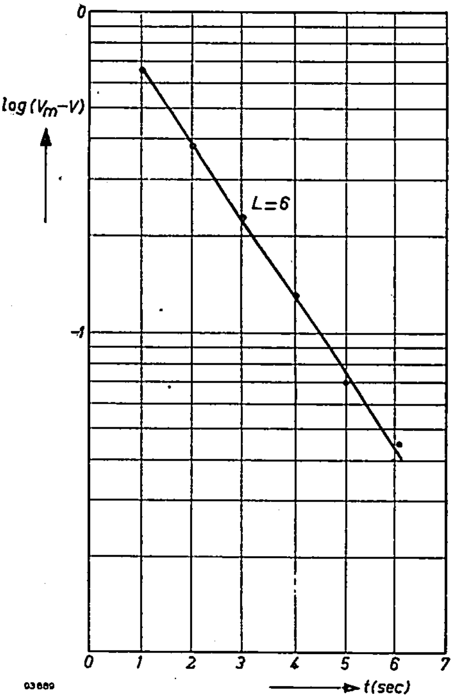

Fig. 5. The linear relation between $\log(V_m - V)$ and the time during irradiation with a constant intensity ($L = 6$ in fig. 4).

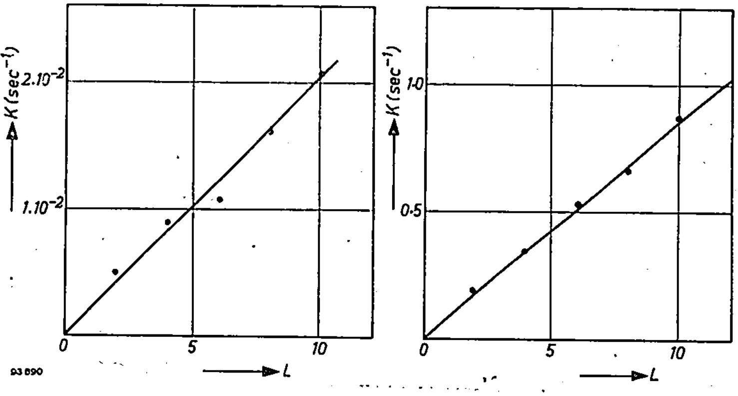

Fig. 6. The values of k from the formula $V = V_m(1 - e^{-kt})$ for the system AL/AL$_2$0$_3$/electrolyte (left) and for the system Ta/Ta$_2$O$_5$/electrolyte (right) as a function of the intensity of irradiation.

Figure 7 shows the proportionality between i and L for the system Ta/Ta_2O_5/Cu in which the electrolyte had been replaced by a transparent layer of copper.

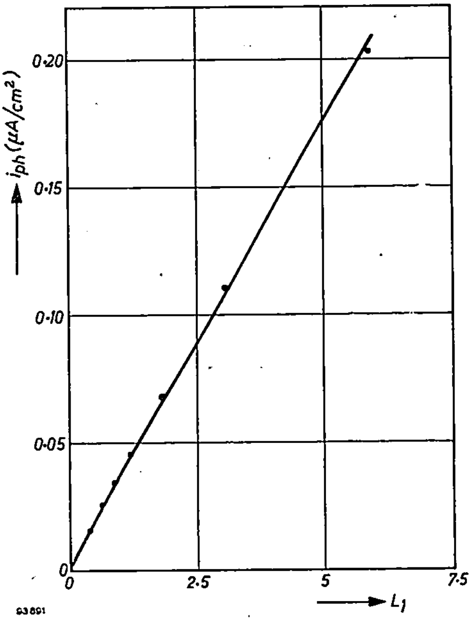

Fig. 7. The photocurrent for the system Ta/Ta_2O_5/Cu, as a function of the intensity of irradiation, no auxiliary voltage being applied.

3.4. *The influence of the thickness of the layer on the photocurrent and the value of k.*

Figure 8 gives the photocurrent as a function of the thickness of the layer, no voltage being applied (for constant intensity of irradiation). The

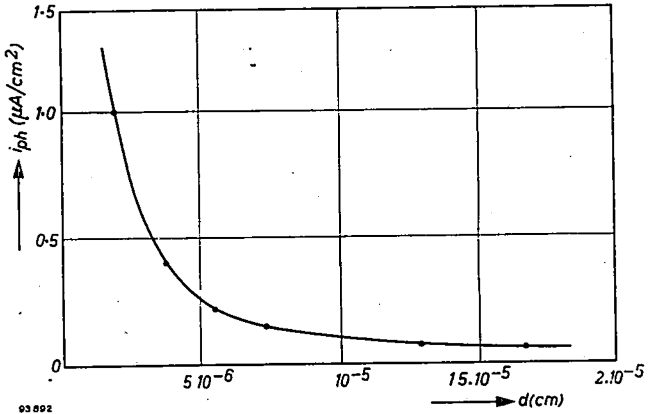

Fig. 8. The photocurrent at constant irradiation with varying thickness of the layer, no auxiliary voltage being applied. The system is Ta/Ta_2O_5/electrolyte.

photocurrent decreases rapidly with increasing thickness. We have found earlier that the photovoltage which is built up during irradiation can be written as $V_{\text{photo}} = V_m\ (1 - e^{-kt})$. The photocurrent is proportional to $(\mathrm{d}V/\mathrm{d}t)_{t=0}$ when measured without an auxiliary voltage and resistance in the circuit. Thus i is proportional to k and again we find k proportional to L.

We also measured k as a function of the thickness under constant intensity of irradiation, this intensity being the same as used with the measurements of fig. 8. Figure 9 shows that k decreases by a factor of 5 when the thickness of the layer increases by a factor of 30. We will come back to this question in sec. 4.4.

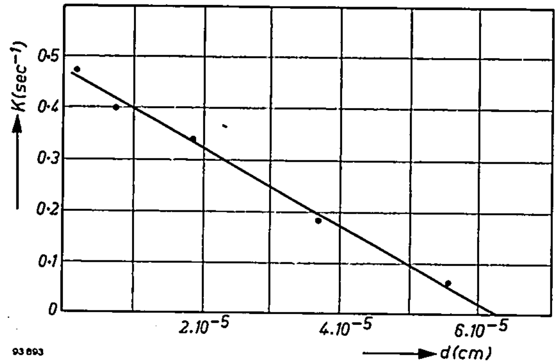

Fig. 9. The constant k at the same constant irradiation as used in fig. 8, as a fuction of the thickness of the layer. System Ta/Ta_2O_5/electrolyte.

So if we want to find the dependence of i on the thickness (L constant), we must multiply the values of i by a factor k_0/k_d, where k_0 is the value of k for a very thin layer. In this way the fact that k changes with increasing d is eliminated. After having done this for the values of i from fig. 8, with the aid of the values of k from fig. 9, we plotted $1/i$ against d. Figure 10 shows the result; we find id = constant for a constant irradiation.

4. Conclusions

4.1. *Photoeffect and i-V characteristics*

To explain the phenomena described, we have to consider the band structure of the oxide layer in contact with the base metal Ta, Al at one side and the electrolyte, semi-conductor or thin metal layer at the other side. We assume that the work function (φ_1) for electrons from the base metal (Ta, Al) to the oxide layer is smaller than the work function (φ_2) for electrons penetrating from the other electrode (electrolyte, semi-conductor or transparent metal layer) into the oxide layer. The situation is shown in fig. 11. Although the electrolytically formed layers are mainly amorphous, the fact that a photocurrent is produced proves that there is electronic conduction, and thus we may speak of a conduction band. We draw our conclusion about the difference in work functions from other experiments which gave rise to the assumption that the oxide layer at the side of the base material on which the oxide layer has grown contains extra metal ions [8]).

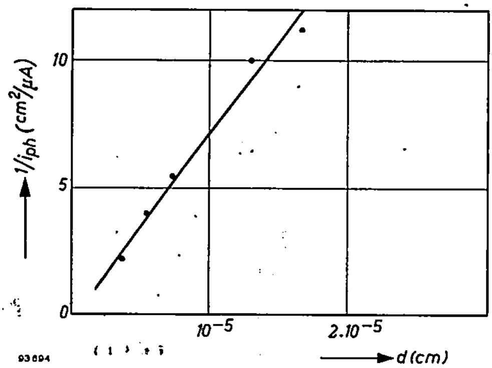

Fig. 10. The reciprocal value of the photocurrent at the same constant irradiation as used in figs 8 and 9 as a function of the thickness of the layer, the photocurrent being corrected for the changing k. It appears that $i_{\text{ph}}.d$ is constant. The system is Ta/Ta_2O_5/electrolyte.

When during irradiation electrons are liberated and are raised from the valence to the conduction band these electrons will drift to the metal even without the application of an auxiliary voltage. If we apply a voltage with the electrolyte negative we see that the slope of the empty band in fig. 11 will increase and that more electrons will be able to cross the layer (fig. 1).

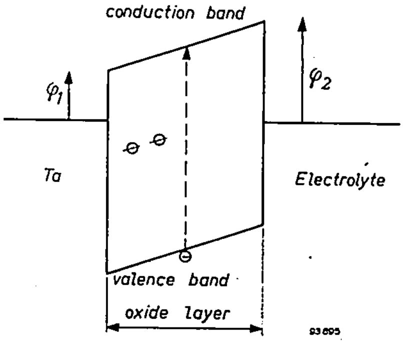

Fig. 11. The position of the energy levels in the system Ta/Ta_2O_5/electrolyte.

As soon as we apply a voltage with Ta negative (forward direction), the slope will decrease and the photocurrent will also decrease, whereas the forward current of opposite sign will increase. At a given value of the voltage no current will flow through the system (fig. 2, A). At a still higher voltage (Ta neg.) the conduction band will be horizontal and, although a forward current is passing, irradiation will have no influence on the current (fig. 2, B). At still higher voltages the photocurrent is reversed.

The resemblance to a barrier-layer photocell is remarkable. The *i-V* characteristics for dark and photocurrent behave in the same way. In our case we have a well-defined insulating layer of constant thickness. With the barrier-layer photocell we are dealing with a Schottky barrier, where the space charge, which comes into existence after the contact between metal and semi-conductor has been established, causes a curvature of the potential in the semi-conductor (fig. 12) [9]).

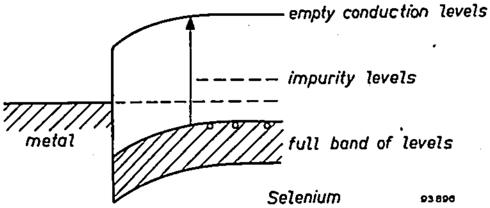

Fig. 12. The position of the energy levels in a barrier-layer photocell.

In this case electrons are liberated from the full band and are raised into the empty band, where they move under the influence of the field to the metal. This process continues until a counter e.m.f. is built up and the empty band has a horizontal position.

A difference between the system Ta/Ta_2O_5/electrolyte and the barrier-layer photocell consists in the fact that for small voltages the forward current of the first system is much smaller than for the second. As soon as a photovoltage is produced the polarity for both systems is such that the metal constitutes the negative pole and a forward current is passing through the system, which is opposite to the photocurrent. If there were no forward current the photovoltage would have a constant value, independent of the intensity of irradiation. For a small forward current, as is the case with our system Ta/Ta_2O_5/electrolyte, the photovoltage is equal to $\varphi_2 - \varphi_1$ for photocurrents which are large compared with the forward current. For weak intensities it is smaller. For forward currents of the order of the photocurrent, as is the case with barrier-layer photocells, the photovoltage is strongly dependent on the intensity of irradiation. Figure 13 gives the photovoltage for a selenium cell as a function of the intensity of irradiation.

1.2. *The photo e.m.f.*

We will try to give an explanation of the inertia of the photovoltage as a function of time, and the fact that the photovoltage would be independent of the intensity of the irradiation if the electrons did not leak back from the metal through the oxide to the electrolyte. The latter fact is rather easy to understand. The photo e.m.f. must be equal to the difference of the work functions φ_2 and φ_1. As soon as $V_{\text{photo}} = \varphi_2 - \varphi_1$, the conduction band in the oxide layer will be in a horizontal position and the increase of the photovoltage will stop (fig. 4).

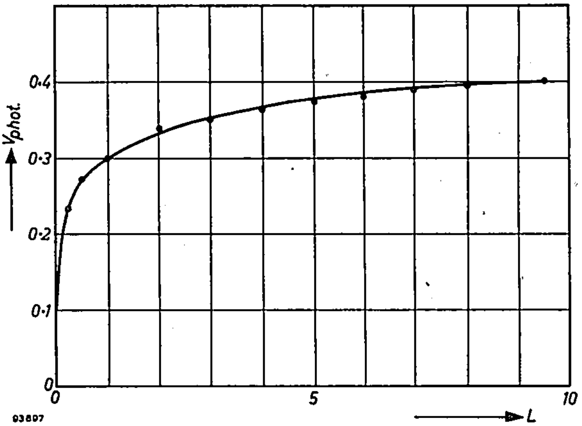

Fig. 13. The photovoltage for a selenium cell as a function of the intensity of radiation.

To explain the build-up of the photovoltage as a function of the time we assume that an electron liberated by a light quantum will have a lifetime τ before it is annihilated. In this time τ it travels as a result of the existing field F along a distance $d = \tau v$, v being the drift velocity proportonal to the field.

The number of electrons which arrive per second at the Ta electrode (fig. 11) will be proportional to the intensity of the light L and to the distance d, i.e., $\mathrm{d}n/\mathrm{d}t = \beta L F$.

Now F can be written as follows: $F = (\Delta\varphi - and)/d$, because the potential difference is equal to $\Delta\varphi$ diminished by the potential difference over the oxide layer, caused by the n electrons which have arrived on the Ta electrode. This potential difference is proportional to nd. So we write $\mathrm{d}n/\mathrm{d}t = \beta L(\Delta\varphi - and)/d$, where a and β are constants. After integration we find $n = (\Delta\varphi/ad)\,(1 - e^{-\beta aLt})$. Hence $and = V_{\text{photo}} = \Delta\varphi(1 - e^{-pLt})$, where $p = \beta a$. We found experimentally that $V_{\text{photo}} = V_m(1 - e^{-kt})$ which is the same formula as we deduced above. Thus $V_m = \Delta\varphi$ and k is proportional to L, in close agreement with our experimental results. Here we did not take into account that electrons are leaking back from the metal through the oxide layer, to the electrolyte.

4.3. *The photocurrent without an auxiliary voltage*

It was found experimentally that $V = V_m\,(1 - e^{-kt})$; hence $\mathrm{d}V/\mathrm{d}t =$ $V_m k\, e^{-kt}$.

The current i_0 through the short-circuited system is equal to $C(\mathrm{d}V/\mathrm{d}t)_{t=}$ and thus $i_0 = CV_m k$. Now $C \propto 1/d$ and $k \propto L$ and because V_m is independent of L, $i_0 d \propto L$. So for $d =$ constant we find $i_0 \propto L$ and for constant L, $i \propto 1/d$. This is in agreement with our experimental results.

It should be mentioned that in fact we have to consider both electron and hole movement, as only this makes a mechanism with a "lightpump" possible. This implies that in fact our calculations do not apply especially to electrons, but (as the number of electrons and holes is equal) to the charge carriers with the lowest mobility. These might be the electrons but it is not necessarily so. Calculations show that a very low mobility (of either charge carriers) is sufficient for producing the observed photocurrents.

4.4. *The influence of the thickness of the layer on the constant k*

We found in sec. 4.2 that $k = \alpha\beta L$, in which α and β are constants. In the first instance it is not evident why α and β should depend on the thickness d. The light L however will be absorbed according to $L(x) = L_0 e^{-x/\mu}$, L_0 being the intensity at $x = 0$ and μ determining the absorption coefficient.

Approximately we may replace L in sec. 4.2 by the average light intensity, i.e.

$$L = \int_0^d \frac{L(x)\,\mathrm{d}x}{d} = L_0\,\frac{\mu}{d}\,(1 - e^{-d/\mu})\,.$$

In first approximation this can be written $L = L_0\,[1 - (d/2\mu)]$, which implies $k = k_0\,[1 - (d/2\mu)]$, which is qualitatively in good agreement with experiments.

The authors wish to thank Mr K. Compaan for helpful discussions.

Eindhoven, October 1957

REFERENCES

1) J. Lifschitz and M. Reggiani, Z. Phys. Chemie A **155**, 431-450, 1931.
2) L. Young, Trans. Faraday Soc. **50**, 164-171, 1954.
3) G. Rosenthal, Z. Phys. **99**, 607, 1936.
4) W. Bär, Z. Phys. **115**, 658-678, 1940.
5) W. Walkenhorst, Z. techn. Phys. **22**, 14-21, 1941.
6) W. Ch. van Geel and B. J. J. Schelen, Philips Res. Repts **12**, 240-248, 1957.
7) O. von Auwers and H. Kerschbaum, Ann. Phys. **7**, 129-175, 1930.
8) W. Ch. van Geel and J. W. A. Scholte, Philips Res. Repts **6**, 54-74, 1951.
L. Young, Trans. Faraday Soc. **51**, 1250-1260, 1955.
9) N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals, Clarendon Press, Oxford, 1940, p. 195.