

PREPARATION OF PHOTOCONDUCTORS CONSISTING OF MICROCRYSTALLINE CADMIUM SULPHIDE AND CADMIUM SELENIDE¹

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Electrical conductors or semiconductors that alter their conductivity as a function of the intensity of radiations falling on them, have been known for a long time. As a classic example for such *photoconductors*, metallic selenium can be mentioned. At a later period, a number of further compounds showing photoconductivity, were discovered. The sulphides, selenides and tellurides of zinc and cadmium are known as an important group of photoconductors; however, photoconductive compounds of a quite different chemical nature are known as well.

Cadmium sulphide and selenide photoconductors according to their design can be divided into two groups; either they consist of a *single crystal* or of a *microcrystalline layer*. The preparation of microcrystalline cadmium sulphide cells is the subject of a number of publications [1, 2, 3]. The procedures and equipments described in these publications are, however, very complicated; for instance, procedure [2] needs a mercury diffusion pump made of fused quartz, most of the procedures need equipment for cathode-sputtering, etc. — The preparation of artificial single crystals of cadmium sulphide had been reported as early as the previous century [4]; however, their production on a larger scale was first made by FRERICHS [5]. According to his method, cadmium vapour and hydrogen sulphide are made to react in a space heated to about 1000° C and the cadmium sulphide thus obtained crystallises then from the vapour phase.

As Frerichs' equipment is much simpler than those described for the preparation of microcrystalline layers, it seemed worth while trying to prepare such layers with this simpler equipment. This looked to be hopeful, as it is easier to prepare microcrystals, than well-developed single ones. Crystal seed formation and crystal growth are — as it is generally known — governed primarily by conditions of supersaturation. An existing crystal seed will grow only if the medium is supersaturated in respect to the material of the crystal. If the supersaturation remains below a certain limiting value, it is only the

¹ Hungarian Patent No. 145.184.

existing crystal nuclei that will grow, but there is no possibility for the forming of new crystal seeds. However, if the supersaturation exceeds this critical value, spontaneous seed formation will occur, and a great number of tiny crystals will appear. In order to grow large single crystals a small degree of constant supersaturation should be maintained. FRERICHS achieved this by slowly cooling the reaction zone at a uniform rate. On the other hand in order to obtain a microcrystalline product we have to produce a considerably higher degree of supersaturation, which can be achieved by choosing lower reaction temperatures.

According to the above, experiments have been made with an apparatus similar to that of FRERICHS [4], with the simplification that the temperature programm device was omitted.

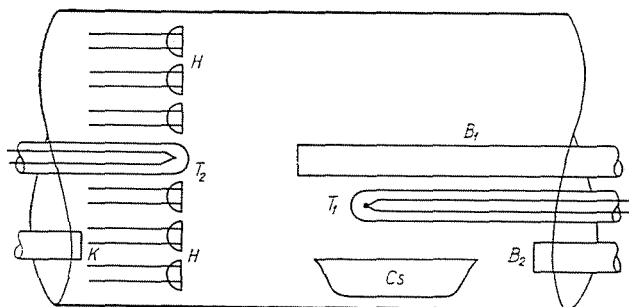


Fig. 1. Apparatus for producing microcrystalline layers of photoconductors

The apparatus (Fig. 1) consists of a quartz tube containing cadmium metal in a little crucible (*Cs*). At one end of the quartz tube there are two inlet tubes; a shorter one (*B 2*) for the introduction of hydrogen as a vehicle gas, and a longer one (*B 1*), which extends over the crucible into the reaction zone, for the introduction of the hydrogen sulphide (or selenide). In the reaction zone there are supports (*H*), upon which the microcrystalline cadmium sulphide or selenide layer is precipitated. These supports are glass hemispheres with a plane ground on one side of them, bearing evaporated gold electrodes and contact wires. Between the two gold electrodes there is a slit of 1 mm width, which will form the effective area of the cell. — Two thermocouples (*T1* and *T2*) are used in order to measure the temperature of the cadmium vapour and that of the reaction zone, further an outlet tube (*K*) for unreacted gases. The operation of the apparatus is extremely simple: air is expelled from the quartz tube by a stream of hydrogen; when the tube is made free of air, the cadmium is heated to about 550° C, and the reaction zone to about 500° C. Hydrogen sulphide (or selenide) is then introduced; precipitation of the microcrystalline layer on the walls of the quartz tube and

on the supports readily occurs. While a run for growing single crystals lasts for 16 to 72 hours [6, 7], the above procedure takes only about 15–20 minutes; moreover, a number of supports can be used at the same time, so this method is highly productive.

The sensitivity of the cells prepared in the above way has been measured by the circuit shown in Fig. 2. Cell voltage was kept at 100 volts throughout the measurements by a potentiometer (P) and a voltmeter (V). The current flowing through the cell (C) was measured by a multi-range electronic microammeter (E). The circuit contained also a current limiting resistor (R) for safety. The current was measured once in complete darkness (i_0) and once with an illumination of 1000 luxes of white light (i). The sensitivity (s) of the cells is defined by the formula

$$s = i/i_0.$$

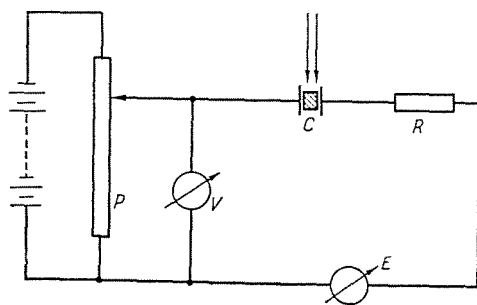


Fig. 2. Circuit used for measuring the sensitivity of photoconductors

The cells prepared by the above procedure show little or no sensitivity at all after completion; full sensitivity is attained only after the cells have been tempered. The tempering of cadmium sulphide photoconductors is described in literature, but the recommended temperatures show a wide scattering; the tempering of cadmium selenide has not yet been described. Therefore a systematic study has been made on the effects of tempering. Temperings were made in air at atmospheric pressure. During each experiment the temperature was kept at a constant value and the temperature of each successive tempering was higher than that of the previous one. Each tempering lasted 5 minutes. After each heating the cells were cooled to room temperature and the sensitivity was measured. The results are shown in Fig. 3, where the logarithm of the sensitivity is plotted against the temperature of tempering. It can be seen that the sensitivity is growing up to a certain temperature, while at higher temperatures it falls again. Selenide cells are especially sensitive to such an *overt tempering*; a slight overtempering of 10 to 20° C practically destroys sensitivity. The tempering affects also the resistance of the cells to a great degree: the dark resistance increases by some two or three orders of

magnitude after tempering. As it can also be seen from Fig. 3, the sensitivity of the sulphide cells is about 10^4 , and that of the selenide cells about 10^3 . Fig. 3 represents typical curves obtained as an average of measurements

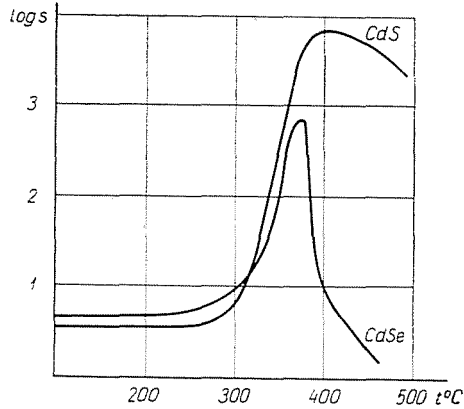


Fig. 3. Sensitivity of photoconductors plotted against temperature of tempering

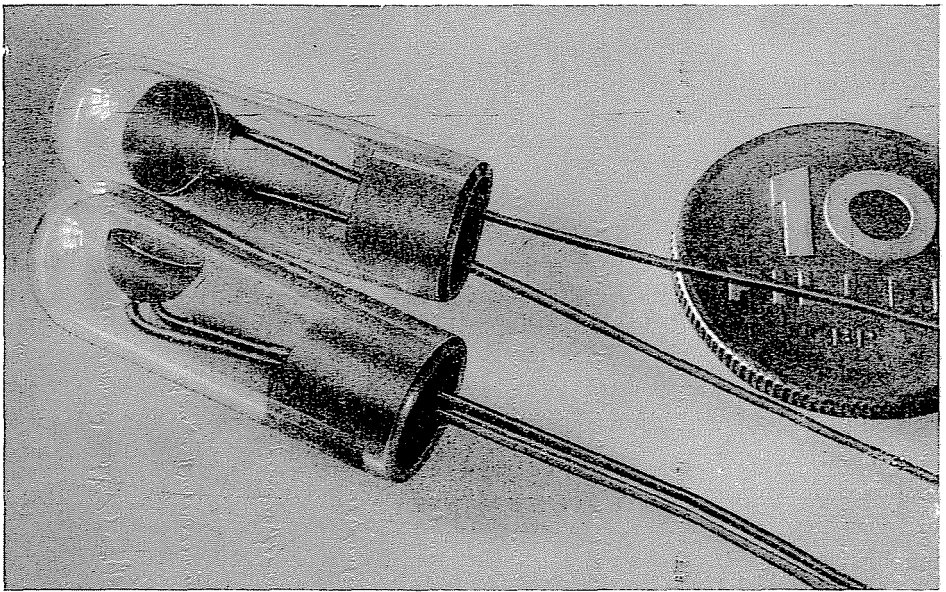


Fig. 4. Photoconductive cells

made on a number of cells, showing more or less deviations from the mean values given; moreover, there were cells which showed little or no increase of sensitivity after tempering.

After tempering the cells were sealed in a suitable bulb (Fig. 4). The most sensitive sulphide cell, prepared by the above procedure, had a sensitivity

of 22 000 and the most sensitive selenide cell of 5400; the above value for the sulphide cell is normal, but the sensitivity of the selenide one is uncommonly high. (The guaranteed sensitivity of the Zeiss selenide cells is 100.)

Cells showing low sensitivity after tempering were subjected to repeated temperings. (This procedure has as yet not been mentioned in literature.) The experiments were carried out with selenide cells; temperings lasted — as in the previous experiments — 5 minutes each and the temperature was 375° C. After repeated temperings the sensitivity of the cells showed a further increase. The sensitivities of four of the cells after repeated temperings are given in Table 1.

Table I

Number of cell	Number of temperings					
	0	1	2	3	4	5
1	1	150	350	500	—	—
2	1	40	80	160	154	100
3	1	55	110	180	130	—
4	1	57	184	210	165	—

As it can be seen, repeated tempering causes a considerable increase in sensitivity; the occurrence of overtempering can also be observed.

The data concerning cell no. 4 deserve special attention. The first tempering of this particular cell lasted one hour in contrast to the routine tempering of 5 minutes, while its further temperings lasted, as usually, only 5 minutes. An increase of sensitivity after the second and third tempering can be seen, just as with the other cells. This suggests that the effectiveness of repeated temperings is not caused by the increase of total tempering time itself, as the first tempering of cell no. 4 alone lasted considerably longer, than the total time of temperings of the other cells. This result is contradictory to VEITH's [1] theory, according to which the active compound forms only during tempering. The above results indicate that it is the number of heating- and cooling cycles, and not the total time of temperings, that may be considered as the effective factor; consequently, it can be assumed that the effects of tempering are brought about by influencing the structure of the microcrystalline layer.

The spectral distribution of the sensitivity of these cells was measured by the monochromator of a type IKSz-11 spectrophotometer. The intensity of light was brought to the same value at each wave-length as measured by the thermocouple sensing element of the instrument, on the assumption, that the sensitivity of the thermocouple is practically constant throughout the spectral

range employed. The spectral distribution curves are shown in Fig. 5 (the ordinate in arbitrary units); these curves are similar to those already known from literature.

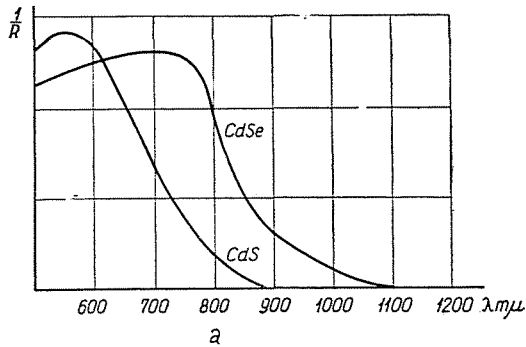


Fig. 5. Spectral distribution of sensitivity of photoconductors

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Summary

A simple, new method is described for the preparation of microcrystalline cadmium sulphide and selenide photoconductive cells by vapour-phase reaction. A new method of repeated tempering has been developed, which, in the case of selenide cells, results in a high sensitivity previously unattained. The spectral distribution of the sensitivity of the cells has been measured.

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