The Influence of Mercury Vapour on Selenium Rectifiers and Selenium Photoelements

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LETTERS TO THE EDITOR

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Selenium rectifiers, if used or stored in a room in which the atmosphere is contaminated with mercury vapour, lose their high resistance in the blocking direction and become useless, as previously stated by the author (1943 a, b) * A similar destructive effect has been observed on selenium photoelements This effect can be accelerated by circulating a stream of air, saturated with mercury vapour at room temperature, through the closed box which contains the element The results of the experiments performed by the above method may be summed up in the following statements

(i) In the circumstances mentioned above, mercury vapour diffuses through the counter-electrode of the rectifier disc (possibly through its pores) and the selenium layer in immediate contact with it is gradually converted into mercuric selenide This is an excess semi-conductor of high conductivity (Henisch and Saker 1952).

(ii) During this process, the form of the function f in the blocking voltage–current characteristic $I_r=af(U_r)$ remains unaltered, and it is only the factor a which gradually increases In other words, the back current will be increased at every voltage in the same proportion. This has been found to be true, with some precautions, from 0·1 volt to 15 volts

(iii) The forward current remains unaltered, except in the neighbourhood of the origin, where the current must also increase in order to preserve the continuity of the characteristic.

(iv) The open-circuit e m f of photoelements decreases rapidly under the influence of mercury vapour, while the primary (short circuit) photocurrent was found to remain unaltered.

Theoretical consequences. The statements under (i), (ii) and (iii) are in good accordance with Schottky's barrier layer theory (1942). Assuming that in consequence of the conversion of the boundary layer of selenium into mercuric selenide only the conductivity κ_B on the boundary is increased, it follows from Schottky's equation (13) that the back current will also be increased in the same proportion; while in accordance with equation (23) the capacity and its variation with the reverse voltage remains unaltered. Similarly, statement (iv) is in good agreement with the fundamental conception (Schottky 1930) that the e m.f of the photoelement is identical with the potential drop of the photo-current flowing back through the blocking resistance; therefore it will vanish if the blocking resistance disappears Furthermore, it follows from these observations that the mechanisms which control the photo-sensitivity, the rectification properties and the self-capacitance, and which together form the true physical model of the photoelement (Kőrösy and Selényi 1931, 1932), are, so to speak, independent of one another · within certain limits one can damage the crystal detector without influencing the photo-response and the capacitance.

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* I learned later, from oral communications and from the B.I.O.S. Final Report No. 725, " German Research on Rectifiers and Semi-Conductors ", that this effect has been still earlier recognized. The explanation, however, given in this Report on pages 31 and 33 (formation of a film of mercury by passing the selenium layer at its edges) is entirely insufficient.