The Effect of Mercury on Selenium

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The Effect of Mercury on Selenium

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ABSTRACT. It is shown that the interaction between crystalline selenium and liquid mercury or mercury vapour results in the formation of mercuric selenide. When produced in this form, this material is an excess semiconductor of high conductivity. The associated volume and surface diffusion have been investigated using radioactive ^{203}Hg. Mercury added to selenium *before* the crystallization process results in material of high resistivity This is ascribed to a reduction of the positive hole mobility.

§ 1. INTRODUCTION

In view of the great industrial applications of semiconducting selenium in the manufacture of rectifiers and photocells, the effect of accidental or deliberately added impurities is a problem of considerable practical importance. Among the various impurities which are important from this point of view, mercury occupies a special place because of the rapidity with which it acts upon selenium and the drastic nature of its effects. The knowledge available at the beginning of this investigation can be summarized as follows:

(*a*) The first recorded observations concerning the effect of metallic mercury on the resistance of selenium specimens appear to be due to Moss (1877). Temporary contact with mercury was found to result in a pronounced decrease in resistance.

(*b*) Brown (1913) found that the resistance of selenium specimens crystallized in the presence of mercury vapour increased on exposure to light. This observation was later confirmed by Tisdale (1918). No clear distinction between bulk and contact phenomena was made in these experiments and the exact interpretation of these observations is therefore uncertain.

(*c*) Williams and Thompson (1941) have reported on the rapid and destructive influence of mercury vapour on selenium rectifiers. In the presence of mercury vapour the rectification efficiency falls until the forward and reverse resistances of the rectifier discs become almost equal.

(*d*) Henisch and François (1950, 1951) have reported that the thermo-electric effect decreases rapidly in the presence of mercury vapour. After prolonged exposure thermo-electric effects of reversed polarity were observed. On the other hand, considerable quantities of mercury (e.g. up to 1·6% by weight) could be added to the selenium before melting and crystallization without causing any significant change of thermo-electric properties.

The experiments described in the following sections were carried out in order to obtain further information on the phenomena involved and, in particular, to investigate the extent to which mercury can penetrate into the selenium specimens. The results show that there is penetration to considerable depths which may be due to diffusion through the lattice or along grain boundaries. The principal electrical effects are shown to be due to the formation of mercuric selenide at the surface. The presence of this distinct phase has been confirmed by x-ray analysis. There is also evidence, from experiments with radioactive mercury, of rapid surface diffusion.

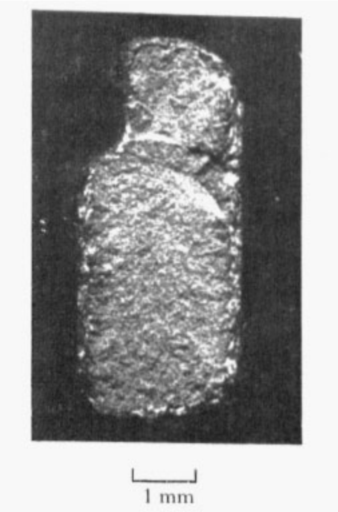

Fig. 2. Photomicrograph of a section through a selenium specimen after immersion in liquid mercury at 100° c for 100 hours.

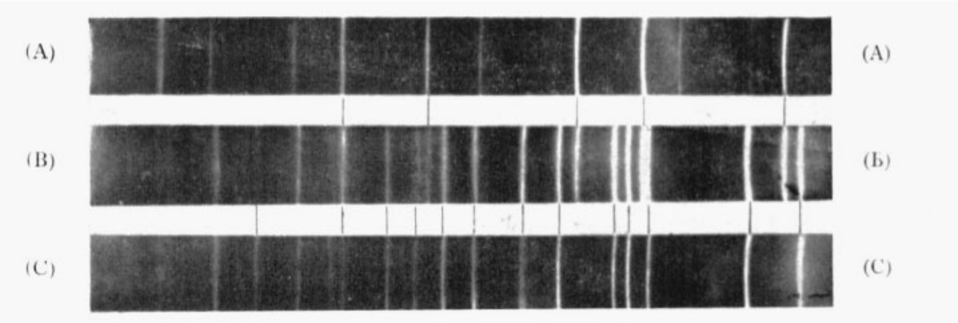

Fig. 3. X-ray powder photographs of:

(A) A surface layer detached from the specimen shown in fig. 2.
(B) Powdered crystalline selenium after exposure to mercury vapour at room temperature.
(C) Pure crystalline selenium.

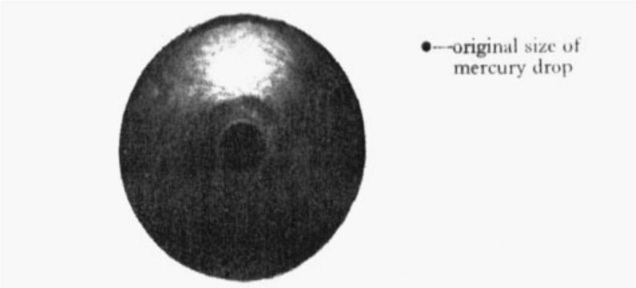

Fig. 7. Autoradiograph showing surface diffusion of mercury on selenium. A selenium rectifier disc (concentric assembly type) without counter-electrode was used for this experiment.

§2. EXPERIMENTAL METHODS AND RESULTS

Effect of Mercury added before Crystallization

Measurements of bulk resistivity were carried out on a series of rectangular specimens (20 mm × 5 mm × 3 mm) to which current electrodes and potential probes of gold had been evaporated *in vacuo*. These specimens were prepared by adding varying amounts of mercury to amorphous selenium powder which was then melted. After subsequent solidification, the resulting glassy solid was crushed to a fine powder, moulded to the above shape in a press and converted to the crystalline modification by heat treatment for 30 minutes at 210° c. The average density of these specimens was 4·27, compared with the x-ray density of 4·82, and did not differ significantly as between the various groups of different mercury content. The table gives the results in summarized form and shows that there is a pronounced *increase* of resistivity with increasing mercury content.

Specimen group	a	e	d	f
Mercury content (% by weight)	0	0·008	0·158	1·58
Mean resistivity (ohm.cm)	469 ± 90	618 ± 70	2766 ± 300	22060 ± 2000

Effect of Mercury Vapour on the Resistance of Crystalline Specimens

Specimens of the type described above were kept in a closed vessel in the presence of mercury, first in air at atmospheric pressure and later at reduced pressures. Typical results for the various groups are shown in fig. 1. It will be seen that the effect of mercury is in every case more rapid at reduced air pressures. No consistent differences were observed as between specimens belonging to the different groups. By the successive removal of thin surface layers and repeated measurements of resistance it was possible to estimate the depth of penetration. For the specimens referred to in fig. 1 this depth was of the order of 5×10^{-3} cm at the end of the experiment. By comparison, the thickness of the barrier layer on a selenium rectifier is usually estimated to be considerably smaller, e.g. between 10^{-5} and 10^{-4} cm. In view of the speed of

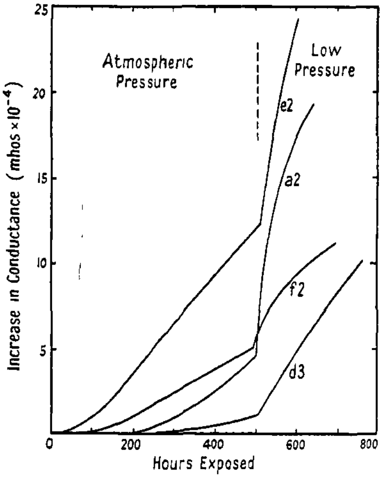

Fig. 1. Effect of mercury vapour on the conductance of selenium specimens.

the above diffusion process, such a layer could be rapidly penetrated in places which are not thoroughly protected by the counter electrode. Alternatively, the barrier layer could be short-circuited by mercury penetration near the edge of the counter electrode.

Action of Liquid Mercury on Selenium

Specimens of the type described above and some others of higher density (4·75), prepared by a casting technique, were kept immersed in liquid mercury at a temperature of 100° c for 100 hours. Sections were then made through the material and one of these is shown in fig. 2 (Plate). The appearance of the surface regions is visibly changed by this treatment, to a depth of about 0·25 mm. Accurate electrical measurements on the surface layer itself were not practicable, but it was confirmed that the layer has a high conductivity.

X-ray Tests

For purposes of identification and comparison, x-ray powder photographs were taken of normal crystalline selenium and also of two specimens which had been exposed to the influence of mercury in two different ways; fig. 3 (Plate) shows the results. The photograph A refers to a surface layer detached from a specimen similar to that shown in fig. 2. The lines are characteristic of a zinc-blende structure and lead to a lattice constant of 6·04 Å. The value quoted by Wyckoff (1931) for mercuric selenide is 6·07 Å. In view of the fact that all these specimens are expected to deviate considerably from stoichiometric composition, the two results are regarded as being in reasonably satisfactory agreement. Photograph B was obtained with a specimen of selenium which had been kept in the presence of mercury vapour in vacuum for 150 days at room temperature. It will be seen that lines corresponding to pure selenium and mercuric selenide are both represented. This shows partial conversion of the selenium into mercuric selenide.

Thermo-electric Tests

The specimen shown in fig. 2 was subjected to thermo-electric tests. It was clamped in a large electrode which was kept at room temperature, and a second contact of very small area was made by a wire which was heated electrically to about 60° c. The resulting thermo-electric force was then measured by means of a sensitive potentiometer circuit. The hot 'point' contact could be controlled by means of a micro-manipulator which made it possible to explore the thermo-electric properties of various surfaces. Results for measurements across one section of the specimen are shown in fig. 4. It will be seen that the thermo-electric effect changes sign at some distance from the exposed surface. The observed polarities correspond to n-type conduction in the surface region and to p-type in the interior. The magnitude of the thermo-electric power is considerably greater in the interior of the specimen than in the surface region. This is consistent with the previous observation that the surface region has a high conductivity. It is of interest to note that the electrical effects of mercury can be detected beyond the visible boundary of the selenide.

The Contact between Selenium and Mercuric Selenide

The above thermo-electric tests show the existence of a 'p–n contact' between the selenium and the mercuric selenide. The behaviour of such a contact is expected to differ somewhat from that of the more familiar p–n contacts in germanium, in view of the fact that the participating substances have not only a different conduction mechanism but also a different lattice. A simple experiment confirmed the existence of rectification in the expected direction. Fig. 5 shows the voltage–current relation of such a contact as obtained by oscillographic methods. Pronounced hysteresis effects were observed at 50 c/s.

Tests with Radioactive Mercury

In order to obtain more sensitive and direct evidence of mercury penetration some experiments were carried out with the radioactive isotope ^{203}Hg which has a convenient half-line of 43·5 days. The activity resulting from exposure to mercury vapour was measured with a Geiger counter and investigated as a function of depth. Fig. 6 shows typical results. In the dense specimen, B, the distribution follows approximately an exponential law of the form $N_x = N_0 \exp(-x/x_0)$, where N_0 and N_x denote the concentration of mercury at the surface and at a depth x respectively. For specimen B the length x_0 after 100 hours, exposure at room temperature and a pressure of 10^{-2} mm Hg was found to be 9×10^{-4} cm. In the amorphous specimen C it is smaller (e.g. 2×10^{-4} to 3×10^{-4} cm). Specimen A was very porous and a simple exponential distribution could not be expected. The term N_0 was found to be almost entirely determined by the roughness of the surface. It is smallest for surfaces which are highly polished. The depth of penetration measured for crystalline specimens is in agreement with the values estimated from electrical measurements.

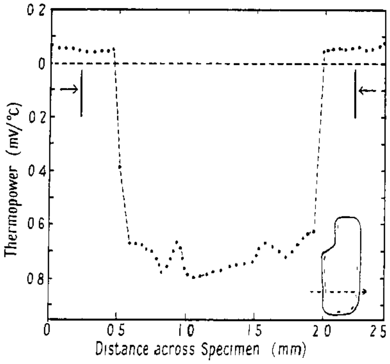

Fig. 4. Variation of thermo-electric properties across a section of selenium specimen exposed to the influence of liquid mercury. The arrows indicate the visible boundary

To test for surface diffusion a small drop of mercury (2 mm in diameter) was placed on a disc of crystalline selenium and kept in a small enclosed vessel for a period of 40 hours. An autoradiograph was then taken and is shown in fig. 7. It will be seen that there is considerable diffusion along the surface. The mosaic structure is not due to the boundaries of individual ordered domains but arises from cracks in the material which are on a much larger scale.

§ 3. DISCUSSION AND CONCLUSIONS

The experiments confirm that the effect of mercury on selenium is not merely a surface phenomenon but is concerned with layers of considerable thickness. When a selenium specimen comes into contact with mercury or its vapour, mercuric selenide is formed on the outside, not only at high temperature as is well known (Mellor 1923), but also at room temperature, though more slowly. When formed under these conditions mercuric selenide is a good conductor of the excess type. The presence of even a very thin film of such a highly conducting n-type material is sufficient to account for the observed decrease in resistance, the reversal of the thermo-electric power already reported, and the deterioration of selenium rectifiers. The experiments, most of which were carried out on micro-crystalline specimens, could not distinguish between penetration of the lattice and diffusion along grain boundaries. The latter mechanism is perhaps more probable in view of the rapidity of the observed surface diffusion effects. The speed of the diffusion process is comparable with that of the thallium diffusion investigated by Gudden and Lehovec (1946).

When mercury is added to a selenium melt, it is able to take part in the subsequent crystallization process and could thus affect the length of the selenium chains (see, for instance, Krebs 1951). Its influence on the electrical properties of the material would thus be quite different from that of mercury added by diffusion after crystallization. The results of the resistivity measurements quoted in the table, together with the evidence derived from previous thermo-electric tests (Henisch and François 1950), indicate that mercury added before crystallization affects the mean free path of the carriers but not their concentration.

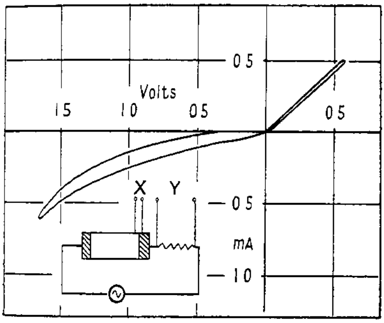

Fig 5 Voltage—current relation of a contact between selenium and mercuric selenide

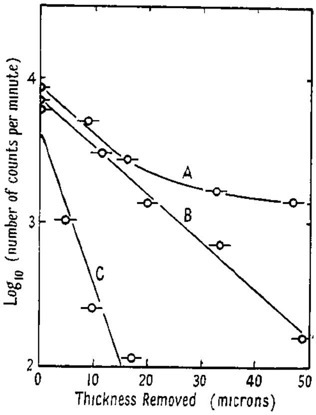

Fig. 6 Mercury concentration (proportional to number of counts) as a function of depth.

It seems desirable that experiments of the type here described should also be carried out on single crystals of selenium. The detailed mechanism of the interaction could also be usefully investigated by micro-balance techniques of the type successfully used in the study of oxidation processes. Lastly, as far as is known, mercuric selenide has not yet been systematically investigated for electrical properties and, in view of the interesting properties of other selenides, such an investigation is thought desirable.*

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*A publication by A. I. Blum and A. R. Regel on the "Electrical Properties of Solid Solutions of Mercury-selenide and Selenium" (*J. Tech. Phys., USSR.*, 1951, **21**, 316) has come to the authors' notice since the preparation of the present paper.

§4. ACKNOWLEDGMENTS

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Impurity Scattering in Oxide Semiconductors

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ABSTRACT The oxide semiconductors are characterized by relatively high concentrations of impurity centres and low electron mobility It is suggested that electron scattering by neutral impurity centres makes an important contribution to the resistivity of these materials The familiar relation $\log \sigma_0 = \alpha + \beta\epsilon$ together with the theory given by Busch are discussed and an alternative explanation involving impurity scattering and a dependence of ϵ on N is given This is compared with experimental results for several oxides, including measurements by the author on the $Fe_2(Ti)O_3$ system

§1. INTRODUCTION

ONE of the features which appears to differentiate the oxide semiconductors from those, such as germanium and silicon, in which the binding is covalent is the high concentration of impurities* required in the former to provide conductivities of the order of 10^{-1} or 10^{-2} $(\Omega\ \mathrm{cm})^{-1}$. This is illustrated in the table, where concentrations and conductivities are given for three oxides and for germanium.

	Type of impurity	Lowest conductivity $(\Omega\ \mathrm{cm})^{-1}$ $N=0$	Impurity concentration	$\sigma(\Omega\ \mathrm{cm})^{-1}$
Nickel oxide	Substituted lithium	$10^{-7}-10^{-8}$	$6{\cdot}3\times10^{21}$	10^{-1}
Ferric oxide	Substituted titanium	$10^{-8}-10^{-9}$	$7{\cdot}8\times10^{20}$	10^{-2}
Magnesium titanate	Excess titanium	10^{-14}	$4{\cdot}2\times10^{21}$	5×10^{-2}
Germanium	Substituted aluminium	$10^{-1}-10^{-2}$	$6\ \times10^{19}$	2×10^{2}

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* Throughout this paper the word 'impurity' has been used to describe lattice defects producing electronic conductivity, irrespective of whether foreign atoms are involved. Although this is not entirely satisfactory, it leads to the accepted term 'impurity scattering'.