58. *On Thermoelectric Phenomena of Thin Metallic Films.*

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At the Annual Meeting of the Physico-Mathematical Society of Japan, 1926, Messrs. T. TSUTSUI and M. TAMANO¹⁾ read a report on the thermoelectric phenomena observed when an apparently homogeneous wire is subjected to local heterogeneous heating. It was considered interesting to investigate the allied phenomena with thin films of different metals deposited upon glass plates. The plates were cut from ordinary window glass into a narrow strip $1 \times 24 \text{ cm}^2$. After depositing the film, it was laid in contact with the plane outside wall of a brass tube, through which water was circulated, in order to keep the plate and especially the leads at the both ends of the film at a constant temperature. The good contact at the lead was secured, without affecting the film, by means of tin foil pressed by a corrugated piece of lead. The thermoelectric effects due to the leads were always insensible. The local heating of the film was given by projecting the image of a 300 watt incandescent lamp upon the film, the straight image being perpendicular to the length of the strip which was laid horizontally, with its plane vertical and facing to the lamp placed in front of it. Disturbing radiations were shielded off by double screens placed between the lamp and the film. The effect of the air current could be put out of account. The galvanometer used was of moving-coil type, with a sensibility of about 2×10^{-8} volts.

At first, films of silver were investigated. They were obtained either by the ordinary chemical methods, or by cathode sputtering executed in a specially devised discharge tube.²⁾ In some cases, chemically deposited films were afterwards thickened by electrolysis in a solution of AgCN and KCN . A copper film superposed upon a silver one was also made by electrolysis of CuSO_4 . Later on, films of bismuth and antimony were prepared by cathode sputtering. Though the results obtained are of a merely qualitative nature, a brief summary

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1) To be published in Sci. Pap. Inst. Phys. Chem. Res.

2) The thicknesses of the films estimated by means of Newton ring method vary from 5 to 10 μ .

of the phenomena observed will be given for the sake of future references.

Uniformly deposited silver film shows no sensible e.m.f. when heated locally. However, if a portion of it be rubbed or polished with paper, chamois with or without rouge, an e.m.f. of the order 10^{-7} volts is observed when the boundary between the polished and unpolished portions is heated. The current is directed from the unpolished towards the polished part, and increases with the number of rubbing, at first rapidly and later slowly. The effect was the same when the entire film was first evenly polished and afterward a limited portion was subjected to a further polishing. Scratching with sand paper, or cutting a grating in the longitudinal direction affects the film in the similar sense as the polishing.

After polishing a portion of the silver film, a celluloid solution was poured on its surface. Upon drying, the celluloid film could be easily stripped off from the glass completely laden with the silver film. The effect of the local heating was quite similar and of the same order of magnitude with the original film on the glass plate. Only when the celluloid behind the polished portion was soaked with amyl-acetate, the effect was observed to change its sign. It could not yet be ascertained whether this change is due to the mechanical strain caused by the deformation of the celluloid or to a chemical effect.

A chemically deposited film was afterwards thickened by electrolysis on its half length.¹⁾ On heating the boundary of the two portions with the different thicknesses and modes of deposition, the thermoelectric current flows from the thinner to the thicker part, i.e. in opposite sense compared with the case of polishing. Thus, it will be seen that the e.m.f. is not determined by the thickness of the film alone. The thermoelectric-current increases with the thickness of the added film (measured by the product current $\times$ time) at first rapidly and later slowly. For a given thickness of the added film, the thermoelectric-current depends on the current density i of the electrolysis; it seems to pass a minimum for a certain value of i .

Plates of different conducting materials were placed in contact with the silver film and one end of the superposed plate was heated in a similar manner. With carbon, tin, bismuth and copper sensible currents have been observed; the last metal showed an e.m.f. in the

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1) The microcrystalline structure of electrolytically deposited silver film has recently been studied by Messrs. HIRATA and KOMATSUBARA of the Kyoto Imperial University. Their results throw some light on the nature of the phenomena here described.

sense opposite to those for the other substances. This may be explained at least qualitatively by the ordinary thermoelectric force of these materials with respect to silver.

Different insulating substances, such as celluloid, ebonite, glass, bakelite, paraffin, glycerin, terpentine etc. were successively placed in contact with, or coated upon the surface of silver films. In the cases of celluloid and paraffin (solid or liquid), e.m.f. of the order 10^{-6} were observed, directed from the coated to uncoated part.

Different electrolytes, i.e. solutions of metallic haloids, sulphate etc. were introduced to the thin interspace between the surface of the silver film and a deck glass placed upon it. With the solutions of NaCl, KCl, ZnCl_2 , Na_2SO_3 , K_2SO_4 and KCO_2CH_3 the current passed from the covered to the uncovered part, while with AuCl_3 and Na_2SO_4 the opposite e.m.f. were observed. The magnitudes of e.m.f. obtained by these means are of the same order with those caused by the coatings of paraffin, i.e. 10^{-6} volts. The magnitudes depend on the concentrations. In most of these cases, the chemical actions are apparent, so that the e.m.f. are probably due to cell actions.

The silver film was placed within an air-tight tube which was evacuated to a few cm. of mercury. No sensible change in the general behaviour could be observed.

A bismuth film¹⁾ upon glass obtained by cathode sputtering shows a remarkable thermoelectric-effect by applying the local heating in the manner above described. It gives an e.m.f. of about 10^{-5} volts at a place, while another place, a few cm. apart from the former, shows an opposite e.m.f. of the same order of magnitude. The transition from the maximum to the minimum is apparently gradual. The distribution of these extreme points seems to vary at random with the different films. The general distribution of e.m.f. is not altered, if the film be heated from the opposite face, viz. from the glass side. It is also not sensibly changed, if the different halves of the breadth of the film at a given point of the length be heated, or if the image of the lamp filament be inclined from the vertical. The film is, therefore, apparently divided into different patches with different properties. On polishing a limited portion of the film, a sensible change is observed, the sense of which is the same with the case of silver. The magnitude of this effect is of the same order as the natural effect.

With Sb film, the number of experiments is scanty. The thermoelectric effect due to the natural heterogeneity is of the same order

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1) The thickness was not determined. The film is not quite opaque.

of magnitude as Bi. However, the effect of polishing appears in the opposite sense compared with the cases of silver and bismuth.

On superposing Ag film upon Bi film by sputtering, a natural heterogeneity similar to the case of the single Bi film was observed. On polishing a portion, an e.m.f. of the order 10^{-5} volts have been obtained. An effect of the same order has also been obtained at the boundary of a Sb film sputtered upon a half length of the glass strip and afterwards covered with Bi film over the entire length.