THE STRUCTURE OF THIN METALLIC FILMS.

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1. *Introduction.*

In an earlier paper,[1] the scattering of light by thin films of metal obtained by evaporation *in vacuo*, has been studied. Some interesting results obtained were given and it was found that a metallic film prepared by the method given in that paper could be divided into three parts, *viz.*, a central metallic part which was highly conducting and scattered very little light, a part which scattered light intensely and had a high electrical resistance, and a part which also scattered light though a little more feebly but was non-conducting. It was suggested from these results that the metallic film has three possible different states : a crystalline state where there is complete regularity of arrangement of atoms and consequently very little scattering of light, a two dimensional gaseous state with random distribution, and an intermediate state between these two. This means that in a metallic film it is possible to have an amorphous modification of the metal. Kramer[2] and Zahn and Kramer[3] have been able to obtain non-conducting films of iron, nickel, platinum, zinc, tin, etc., by cathodic sputtering as also by evaporation *in vacuo*. They suggest that in the anomalous non-conducting condition the metallic film is amorphous. They also find that on heating above a certain critical temperature the non-conducting modification becomes highly conducting. They suggest that this is due to the formation of a metallic lattice at the critical temperature.

All evidence obtained so far regarding the amorphous state of thin metallic films is, however, indirect. More direct evidence can be obtained by examining them by the method of electron diffraction which has been developed in recent years by G. P. Thomson,[4] G. I. Finch[5] and others. The surface of polished metal, for instance, has been shown to be amorphous by

[1] S. Rama Swamy, *Proc. Ind. Acad. Sci.*, A, 1934, 1, 347-353.
[2] J. Kramer, *Ann. der Physik*, 1934, 19, 37-64.
[3] H. Zahn and J. Kramer, *Zs. Phys.*, 1933, 86, 413-420.
[4] G. P. Thomson and G. G. Fraser, *Proc. Roy. Soc.*, A, 1930, 128, 641.
[5] G. I. Finch, A. G. Quarrel and H. Wilman, *Trans. Farad. Soc.*, 1935, 31, 1051.

this method.[6,7,8] The present work was taken up with a view to obtain direct evidence of the amorphous state of metals in thin films by their study with the help of the method of electron diffraction.

2. *Experimental.*

Films of silver and gold were obtained by evaporation of the metals in vacuo in a slightly modified form of the apparatus previously employed.[9] The modification consisted firstly of an improved method of passing the heating leads through the bed-plate as shown in Fig. 1. The heating lead C (Fig. 1) which was a stout copper wire passed through a small brass plate B to which it was soldered to make a vacuum tight joint. The plate B was then stuck on with Metropolitan Vickers' black wax, to one of the faces of a piece of plate glass A, both sides of which had been ground flat with very fine carborundum powder. A glass tube E, the ends of which were ground flat was slipped over C, as shown, for purposes of insulation. The whole arrangement was then passed through holes in the bed-plate D as shown, with a thread of Metropolitan Vickers' vacuum putty F between the ground-glass piece and the bed-plate and pressed home. The vacuum further pulled this down tight thus forming a very effective joint. Further, instead of the conically wound heating spiral previously used, the type of filament recommended by Ritschl[10] was used. The metals were evaporated on to surfaces of freshly split pieces of mica kept inclined in the apparatus as previously.

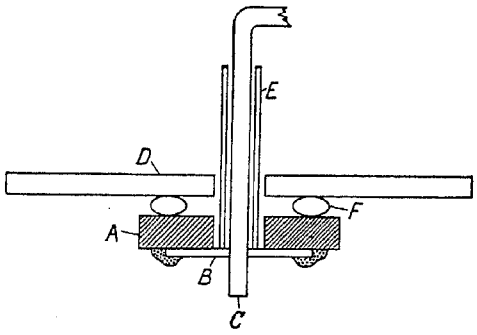

FIG. 1.

The electron diffraction camera was a standard outfit made by "Seemann Laboratorium" using a hot filament of tungsten as the electron emitter. The high potential necessary for working the apparatus was supplied by a standard equipment consisting of a high tension transformer, two hot

[6] R. C. French, *Proc. Roy. Soc.*, A, 1930, **140**, 637.
[7] C. S. Lees, *Trans. Farad. Soc.*, 1935, **31**, 1102.
[8] H. G. Hopkins, *Trans. Ferad. Soc.*, 1935, **31**, 1095.
[9] S. Rama Swamy, *loc. cit.*
[10] R. Ritschl, *Zs. Physik*, 1931, **69**, 578.

cathode rectifiers and two suitable condensers connected in the Greinacher circuit. The outfit was fed on the primary side by a suitable motor generator set working off the 25 cycle 220 volt A.C. supply of the Institute. The potential applied to the electron diffraction tube by these means was found to be quite steady and could be maintained so over quarter of an hour after thoroughly degassing the hot cathode.

The specimens used for examination were cut from various parts of the mica on which the metallic film had been deposited. They were about 2 mm. wide and about a centimetre or so long. In order to avoid burring of the edges of the specimens, which would either hide the diffraction pattern produced by the metallic film or give a pattern of mica dust, the following procedure was adopted. The specimen was kept on a piece of clean Bristol board with the metallic film side up and the edges cut by a single stroke of a keen edged razor held slightly inclined.

Previously to introducing them in the diffraction camera the specimens were soaked and washed in petroleum ether about half a dozen times in order to remove all traces of grease which may have been present. Immediately after washing, they were inserted in the electron diffraction camera and the pattern given by the metallic film on the specimen strip obtained by the well-known method of reflection of G. P. Thomson. Some of the patterns obtained are reproduced in Figs. 2–5.

3. Results.

In Fig. 2 is given a pattern obtained from the central opaque portion of a gold film. This part of the film does not scatter any light whatever. From the pattern in Fig. 2 we find that this part of the film consists of preferentially oriented crystals, the preferred plane being *111* which was parallel to the surface of deposition.

The next part of the gold film studied was green by transmitted light and had the characteristic golden colour by reflected light. The pattern obtained from this part is shown in Fig. 3 and consists of continuous rings showing random orientation of the crystals in the film.

Fig. 4 is a pattern obtained from a part just prior to the start of the intense scattering of light. The pattern consists of rings as before but they are definitely diffuse and the innermost rings (*111* and *200*) are beginning to fuse together showing that the crystallites are much smaller than in the previous part.

In Fig. 5 is given the pattern produced by the part of the film just at the start of the intense scattering of light. In the case of gold films the colour

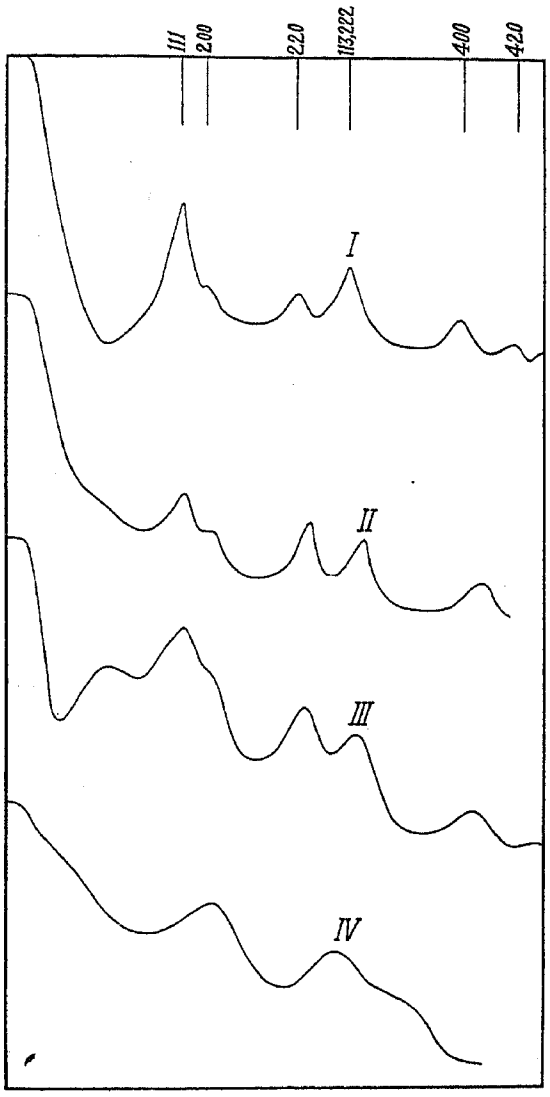

FIG. 6.

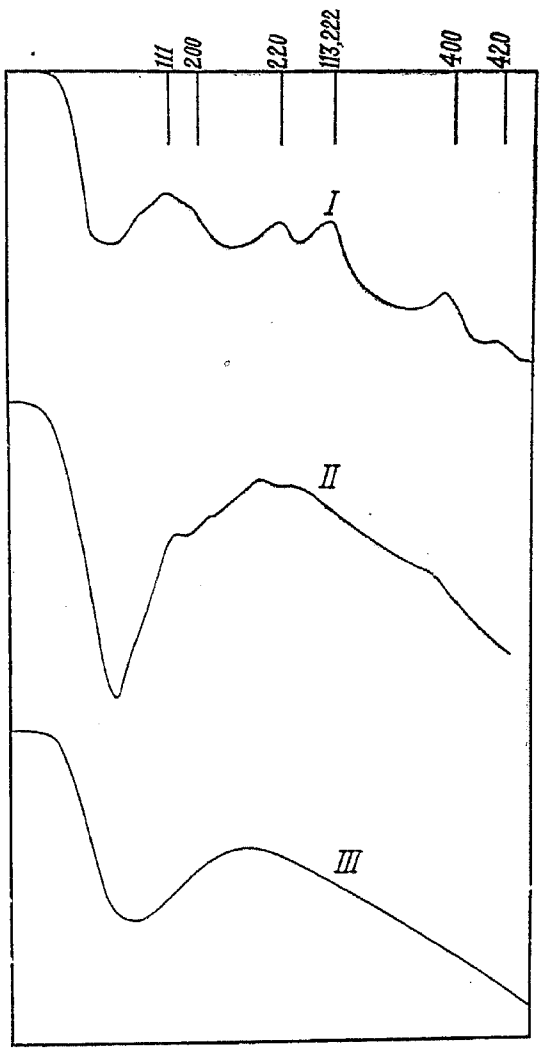

FIG. 7.

of this portion by scattered light is a deep red while for silver it is orange. The pattern from this part of the film consists of one or two haloes, as shown in Fig. 5, indicating thereby that the film is no longer crystalline but amorphous.

It was not possible even to observe the pattern given by the next non-conducting part of the film due to its rapid charging up by the electron beam. But from a study of the previous pattern and the manner in which the sharp rings gradually become diffuse haloes one may reasonably infer that this part of the film is amorphous.

Microphotometer records of these patterns are given in Fig. 6 which bring out the points mentioned above in a striking manner. In Fig. 6, *I* and *II* correspond to the opaque and transparent metallic portions of the

gold film ; *III* corresponds to the part just before the scattering of light starts and *IV* to the portion immediately after the start of the scattering.

Exactly similar results were obtained with silver films, microphotometer records of the patterns given by one of them being reproduced in Fig. 7. Here *I* corresponds to the central metallic part of the film, *II* to the part just before the scattering of light starts and *III* to the part which scatters light.

It is with much pleasure that I take this opportunity to express my sincere thanks to Sir C. V. Raman, F.R.S., for the kind and helpful interest he has taken in the progress of this work and for the facilities afforded in his laboratory for its execution.

4. *Summary.*

The structure of thin films of gold and silver obtained by evaporation *in vacuo* has been studied by electron diffraction methods. Direct evidence has been obtained for the existence of these metals in the amorphous state as suggested in an earlier paper by the author. Films of gold and silver which are thin enough to scatter light, as discussed in the earlier paper, are found to give electron diffraction patterns corresponding to an amorphous structure. Thicker films having metallic reflection and high electrical conductivity give patterns corresponding to a polycrystalline structure.