PHYSICAL PROPERTIES OF THIN METALLIC FILMS.[1]

II. Magneto-Resistance Effects in Films of Bismuth.

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Synopsis.

Increase of resistance of bismuth films in a magnetic field; the effect of heat treatment.—Films of bismuth one centimeter long by 3 millimeters wide were sputtered from chemically pure bismuth on glass slides to resistances varying from 25 ohms to 200 ohms. If especial care is taken to avoid heating these films during the sputtering, by allowing the process to go on intermittently at short intervals, there is little or no change produced in the resistance of such films when placed in a transverse magnetic field of 16,000 gauss. If the films are heated to a temperature near the melting point of bismuth and allowed to cool and this process repeated several times, after each heating the film exhibits a greater change of resistance in the magnetic field than before it, until a certain upper limit is reached, beyond which further heating, if the previous maximum temperature is not exceeded, has little effect. Likewise, heating to successively higher temperatures, beginning at a fairly low maximum and gradually approaching the melting point of the metal in each successive heating, restores the property under investigation to a greater and greater degree. Heating to temperatures under 150° has very little effect towards restoring this property, while heating to temperatures above this value has a correspondingly larger effect. If the film is strongly heated while being sputtered the initial increase of resistance in the magnetic field is comparatively large and further heating produces only slight increases in this initial value. The increase of resistance in weak fields or where the total effect is not large is strictly proportional to the square of the field strength.

Negative temperature coefficient.—The heating as above described produces no observable change in the negative temperature coefficient of resistance of these films, which was carefully measured before and after each heating.

THE present investigation is a continuation of the work reported in the previous paper[2] on this subject, the aim being to obtain more exact quantitative measurements of the effect under investigation.

A bismuth cathode was cast from a stick of chemically pure bismuth, an aluminum wire being inserted in the molten metal and allowed to harden in place to serve as an electrical connection and a support within the jar. The face of this cathode was carefully polished with very fine emery paper and a piece of mica of slightly larger size was clamped to the back with short pieces of aluminum wire. The aluminum stem

[1] Second of a series of articles on this subject from the Physical Laboratory of Cornell University. The authors are pleased to acknowledge aid from the Rumford Fund in carrying out this work.

[2] J. A. Becker.

was then cut to the proper length and a piece of glass tubing of small bore slipped over it. Thus all parts of the cathode except the face were covered as well as possible in order to concentrate the effects of the discharge upon it. Aluminum was used for the connecting wire and clamps since it does not sputter in air.

The bismuth was sputtered on to small pieces of ordinary glass about 2 cm. long, 1.5 cm. wide, and 1.5 mm. thick. These glasses were prepared for sputtering in the following manner. After having been cleaned chemically and rinsed with distilled water they were allowed to dry. They were then covered through the center squarely from side to side by a piece of glass with edges ground true to a width of one centimeter. The glass slide thus covered was put in a bell jar under a gold cathode, the jar evacuated, and a thick film of gold sputtered on to the exposed ends. These terminals were to provide contact with the bismuth film yet to be sputtered, gold being used because films of this metal of the thickness used, as was found upon testing them, had a negligible resistance in comparison with that of the bismuth film. These blanks were then removed from the jar and baked in an open furnace at about 250° for several hours to make the gold adhere more firmly to the glass. They were then covered lengthwise, except for a strip 3 mm. wide through the center, by gluing thin pieces of mica to the glass, a piece of glass 3 mm. wide with true edges serving as a guide. Thus prepared, the blanks were put into a small bell jar a little over a centimeter beneath and parallel to the face of the bismuth cathode described above. To each of the gold terminals was attached a metal spring clip which was fastened to a wire which led through the side of the jar. These two wires were connected to a Wheatstone bridge. With this arrangement the resistance of the films could be measured in situ and films could be sputtered to any desired initial resistance, the films being 10 × 3 mm. in area. No attempt was made to measure the thickness of these films since, for the purposes for which they were used, the electrical resistance has a far greater significance as indicating the character of the film than the thickness as measured by the usual methods.

The jar was evacuated by means of a rotary oil pump and a Gaede mercury pump in series, a McLeod guage being connected for measuring pressures. A vacuum which gave a dark space of a little over a centimeter was, in general, found to be best.

The discharge was produced by a 10,000-volt, 1/2 kilowatt transformer connected through a variable resistance to the 110 A.C. circuit. By means of the resistance the rate of sputtering could be controlled. No attempt was made at rectification, which, although desirable to avoid excessive heating, is not necessary since the aluminum, of which the anode was made, does not sputter.

After having been sputtered in this manner, the films were removed from the jar and provided with leads as follows: Pieces of lead foil were cut to the proper size and bent over the gold terminals and then several turns of copper wire were twisted around the whole until the lead and gold were firmly clamped together. Copper leads were then soldered to these ends. This arrangement gave good contact but it could not be heated above 190°—the melting point of the solder.

Attention was accordingly turned toward devising some method of making contact with the gold terminals which would not involve the use of solder. Becker[1] had plated terminal wires on some of his films with copper and found them fairly satisfactory, but this seemed too slow a process for the present work. Finally a new type of clamp was designed which, for the most part, gave good service. It consisted merely of two narrow brass strips which projected over the edges of the glass far enough so that screws could be fitted to them and thus firmly clamp the lead foil on to the gold. These clamps at first seemed to expand and loosen at the higher temperatures, giving poor contact, which usually became good again on cooling. It was found, however, that this trouble could be avoided to a great extent by slightly bowing the ends of the brass strips outward before clamping in place and putting between them and the lead foil bent pieces of spring brass. If then the screws were not turned down too tightly the elasticity of the system compensated for the expansion when heated and it was found possible to maintain good contact as high as 240°, and, in some cases, even higher. The lead wires were inserted under the heads of the screws.

The magnet used was one of the more powerful types built by the Geneva Society. It was water-cooled and designed to carry twenty-two amperes at full load, but the maximum employed in these experiments was only six amperes. With this current it gave a field of about sixteen kilogauss, when the pole pieces, with faces 2 cm. in diameter were placed 1 cm. apart. It was arranged in this manner throughout these experiments.

It was found during the early part of this work that if the discharge was suddenly stopped and a series of successive measurements of resistance made with the film still in place in the jar, the resistance of the film increased, at first rapidly and then less rapidly. Since films made by Patterson[2] and also by Becker[3] had shown a negative temperature

[1] Loc. cit.

[2] Phil. Mag. (6), 4, p. 652, 1902.

[3] Loc. cit.

coefficient this increase was obviously due to the cooling of the film, after having been heated during the sputtering process.

Obviously the temperature reached during sputtering depends upon the time and rate of sputtering. Since films that had been prepared with no precautions to eliminate heating had shown an appreciable increase in resistance when placed in a magnetic field, and since Becker[2] had shown that the higher a film is heated the greater will be its change of resistance in a field of given strength, it seemed probable that the results obtained by Patterson,[1] namely, that the change of resistance in a given field increased with the thickness, were due not so much to variation in thickness as to the higher temperature reached by the thicker films during the longer time required for sputtering. To test this point, excessive heating during the preparation of a film was prevented by sputtering intermittently, closing the switch in the primary circuit of the transformer for ten seconds and then holding it open for twenty seconds, until a film of about the same resistance of the previous films had been obtained. It was found that a film so sputtered had an initial increase in the magnetic field much smaller than that for films previously prepared by continuous sputtering.

For example, data obtained for two films, one of which, *A*–7, was allowed to sputter continuously, the other, *A*–9, intermittently, is given below:

Film.	Field.	Resistance.	*dr*.	*dr/r*.
A–7	0 16,000	237.13 237.41	0.28	0.001
A–9	0 16,000 16,000	230.300 230.325	0.025	0.0001

After heating for half an hour in an open furnace at about 200° Film *A*–9 gave the following data (note the increased resistance in zero field):

Film.	Field.	Resistance.	*dr*.	*dr/r*.
A–9	0 16,000	256.50 256.56	0.06	0.00023

This shows that films sputtered intermittently have a very slight increase of resistance in the magnetic field when first sputtered. Indeed, several films were prepared in which the change of resistance in a field of 16,000

[1] Loc. cit.

gauss, if present, was too small to be detected by the methods used. It also shows that this property can be restored by heating to fairly high temperatures and that this heating is accompanied by a permanent increase of resistance when the heating is done in air, an effect which is undoubtedly due to oxidation.

To accomplish this intermittent sputtering automatically, a rotating fiber disk with a brass sector was arranged so that contact was made during a fractional part of a rotation. This was put in the primary circuit of the transformer and all films referred to in the remainder of this article were made in this manner. Some of these, however, as mentioned later, became heated because of the high current density used.

Heating the films in air caused an increase in resistance which was greater the higher the temperature. The heating was next tried by inserting the film, together with a mercury thermometer, in a large test

Film A–10.

Resistance in Zero Field before Heating 75.98 *Ohms; after Heating to* 220°, 71.10 *Ohms.*

Field.		dr/r.			Ratios.		
H.	$H^2/10^7$.	Bi in Bulk (1).	A_{10}–0 (2).	A_{10}–1 (3).	(2)/(1).	(3)/(1).	(2)/(3).
1,000	.1	.014					
2,000	.4	.038	.00007	.00013	.0018	.00342	.54
3,000	.9	.073	013	031	018	425	.42
4,000	1.6	.119	026	059	218	495	.44
5,000	2.5	.169	043	095	254	552	.452
6,000	3.6	.223	067	145	300	650	.462
7,000	4.9	.279	090	201	323	720	.447
8,000	6.4	.339	115	266	339	785	.432
9,000	8.1	.395	145	332	367	840	.437
10,000	10.0	.454	180	408	396	900	.441
11,000	12.1	.514	212	490	412	952	.443
12,000	14.4	.572	252	575	440	1002	.438
13,000	16.9	.630	295	672	468	1066	.439
14,000	19.6	.687	338	770	492	1120	.439
15,000	22.5	.747	380	875	508	1171	.435

tube and lowering this down into a bath of oil in a large Pyrex beaker. The oil was heated by means of a coil of nichrome ribbon wound on porcelain tubes placed in the bottom of the bath. The current through this could be controlled by a rheostat and the temperature could be raised, lowered, or held constant at will. Resistance measurements were taken about every twenty degrees. That this heating did have a considerable influence upon the property of the films under examination is shown by the following data obtained by heating film A–10 as described above to about 220°. Since the film was still exposed to the air by this method there was a considerable increase of resistance due to oxidation. The method did possess an advantage over the former method in that the temperature could be controlled and maintained constant with much greater ease and accuracy. In the table data obtained from the calibration curve of a Hartmann and Braun bismuth spiral is included for comparison with the results obtained from the film.

In the above table the notation A_{10}–0 refers to this film before heating and A_{10}–I refers to it after the first heating. A similar notation is employed in labelling the curves.

The results as represented by columns (2) and (3) above are shown graphically in Fig. 1.

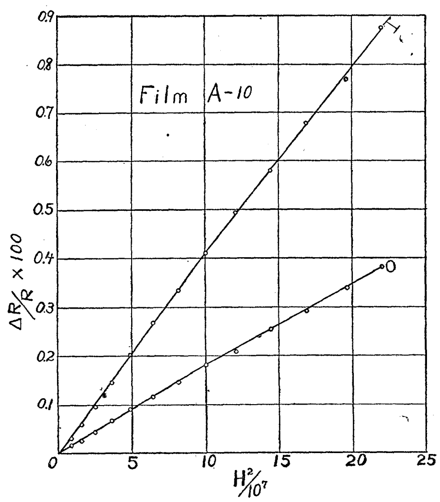

Fig. 1.

Film A–10, showing the effect of a single heating in air upon the increase of resistance in a magnetic field. The percentage increase of resistance is plotted against the square of the field in gauss.

This film is peculiar in that after heating its resistance was found to have *decreased*, although the heating was done in air. All similar films, heated in this manner, increased in resistance upon heating, in some cases very much. Since this seemed to be due to oxidation, a coating of Bakelite was applied to one of the films, A–15, to see whether this would protect the metal from the action of the air. The results obtained from this film are shown graphically in Fig. 2, where, as in Fig. 1, $dr/r \times 100$, or the percentage increase of resistance, is plotted against the square of the field strength in gauss divided by 10^7. It is to be noted that for the weaker fields this effect seems strictly proportional to the square of the field, and that at a rather definite point there seems to be a break in the curve. Beyond this break, which occurs when $H^2/10^7$ has a value of about 10, the curve appears still to be a straight line with a smaller slope than before. Furthermore this break apparently occurs at the same value of the field strength for all of the curves. The above statements apply equally well to Film A–10, Fig. 1.

During the above heatings the resistance of this film in a zero field had increased from 70 to 141 ohms. Hence the Bakelite was not a very efficient protection against oxidation under these conditions.

The next step taken toward reducing and eliminating, if possible, this oxidation was to fill with oil the test tube in which the film and thermometer were placed. Becker had found a similar method rather successful, although Patterson[1] had failed to find any oil which would not ruin his films. The first film heated in this way showed a *decrease* in resistance after the first heating. This, however, was not always true but the increase of resistance as the result of such heatings was much smaller than before in all cases.

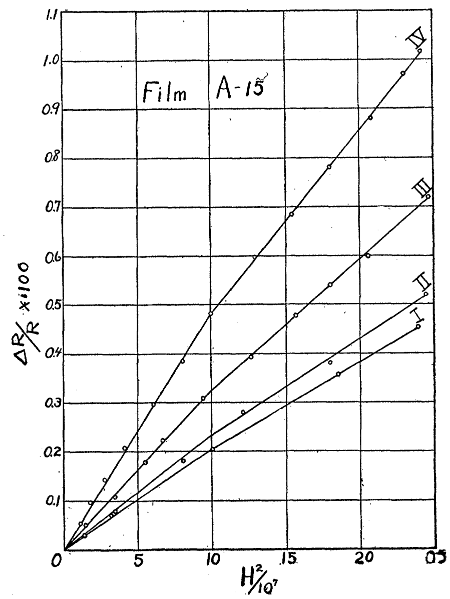

Fig. 2.

Film A–15, showing the effect upon the increase of resistance of four successive heatings in air to approximately the same temperature (230°).

Fig. 3 shows graphically the results obtained from six such heatings to 230° for Film A–18. Since there was much less permanent increase of the resistance as the result of heating the maximum dr/r is slightly larger than for Film A–15 (Fig. 2).

In order to measure the temperature of the films in the bath rapidly and accurately it was found desirable at this stage of the work to construct a resistance thermometer. A platinum thermometer was made in the usual way by winding about six feet of fine platinum wire around a strip of mica just large enough to slip down inside the test tube. At each end of this platinum coil two copper wires were welded, one pair to serve as current leads, the other as potential leads, since the resistance of the coil was to be measured by the fall of potential method, thus obviating the necessity of making corrections for lead resistance. A storage cell and a standard resistance of about the same order of magnitude as the resistance of the platinum coil were placed in series with it, and, by means of a double-pole double-throw switch, the potential drop around either the coil or the standard resistance could be quickly measured by means of a Leeds and Northrup potentiometer. Three good-

[1] Loc. cit.

sized holes were blown in the test tube near the bottom to permit the oil of the bath to circulate through around the platinum coil and the film when it was in place. A mica sheath protected the resistance coil from the film. One pair of leads was brought out through one of these holes and the other pair through another, being held apart by bands of mica wired around the outside of the test tube. This left the inside of the test tube free for the leads to the film.

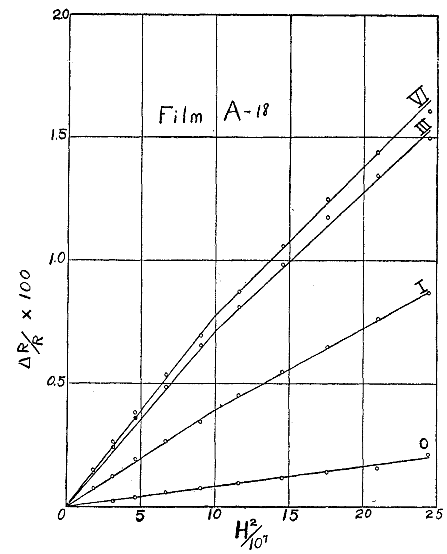

Fig. 3.

Film A–18, showing the effect of six successive heatings to 230° in an oil bath upon the increase of resistance in a magnetic field. II., IV., and V. are not shown.

The data for the next film of interest is represented in Fig. 4. This film, A–20, was strongly heated during the sputtering by the use of a heavy current through the transformer. It was tested as usual in the magnetic field after sputtering and then heated several times as indicated. The initial effect was exceptionally large and, as can be seen from the graph, further heating had very little effect upon the change of resistance in the field. This fact seems to strengthen the theory that heating plays an important part in the restoration of the change of resistance property in these films.

The effect of heating films to successively higher and higher temperatures was also studied with some significant results. The usual method was to heat the film first to 100° and then allow it to cool and test it in the magnetic field; then to repeat the process for 150°, 200°, and 230°. It was found impossible in most cases to heat the films much higher than the last-named temperature. The difficulty seemed to be that, when the oil was heated higher, both the gold and the bismuth became very soft and spongy, sometimes being soaked loose from the glass, and the resistance of the films under those conditions became very high or infinite.

This difficulty is similar to that experienced by Patterson. As mentioned above, he failed to find any oil in which films could be heated without ruining them. Figs. 5 and 6 represent data obtained from

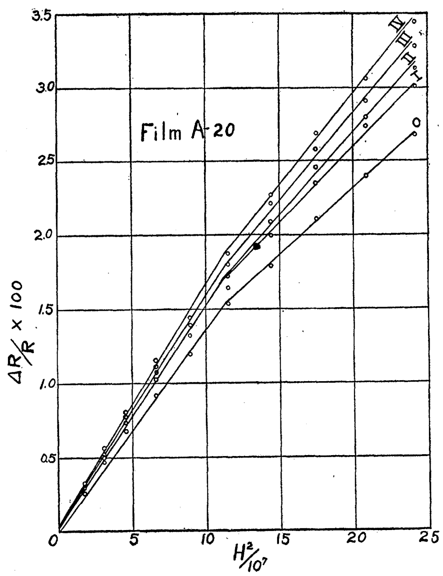

Fig. 4.

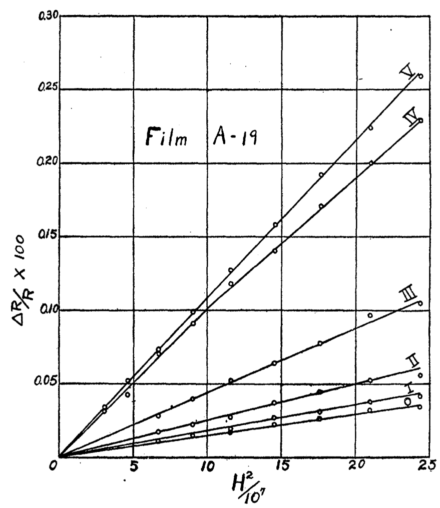

Fig. 5.

Film A–20 was strongly heated while sputtering. These curves show that in such a case subsequent heating has a comparatively small effect upon the increase of resistance in the magnetic field.

Film A–19, showing the effect of successive heatings to higher and higher temperatures upon the increase of resistance in the magnetic field. I—100°, II—155°, III—208°, IV—230°, V—230° (max. temp.).

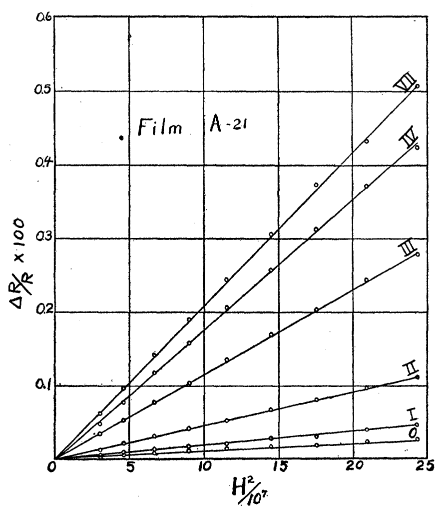

Fig. 6.

Film A–21, showing results similar to those in Fig. 5. I—100°, II—155°, III—212°, IV—240°, V—240° (max. temp.).

films A–19 and A–21 respectively, both of which were heated as described above. It is to be noted that for both films the maximum effect is comparatively small and that the effect here is much more nearly proportional to the square of the field throughout the whole range. Also the higher the temperature to which the film is heated the greater the degree to which the property is restored.

For all the films studied after the platinum thermometer was prepared, which includes all films of the series beyond film A–18, the temperature coefficient between 25° and 35° was carefully measured. In particular an effort was made to determine whether there was any change in this

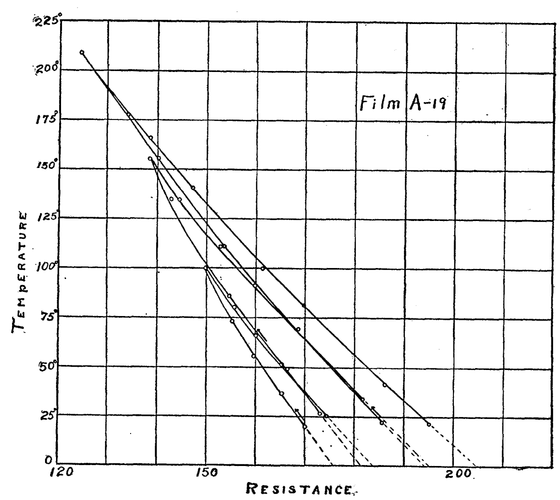

Fig. 7.

Temperature-resistance curves for film A–19 showing the absence of any noticeable effect of heating upon the temperature coefficient. They also show how these films increase permanently in resistance as a result of heating them.

coefficient simultaneous with the change in the increase of resistance in the magnetic field. The temperature coefficients for the various films had a value from −0.0016 to −0.0029. As far as could be determined from the measurements made, heating had very little effect upon this coefficient. This is shown well graphically in Fig. 7 which is the temperature-resistance curve for the first three heatings of film A–19 and is a typical example of the results obtained from these measurements.

Summary.

From a consideration of the foregoing results the following conclusions are evident:

1. Bismuth films prepared by cathodic sputtering exhibit little or no increase of resistance in a magnetic field of 16,000 gauss, if they are not heated much during the sputtering.

2. Heating to temperatures near the melting point of bismuth will partially restore this property of an increase of resistance in the magnetic field.

3. The higher the temperature to which the films are heated the greater the degree to which this property is restored, provided, of course, the melting point is not exceeded.

4. Films strongly heated while sputtering show this effect to a comparatively marked degree and subsequent heatings have very little effect upon such films.

5. There is no perceptible change in the negative temperature coefficient of these films produced by such heatings.

6. As long as the effect is small and for weak fields the effect is strictly proportional to the square of the strength of the magnetic field, but for strong fields where the effect is large this does not seem to be true. To illustrate this last statement and to a given basis of comparison between these films and bismuth in bulk, curves representing the results obtained from film A–20, which showed the largest change of the films here studied, and also the change of resistance for bismuth in bulk for the same field strengths has been plotted and is shown in Fig. 8. The curve for the bismuth in bulk is taken from the calibration curve for a bismuth spiral used in measuring the strength of the magnetic fields.

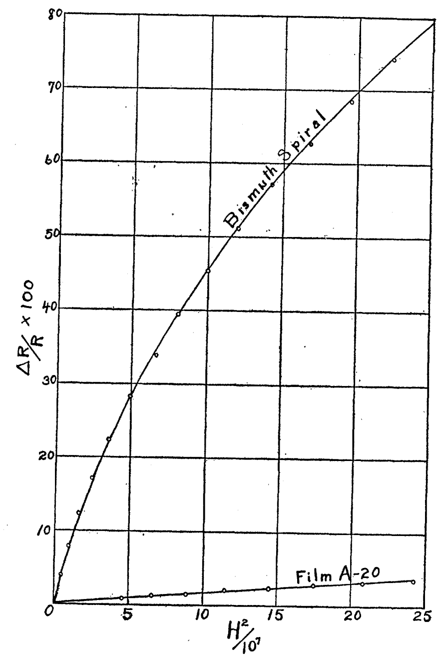

Fig. 8.

A comparison between the results obtained from film A–20 (Fig. 4), and the change of resistance of a bismuth spiral in fields of the same strength.

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