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This paper describes the patterns obtained by disintegration of the cathode in the discharge of electricity in a high vacuum. By sputtering through apertures of different size and shape and through glass and metal cylinders, a set of patterns was obtained that suggested a wave effect associated with the motion of the particles. For a definite value of the voltage, it was found that the ratio between the height and diameter of a cylinder influenced the character of the deposit formed inside. For values of this ratio greater than unity, no deposit is allowed to form on the inside of the cylinder.

The wave length that would produce these effects was found to be much longer than that given by the wave-mechanics. From considerations of the character of the deposits it was shown that most of the particles must carry a charge.

Apparatus for the measurement of the Hall effect in thin films is described and results are given for films of bismuth. An attempt was made to measure the effect in antimony but the work was not completed.

# A STUDY OF PATTERNS IN SPUTTERED FILMS

by

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# A STUDY OF PATTERNS IN SPUTTERED FILMS

## INTRODUCTION

# A STUDY OF PATTERNS IN SPUTTERED FILMS

## INTRODUCTION

One of the most interesting of the phenomena observed in the discharge of electricity through gases is the disintegration of the cathode, commonly called sputtering. In spite of the fact that the phenomenon was observed by Plücker as far back as 1858, and that much use has been made of it for the production of thin films of metal, an explanation of the actual process by which the metal is deposited has not been discovered. Results reported by different observers are contradictory and none of the theories advanced has been generally accepted. Since the effect varies with voltage, pressure, composition and shape of the cathode, distance between anode and cathode, position of the plate to be sputtered, and character of the residual gas in the chamber, it is not surprising that the results of different observers do not agree.

Sputtering occurs with either alternating or direct current; when alternating current is used, the anode and cathode form a point to plane rectifier. Different values of voltage from a few hundred to several thousand may be used, but it is usually difficult to get any discharge with the lower voltages when the pressure is less than ten microns.

The amount of disintegration varies with the kind of gas in the sputtering chamber, increasing with increasing atomic weight of the gas. Sputtering is not confined to metals but has been found to occur with such substances as rocksalt, glass, mica, quartz and carbon. However, some substances sputter much more easily than others. Among the metals easy to sputter are cadmium, lead, antimony, gold, bismuth, tin, copper and platinum while those hard to sputter include zinc, aluminum and magnesium. The difficulty is probably due to the thin layer of oxide which is known to form easily on them.

If one makes a column of $\varphi$, the work necessary to extract an atom from pieces of different metals, and if one also arranges the metals in the order of ease of sputtering, the two columns are found to agree roughly.[16] In some of the older observations it was apparently found that the disintegration varied with voltage according to the relation

$$D = C\,(V-V_o)$$

where V is the energy of the positive ions and $V_o$ the critical voltage, 300-400 volts, below which the cathode failed to disintegrate. However, it was later found that if the plate was carefully degassed there was no critical voltage below which disintegration failed to occur. It has been shown that the amount of disintegration varies linearly with time[2] but no consistent results have been published for the variation of the amount with discharge current. In a recent paper[10] Ingersoll and Sordahl have shown that the rate of disintegration increases with increasing temperature of the cathode.

At first it was believed that the particles were rather large, containing hundreds or perhaps thousands of atoms. However, the latest evidence shows that the great majority of the particles are not deflected by a magnetic field and that a uniform layer of metal only a few atoms thick can be deposited. It is known that some elements form volatile compounds with the gases present in the chamber so that some disintegration undoubtedly takes place in this manner.

As previously mentioned, no theory as to the actual process by which disintegration occurs has been generally accepted. Von Hippel supposes that the positive ions strike the cathode and that the impact raises the temperature enough to volatilize the metal. Another supposition is that the impact of a positive ion knocks out an atom or atoms from the cathode just as a stone dropped into a mud puddle will throw drops of mud and water in the air. Another theory states that the absorbed gases in the metal expand and throw bits of metal in all directions. More will be said about the relative merits of these theories after the discussion of the experimental part of this investigation.

# EXPERIMENTAL WORK

EXPERIMENTAL WORK

A diagram of the sputtering chamber is shown on page 5. The chamber itself is made of pyrex glass and is provided with a carefully ground steel lid. The flat cathode, made of rolled or cast sheet of the metal to be sputtered, is supported by a glass cylinder five inches high cut from a gallon jug. Cathodes were made of bismuth, antimony, lead and tellurium. The pointed aluminum anode projects through the bottom of the glass chamber. A 12,000 volt neon sign transformer usually supplied the field, but was occasionally replaced by a 25,000 volt Thordarson transformer. The plate to be sputtered was placed on a glass about 5 cm below the cathode.

The chamber was evacuated with a Hyvac oil pump which brought the pressure down to as low as one-tenth micron. Phosphorus anhydride was used to collect any water vapor present. A McLeod gauge, readable to one-tenth micron, was used to measure the pressure. The system included a mercury vapor pump, but this was not generally used since most of the sputtering was done at pressures of from five to thirty microns. The best deposits were obtained when the vacuum was such that the plate to be sputtered was at the edge of the Crookes dark space.

It is well known that so-called flare spots (Fig. 1, 2, 3, 4, 5, 6, 8) are sometimes formed near the corners of rectangular sputtered films. It is significant that the film is not merely thinner on these spots but actually absent on some specimens. The existence

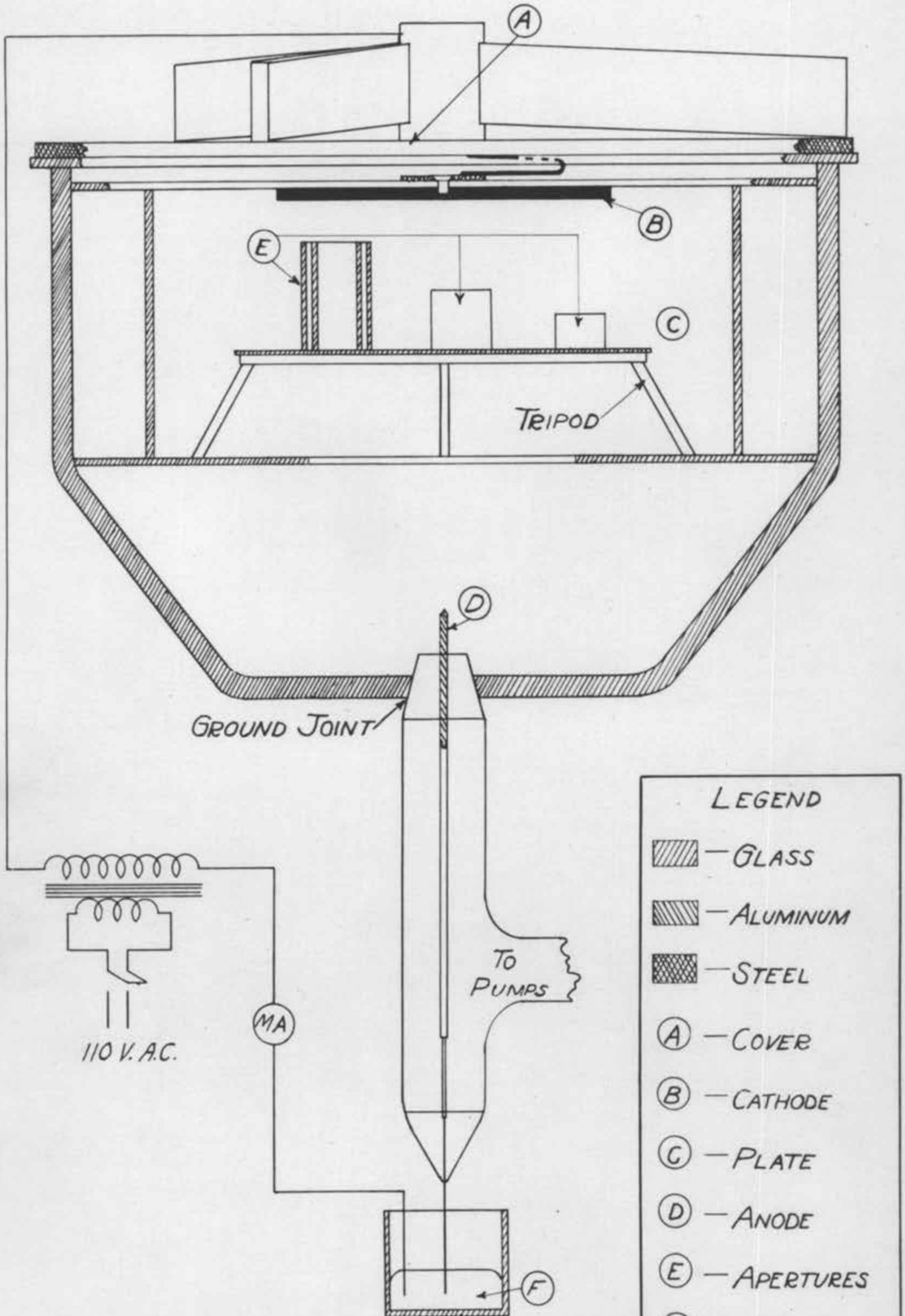


FIG. 1 — SPUTTERING CHAMBER DETAILS

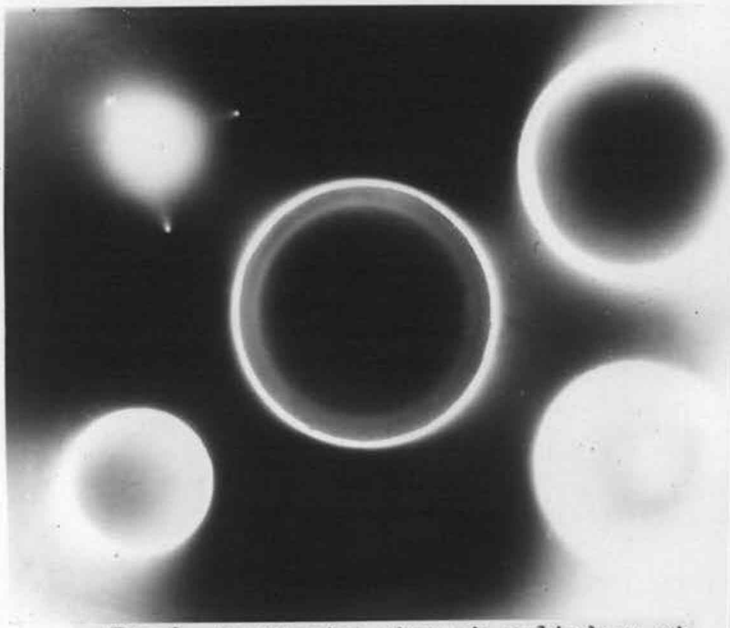

Fig.1- Sputtering through cylinders at 6000 volts. Upper left corner, cylinder on pegs.

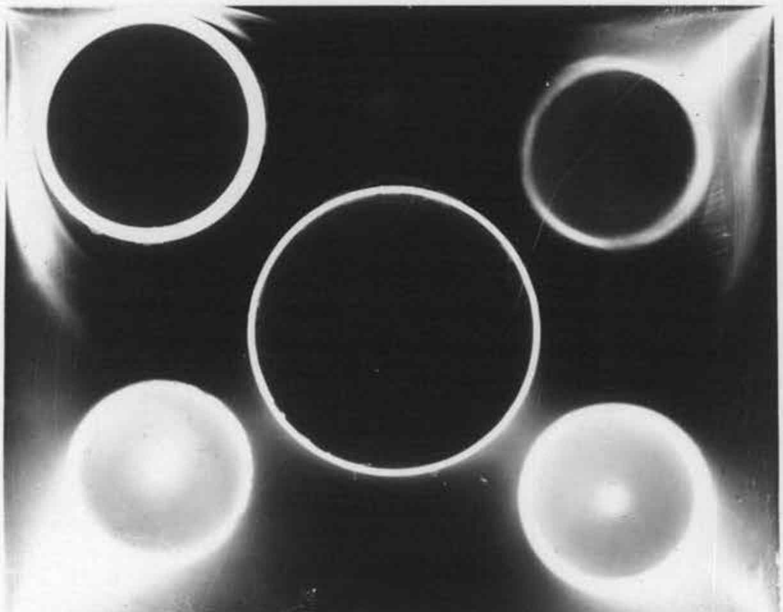

Fig.2- Sputtering through cylinders at 14000 volts. Note the exaggerated flares.

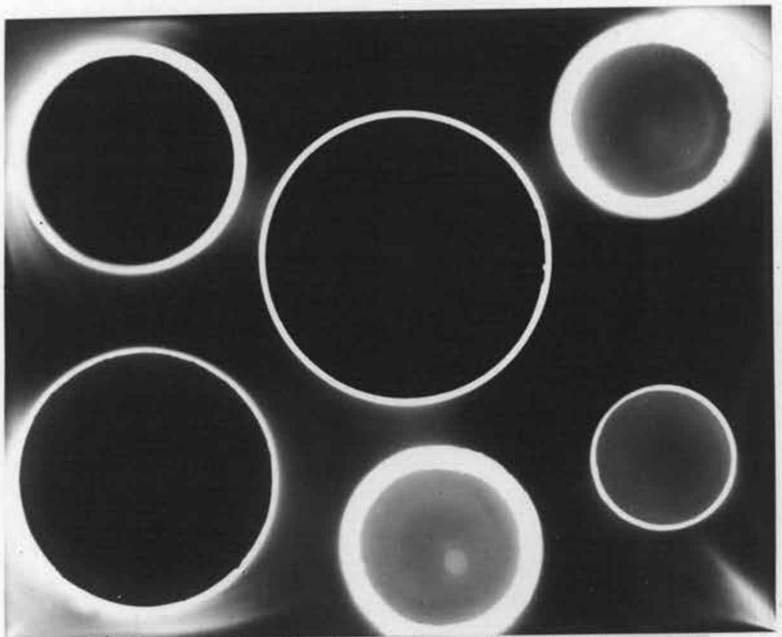

Fig.3- Sputtering through cylinders at 25000 volts.

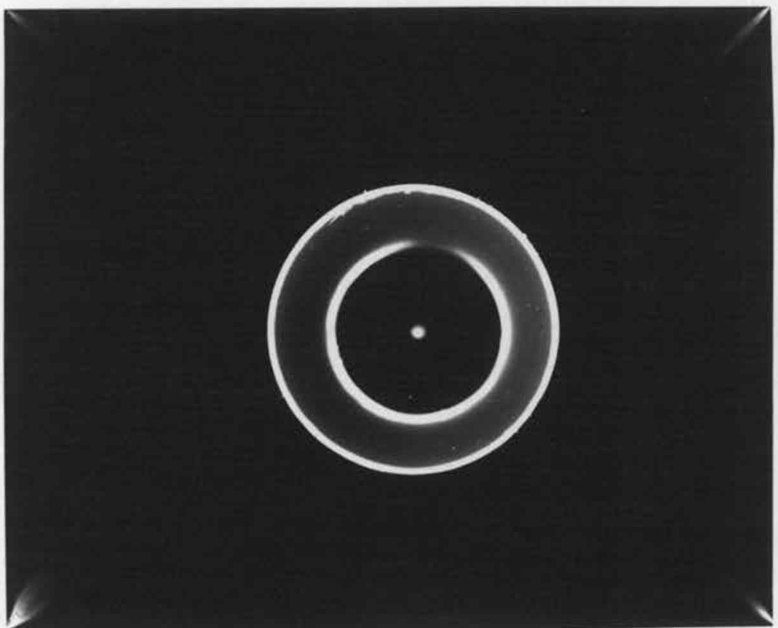

Fig.4- Two coencentric cylinders.

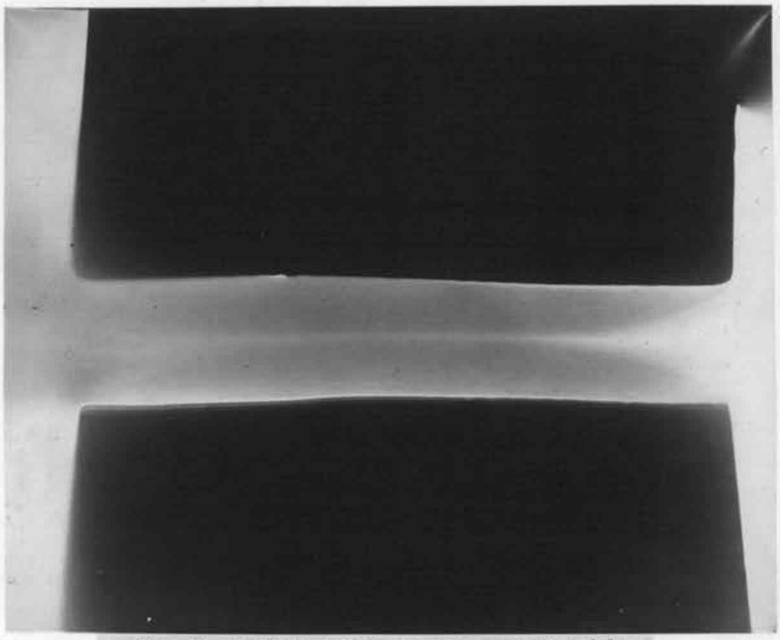

Fig.5- Metal strips one inch wide.

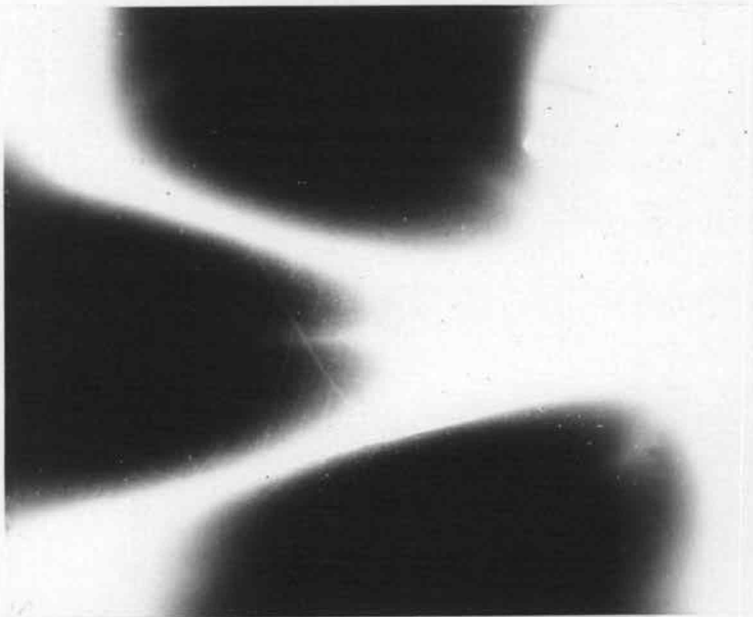

Fig.6- Same strips as fig.5 with ends set together.

Fig.7- Sputtering through a large aperture at 14000 volts.

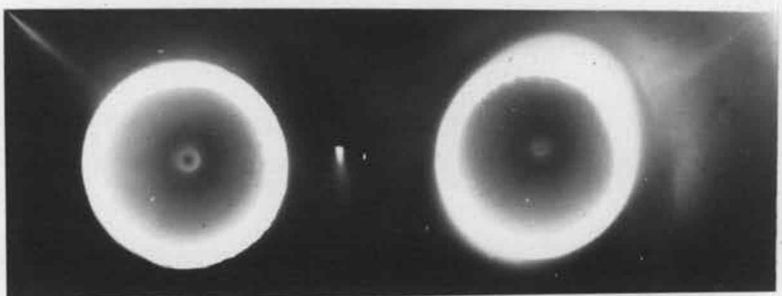

Fig.8- Examples of center spot and ring.

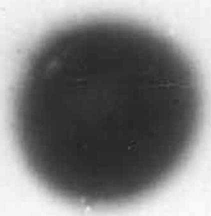

Fig.9- Small aperture at 14000 volts.

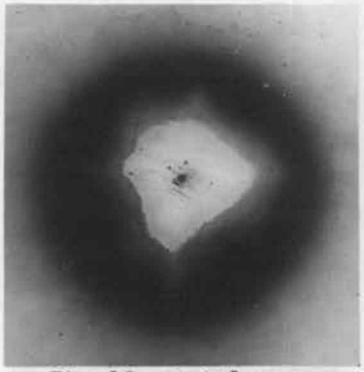

Fig.10- Metal aperture at 14000 volts

of these spots has never been satisfactorily explained.

If one sets a hollow cylinder on the plate to be sputtered, a pattern is obtained that bears some resemblance to a diffraction pattern, as illustrated in Figures 1, 2, 3, 8. If the ratio of the height to the external diameter is very close to unity a single spot of metal about one millimeter in diameter appears in the center and the rest of the plate inside the cylinder receives no deposit. If the ratio is greater than unity, no deposit of any sort is formed, while if it is less than unity the metal deposits on the plate inside of the cylinder, (Fig. 1, 2, 3, 8) This deposit is not uniform but consists of a central bare spot surrounded by rings of varying width. The same pattern is obtained irrespective of whether the cylinders are made of metal or of glass. The outside of a glass cylinder becomes coated with metal and if the ratio of height to diameter is less than one, the inside wall of the cylinder is coated likewise. However, for the taller cylinders, the inside does not become coated except for a ring three or four millimeters in width at the upper end, the outside becoming coated as before. If set on pins so that the cylinder clears the plate by two or three millimeters (Fig. 1) the ratio of height to diameter must be doubled before the deposit fails to appear on the plate underneath. The shorter cylinders on pins give much the same pattern as when directly on the plate except that the bare spot in the center is two or three times as large.

As may be seen in Fig. 1, 2, 3 the presence of a conductor near the corner of the plate has a marked effect on the size and shape of the flare spots produced.

Two concentric cylinders (Fig. 4) two centimeters high allow the deposit to form between them if not closer together than two or three millimeters, but there is a thin concentric circle midway between them that receives no deposit. The bare spot and surrounding rings appear in the center of the inner cylinder as before. Surrounding the central bright spot one can see three rings not more than a millimeter apart and the deposit from there on out is more uniform. In other words, the rings are more pronounced close to the center of the pattern.

The critical ratio between height and diameter involved the external and not the internal diameter. A glass cylinder whose ratio of height to internal diameter was 3:1 was surrounded by a metal cylinder of the same height and of such thickness that the ratio of the height to the external diameter was unity. The metal deposited on the plate inside the glass cylinder proving that the external diameter is the one involved.

All of the patterns described thus far were produced with a difference of potential of 14,000 volts between anode and cathode. When reduced to 6,000 volts, it was found that the central bright spot was not so well defined as before and no evidence of any rings could be noticed. At 25,000 volts the ratio of height to diameter could be increased to 3:2 before no deposit was formed on the plate inside of a cylinder.

Some additional patterns were obtained by interposing a glass plate with a hole in it between the cathode and the plate to be sputtered. The distance between anode and cathode was about fifteen centimeters. The glass plate with the aperture was supported about fifteen millimeters below the cathode and the plate to be sputtered about twenty millimeters below that. With a difference of potential of 14,000 volts and a circular aperture from two to five centimeters in diameter, a spot was formed on the lower plate very nearly the size and shape of the aperture. (Fig. 7, 9) With a difference of potential of 6,000 volts the spot formed was about the same shape as the aperture but about twice the size. With an aperture less than one centimeter in diameter, it was difficult to get any appreciable amount of deposit on the plate; there was a bare spot directly under the hole with a ring of metal surrounding it.

When a metal plate with an aperture was used the bare spot in the center was much larger, (Fig. 10) over half the size of the aperture, and rings of metal appeared around that. Sputtering through slits formed by laying glass plates with their edges four or five millimeters apart on a stand twenty millimeters above the plate, the plate becomes completely coated, but with alternate thick and thin strips, the thin strips being directly under the slits. A single slit one centimeter wide made from two glass plates yielded a pattern consisting of a thin strip of metal one-half centimeter in width directly under the opening and a heavier deposit on either side. The edge of the thin strip was well defined.

Using a slit cut in a metal plate the same result was obtained as with the single glass slit except that the deposit was even lighter directly under the opening.

A metal strip bent in the shape of a rectangle ten centimeters long, four centimeters wide and two and one-half centimeters high did not disturb the deposit in the least, the metal coming down evenly all over except, of course, where the metal touched the plate. Leaving the ends of this box open and bringing the sides closer together, the metal deposited evenly on the inside except for a single line midway between the plates which received no deposit. (Fig. 5) Bringing the ends together to form a wedge seemed to disturb the field immensely and a very uneven deposit resulted. (Fig. 6)

It was noticed that after the switch had been closed for a short time, from a few seconds to a minute or more, a peculiar discharge occurred in the chamber and apparently followed down the sides. The milliameter in the circuit showed that the current changed direction with the appearance of this intermittent discharge, flowing from plane to point instead of from point to plane. The nagnitude of the current was not changed appreciably, being from four to twelve milliamperes in either direction, depending on the pressure. The current reversed sooner when new glass or metal was in the chamber, indicating that the effect was due to adsorbed and absorbed gases. Although a similar phenomenon is said to occur in X-ray and kenotron tubes that have not been properly outgassed, a satisfactory explanation has not been given. All patterns were made with the current flowing in one direction so that no complications should arise due to this effect. It is hoped that we may get the use of a kenotron in the near future to test the results from sputtering with direct current at the higher voltage.

# DISCUSSION OF THE EXPERIMENTAL RESULTS

## DISCUSSION OF THE EXPERIMENTAL RESULTS

It is evident that the direction of the electric field has some effect on the distribution of the deposited metal. This is indicated by:

(1) the fact that it is the ratio of the height to the outside and not the inside diameter of a cylinder that determines the character of the deposit; a tall charged cylinder approximates a charged hollow conductor, within which there is no charge.

(2) The difference between the deposit through apertures in metal and in glass; the field will diverge more rapidly under the metal. On the other hand, there is no conceivable distribution of field intensity that will account for the formation of rings in the deposit. The rings suggest wave effects.

The idea that wave phenomena may be associated with the motion of material particles is of course not new. The work of De Broglie, Heisenberg and Schrodinger in wave-mechanics, Davisson and Germer on the diffraction of electrons, Esterman and Stern on diffraction with hydrogen and helium atoms, Ellet and his students with metallic atoms, and many other experimenters have shown beyond a doubt that wave characteristics are associated with moving particles. All of this work has involved the reflection and consequent diffraction of particles from the face of some crystal. Due to the extremely short wave lengths associated with the particles, ordinary diffraction effects through small apertures have been very difficult to obtain and only first order spectra have been observed in such experiments.

According to De Broglie[14] the wave length associated with a particle should be given by the equation

$$\lambda = \frac{h}{mv}$$

where h is Planck's constant, m the mass of the particle in grams, v the velocity in centimeters per second and the wave length in centimeters. The wave length associated with the larger particles should be of the same order of magnitude as that associated with the electron, the smaller velocity compensating for the greater mass.

Baum[1] has made the most accurate measurements on the velocity of sputtered particles, giving 57,000 cm per second for sputtered silver. This is about the same as the velocity of silver atoms freed by evaporation, 54,000 cm per second. The melting point of antimony is 630.5° C. as compared to 960.5° C. for silver. One should expect the velocity to be somewhat less for sputtered particles of antimony than for silver, if there is a correlation between velocity of sputtered particles and velocity of evaporated atoms, but they should be of the same order of magnitude. That such a correlation probably exists is shown by the increase in rate of sputtering with increasing temperature of the cathode.[11]

If we assume the velocity to be proportional to the absolute temperature of the boiling point of the metal, we get a value of 43,000 cm per second for sputtered antimony. If we further assume that the sputtered particles are atoms, of which we know the mass, we may substitue in De Broglie's equation and get a value for the wave length which should be associated with them.

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-27}}{2.0 \times 10^{-22} \times 4.3 \times 10^{4}} = 7.6 \times 10^{-10} \text{ cm}$$

The rings produced by wave lengths of this size through apertures such as were used in these experiments would not be visible to the naked eye and the appearance of the rings during these experiments cannot be accounted for on this basis. By measuring the distance between rings and taking into account the diameter of the apertures used, it was found that the wave length should be of the order of 0.005 cm. If we substitute this value in De Broglie's equation, assuming the particles to be atoms, and solve for v we get

$$v = \frac{h}{m\lambda} = \frac{6.6 \times 10^{-27}}{2.0 \times 10^{-22} \times 5 \times 10^{-3}} = 6.6 \times 10^{-3} \text{ cm/sec}$$

which is far too small.

It is highly possible that the velocity of many of the particles is much less than that given by Baum.(1) It is a well established fact that a deposit often appears on the side of the plate away from the cathode,(11) indicating that many of the particles move in a slow cloud rather than with great velocities. This idea is substantiated by the fact that the particles will not enter a cylinder for any great distance. If their velocities were very great, the inertia of the particles should be sufficient to carry them through any such obstruction and on down to the plate. If they are uncharged atoms, what retarding force is there that keeps them from going on through the cylinder to the plate?

If the cylinder is set on pins so that it clears the plate by a few millimeters the particles are able to get through to the plate, the cylinder being too tall to let them through otherwise. This suggests that the particles already present in the cylinder, moving in a slow cloud, build up a sort of pressure and keep others from coming in. This should decrease the deposit but should not keep it out all together. The particles descend only a very short distance into the longer cylinders, less than the diameter. The charge on the cylinder does not repel them because they deposit on the outside wall and also on the plate right next to it. Again the appearance of rings is not accounted for.

If one sets a rectangular plate about ten centimeters from the cathode, about two-thirds of the distance to the anode, the flare spots are much smaller than when the plate is sputtered up closer. If one then takes the same plate and brings it up near the cathode and sputters it again, the flare spots become much larger, indicating that the plate itself acts as a cathode and becomes disintegrated partially. This would hardly account for the patterns obtained by other means.

Experimental work is still being done on the problem and it is hoped that the collection of more patterns will result in a clue to a plausible explanation. Arrangements have been made for the use of a transformer delivering voltages from 25,000 to 75,000. Since most of the patterns are most pronounced using 14,000 volts rather than 6,000, it is conceivable that the use of higher voltages will yield some interesting results. No pattern plain enough to allow accurate measurement of wave length has been produced and some method of doing this is necessary to permit of quantitative work on the subject.

# CONCLUSIONS

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The experimental work on this subject has not progressed far enough to permit of really definite conclusions. The facts that have thus far been established are:

1. The particles have some sort of wave motion associated with them.
2. Some of the particles are charged electrically.
3. The particles move with small velocities.
4. The wave length associated with them is much longer than that given by De Broglie's equation.
5. The presence of a conductor influences the distribution of the particles.
6. If close enough to the cathode, the metal on the plate to be sputtered is itself disintegrated.

Before drawing definite conclusions as to the fraction of particles that are charged, it will be necessary to build an apparatus so that sputtering can be done in an intense magnetic field.

ADDENDUM

## ADDENDUM

The apparatus used by H. L. Jones last year for measurements of the Hall effect in thin films of bismuth was available and an attempt was made to measure the Hall effect in some of the films prepared this year. The electromotive force produced between two points initially on an equipotential line, due to the application of a magnetic field in the surface of the film but at right angles to the direction of the initial current, is known as the Hall electromotive force. The effect is greater in bismuth than in any other metal with the exception of tellurium; hence bismuth was used first in order to perfect the technique of making the measurements. With the apparatus available, it was possible to adjust the contacts until the difference of potential between two points near opposite edges of the film was less than ten microvolts. B batteries were used for the primary current and a magnet capable of producing a field of about 3,500 gauss was available. The galvanometer used to measure the Hall current had a sensitivity of $1.4 \times 10^{-9}$ amperes per millimeter.

Values of the Hall coefficient as determined are given below, checking reasonably well with the results obtained by Hargitt[7] and by Jones[13].

| Thickness | Hall coef. |
|---|---|
| $2.1 \times 10^{-5}$ | 0.43 |
| $5.5 \times 10^{-6}$ | 0.38 |

An attempt was made then to measure the Hall coefficient in films of antimony, using the same apparatus. It was found that the resistivity of thin films of antimony increases to as much as 100,000 times the value for the bulk metal, the resistance of the films running from $4 \times 10^5$ to $3 \times 10^7$ ohms. The magnitude of the Hall electromotive force is given by the equation

$$E = \frac{RHI}{t}$$

where R is the Hall coefficient, H the field strength in gauss, I the primary current in abamperes, t the thickness of the film in centimeters and E the electromotive force in abvolts. As may be seen from the equation, the Hall electromotive force is directly proportional to the primary current which is in turn inversely proportional to the resistance of the film. Due to the high resistivity of the films, the primary current was very small, only a few microamperes for the thinner films, so that as a consequence the Hall electromotive force was very small, of the order of a microvolt or so. The resistance across the film between the adjustable contacts was in series with the galvanometer and the large value of this resistance, several thousand ohms, did not allow currents to flow that were large enough to be measured by the galvanometer. It was computed that the Hall current should be of the order of $10^{-11}$ amperes, a hundred times smaller than the sensitivity of the available galvanometer. A direct current amplifier using an FP-54 tube[(4),(17)] was built that was capable of measuring currents of the order of $10^{-13}$ amperes.

Unfortunately, time did not permit any actual measurements on antimony or tellurium, but it is hoped that this work may be continued. Tellurium has a very high Hall coefficient, 500, but since its resistivity is 5,000 times that of antimony, it should give Hall currents of the same order of magnitude.

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