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TEMPERATURE OF THE CATHODE AS A FACTOR IN THE SPUTTERING PROCESS

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Abstract

Effect of high cathode temperatures on the rate of sputtering of metals.—Gold, platinum and nickel show an increase in the rate of sputtering in argon with increase in cathode temperature. The lower the sputtering voltage the more pronounced the effect. Films sputtered from a hot cathode show considerable initial aging, i.e., suffer less change in resistance on baking and show a more definite crystal structure than those from a cold cathode. While evidence is presented to show that the "explosion theory" of sputtering may have a certain basis of fact, especially as regards starting conditions, the results are, on the whole, consistent with the explanation of sputtering as essentially a vaporization process. The indications are, however, that ordinary evaporated films, even when produced under the same pressure as sputtered films, contain less gas, pointing to the excitation accompanying the discharge as an important factor in the process of gas occlusion in the films.

Introduction

A SURVEY of present day theories[1] of the process of cathodic sputtering readily leads one to the conclusion that the temperature of the cathode ought to be a factor in the rate of sputtering. Previous experimental evidence, however, does not support this conclusion. Grandquist,[2] sputtering from platinum cathodes in air at temperatures up to "red heat," found substantially the same amount of metal lost by the cathode at the higher temperatures as at the lower ones. Blechschmidt,[3] sputtering silver in hydrogen at 1500 to 2000 volts got the same deposit with the cathode at 500°C as at room temperatures. Feeling that this could hardly represent the general law and that a more thorough study of the problem was called for, we carried out the following experiments.

Experimental

A large series of films, over four hundred in number, were sputtered from cathodes of nickel, platinum and gold in a residual atmosphere of argon. A few nickel films were also made in hydrogen. The cathode *C*, Fig. 1, was in the form of a hairpin strip which could be heated by battery current to 1000°C or higher. The anode *A* was a square hollow copper block, cooled by circulating water. On its four sides were fastened the $22\times36\times0.25$ mm pieces of microscope coverglass *F* on which the films were deposited. The anode was carried by a ground joint which allowed

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[1] For good summaries and references see A. Güntherschulze, Zeits. f. Tech. Physik **8**, 169 (1927); Zeits. f. Physik **36**, 563; **37**, 868; **38**, 575 (1926): A. v. Hippel, Ann. d. Physik. **80**, 672; **81**, 1043 (1926): E. Blechschmidt, Ann. d. Physik **81**, 999 (1926): T. Baum, Zeits. f. Physik **40**, 686 (1927). For a resume of earlier work see V. Kohlschütter, Jahrb. d. Radioakt. u. Elekt. **9**, 355 (1912).

[2] See Kohlschütter, reference 1, p. 384.

[3] See Blechschmidt, reference 1, p. 1015.

each glass in succession to be turned towards the cathode and at a distance of 9 mm.

Sputtering chamber. This was a cylindrical glass jar large enough (14×24 cm) to avoid the complications due to surface charges. The joint at the top was sealed with gasket and wax, allowing the vessel to be withdrawn readily for the removal of a set of films. The metal and glass tubes were sealed in with De Khotinsky cement. The whole was frequently baked at 300°C with a fair vacuum inside, the joint and brass top-plate on such occasions being water-cooled.

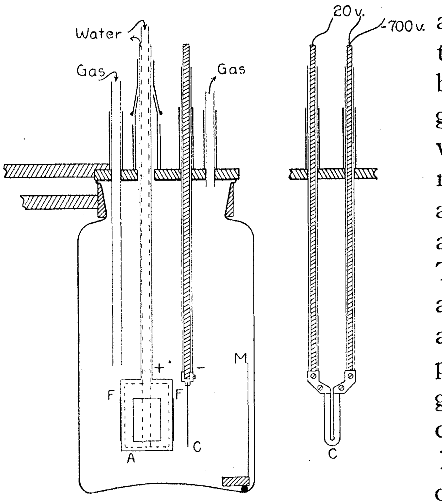

Fig. 1. Diagram of sputtering chamber.

During sputtering the residual gas, argon, was allowed to flow slowly through the chamber, being drawn off by a Hyvac pump. The argon was very good (A 98.2%, N_2 1.4%, O_2 0.4%) but was further purified by passage over magnesium turnings at about 600°C, and in most cases also through a copper and copper-oxide purifying system. These precautions, while perhaps not absolutely necessary, seemed desirable as we had previously found that a small percentage of impurity in the residual gas may produce a marked effect on the deposit. The chamber further had liquid-air traps on both inflow and outflow sides, and in view of the continual flow of gas—inflow tube almost down to the film— and the relatively high pressure (about 1/3 mm) it was not considered that wax vapors from the joint could produce any contamination.

Cathodes. These were 99.5% nickel, Baker furnace platinum and very pure gold, respectively. The nickel cathode was of 0.1 mm strip in the form of a hairpin about 12×46 mm overall with 1 mm between the inside edges of the strip. The platinum and gold were somewhat thinner.

Temperatures were measured with an optical pyrometer. To keep a small area of the side wall of the chamber free of deposit for this purpose, a small mica shield *M*, magnetically operated, was arranged. The "cold" temperatures of the cathode, i.e. no heat input save that due to the discharge, were calculated from radiation considerations and from measurements on the increase of the dark space as the strip heated with the discharge. The two methods gave concordant results of from 150 to 360°C according to circumstances. The unheated parts of the cathode, i.e., aluminum leads, nickel clamp, etc., were sheathed with glass or mica and were specially designed to give a minimum of exposed area.

Films. The sputtering was all done with the aid of a small d.c. dynamo, the potential, for reasons which will appear later, being relatively low,—

from 500 to 800 volts. The films were all deposited in sets of three, the fourth being a blank used in connection with the adjustment of discharge conditions. In general the first and third films were made under identical conditions, cathode cool, say, the second film then being with cathode hot. To secure uniformity of results it was found best to precede each film by several minutes of sputtering on the blank under exactly the same conditions as were to be used in making the film.

All films were sputtered with cathode dark space as nearly as possible 7 mm, or about three-quarters of the distance cathode to film. This necessitated a somewhat higher pressure, about 0.40 mm at the high-temperature sputtering, than the 0.24 mm used with the cathode cool. When correction was made for the fraction of the cathode not subject to heating, it was found that the "net" sputtering current (around 6 milliamp.) was, for a given voltage, almost exactly the same in the hot and cold cases. The time of deposition varied greatly but was usually from 15 to 30 minutes.

While in the preliminary results the film thickness measurements were on the basis of optical density determinations, all the final data depend on direct weighings of the deposits. As the mass of the piece of film under test was usually only a few tenths of a milligram, careful micro-balance weighings were necessary, and for these we are indebted to Mr. Rex Robinson of the Department of Chemistry of this University. The glass on which the film was to be deposited was acid-washed and, generally, baked at 600°C. After sputtering, a small section, one or two sq. cm in area and of nearly uniform density, was cut from the film and then baked (so that the hot- and cold-sputtered films might be on the same basis as regards gas content) at 475°C for a few minutes in 2 mm of argon. The film-on-glass was then weighed, the film removed with acid and the glass alone weighed. All weighings were repeated, the two determinations usually checking to 0.002 mg.

Evaporation. It is obvious that if the cathode is heated to a sufficiently high temperature ordinary vaporization will begin to play an important part. This effect in connection with sputtering has been noted by many observers, particularly with the more volatile metals. In the present work the temperature, save in a few cases, was kept below the point where this phenomenon entered as a factor.

Vaporization was tested for by running the cathode at the desired temperature, without the accompanying electrical discharge and with the gas pressure at its normal value (about 0.40 mm for A) for hot sputtering. The deposit was negligible in all cases save for the highest temperature at which each metal was sputtered. At the highest temperature for platinum (1350°C), however, evaporation accounted for about 11% of the sputtered deposit, and a correction of this magnitude was accordingly made, while for gold at 960°C the correction was 22%. In the case of nickel a correction of 1% was subtracted from the deposit at 1100°C.

It may be remarked as a matter of theoretical interest that the extent of the deposit, i.e. breadth of deposit on glass plate for a given cathode, was very nearly the same for evaporation as for sputtering at the same pressure, indicating that each process involves substantially the same considerations, i.e. diffusion.

RESULTS

Table I gives a synopsis of the results. While the results show some scattering the consistency is quite satisfactory in view of the irregularities inherent in all sputtering operations. The rate of deposition of metal is decidedly larger at higher cathode temperatures, the curves, plotted in Fig. 2, being exponential in form. This fact, together with the rather striking one, shown in the last column of the table, that the increase for higher temperatures is greater for lower voltages, explains why previous observers have not found this temperature effect. For Blechschmidt, for example worked only up to 500°C and at 1500 to 2000 volts.

TABLE I. *Rates of sputtering in argon.*

Metal	Potential (volts)	Net current (ma.)	Cathode temperature (°C)	Deposit (mg/cm²min.)	Deposit (hot) / Deposit (cold)
Gold	500	3.9	150	0.00353	
			960	0.00481	1.36
Platinum	500	3.9	150	0.00165	
			1120	0.00240	1.45
			1350	0.00352	2.13
Platinum	700	about 7	about 250	0.0123	
				0.0120	
			1185	0.0144	1.17
				0.0141	
			1200	0.0134	
Nickel	800	—	about 360	0.00427	
				0.00413	
			1100	0.00597	1.42
Nickel	700	7.3–7.5	330	0.00248	
				0.00261	
				0.00252	
				0.00219	
			700	0.00279	
			850	0.00302	
			980	0.00365	
			1050	0.00361	
			1100	0.00418	1.73
				0.00460	
				0.00416	
				0.00402	

Although the curves show a decidedly upward trend this is by no means as rapid as that of the vapor pressure curve, plotted (the actual ordinates are not given) for the case of nickel from the results of Jones, Langmuir and Mackay.[4] The rate of rise of the sputtering curve undoubtedly varies

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[4] H. A. Jones, I. Langmuir and G. M. J. Mackay, Phys. Rev. **30**, 201 (1927).

with the gas. From the few films of nickel sputtered in hydrogen it was concluded that the increase of sputtering with temperature is not as great in this gas as in argon.

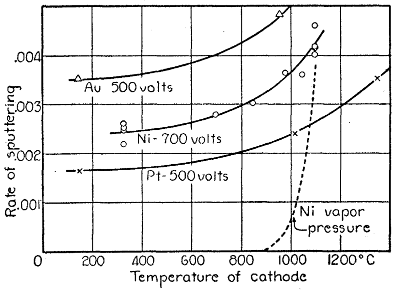

Fig. 2. Rate of sputtering of gold, nickel and platinum in argon as dependent on the temperature of the cathode. (Ordinates are milligrams of metal per square cm per min.)

Theory. The most complete theory of the process of cathodic sputtering is that of v. Hippel,[5] who has developed quantitative formulae in a fairly successful manner. The positive ion impinging on the cathode is supposed to expend its energy in heating a little area of surface ΔF so that it remains for a time Δt at a high average temperature, causing rapid localized evaporation. Most of this vapor is condensed on the cathode, but a fraction diffuses over and deposits as the sputtered film. v. Hippel's final expression for the amount of this deposit is a somewhat complicated one, involving $\Delta F \cdot \Delta t$ as a factor and an exponential term in T, the momentary temperature of the bombarded element of area.

In attempting to fit this theory with the facts, particularly as regards the form of the temperature-sputtering curve for nickel, two separate assumptions have been tried. The first is that the temperature T of the momentary hot spots on the cathode is independent of the actual cathode temperature—being in any case very much higher than this—and that heating the cathode increases the sputtering through an increase in ΔF and Δt. This reduces the problem to one of heat conduction, involving an instantaneous point source, for which, with certain simplifying assumptions, the theory is readily available.[6] Calculations on this basis give a curve of the same general form as those of Fig. 2, but flatter.

The second assumption is to the effect that $\Delta F \cdot \Delta t$ is to be considered the same at the higher cathode temperature as at the lower, and that T is increased by just the amount of the cathode rise. This does not lead to very satisfactory results. It may be observed that neither of these assumptions fits the actual case, which undoubtedly involves increases in T, ΔF and Δt on heating the cathode. Dr. v. Hippel (letter) also suggests that surface layers of adsorbed gases on the cold cathode may cause reflection of the positive ions and also serve to increase the atomic emission-work, causing less sputtering than at higher temperatures when the gas layer is largely driven off.

The fact that the increase of sputtering at high cathode temperatures is less at higher voltages is perhaps to be accounted for by supposing that the greater the energy of the impinging ion the less important as a factor is the molecular energy, i.e., temperature, of the cathode.

[5] A. v. Hippel, Ann. d. Physik **81**, 1043, (1926). Dr. v. Hippel has also kindly let us see the manuscipt of a forthcoming paper in the Annalen involving an extension of this theory.

[6] See, e.g., Ingersoll and Zobel, "Mathematical Theory of Heat Conduction" (Ginn and Co.) p. 129.

Physical properties of the films. Hot and cold-sputtered films show a slight difference of color, the latter being generally somewhat brownish and the former dark gray, sometimes with a bluish color. Baking for a few minutes at 475°C usually brings them to substantially the same color, i.e., that of the hot-sputtered film.

As is well known, sputtered films suffer a rapid and irreversible change in resistance on heating, known as aging. Many measurements of resistance at various temperatures were made in the present case and typical curves are shown in Fig. 3. While these tests were carried out in high vacuum, substantially similar results, at slightly higher temperatures however, occur under one atmosphere of argon. The straight lines are essentially cooling curves, although actually made by cooling down to room temperature from the highest point and then measuring the resistance on heating up again. Platinum gives curves of the same type. It is evident from the figure that the hot-sputtered film is largely aged as deposited, and this is undoubtedly due to the heating of the film surface, in spite of its water-cooled backing, due to the neighboring hot cathode and to the discharge. The curves for the cold-sputtered films are quite similar to those given by Bartlett.[7]

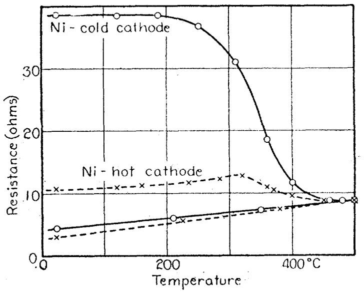

Fig. 3. Effect of heat treatment on hot and cold-sputtered films of nickel.

While the crystal structure of these films has been studied at length in some cases, only a preliminary statement will be made here as the matter is somewhat complicated and is being further investigated. In general it may be said that hot-sputtered nickel films resemble the massive metal while cold ones may initially be amorphous or else show a crystal structure with a somewhat swollen lattice, indicating a not impossible nickel-argon compound. In line with this is the fact that cold-sputtered nickel films are generally non-magnetic and hot ones magnetic. Aging by heat treatment, i.e. baking, drives out the gas[8] in the film and brings about more complete crystallization. As already remarked, hot-sputtered films show large initial aging.

Other effects. It has been recognized for a long time that a gas-filled metal evaporates much more readily than one which is out-gassed. Berliner,[9] who first studied this effect, suggested that the gas may likewise influence cathodic sputtering. As further developed by Bush and Smith[10] this has given rise to the "explosion" theory of sputtering, whereby the positive

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[7] R. S. Bartlett, Phil. Mag. **5,** 848 (1928).

[8] While there is every reason to believe this statement it must be admitted that this gas has not actually been found and measured, save in some special cases such as palladium-hydrogen. The matter is to be studied further.

[9] A. Berliner, Wied. Ann. **33,** 289 (1888).

[10] V. Bush and G. C. Smith, Jour. Am. Inst. of Elect. Eng. **41,** 627 (1922).

ions are imagined as developing, on being shot into the cathode, such pressures that miniature explosions of the metal take place.

Our apparatus seemed to offer opportunity to make a quasi-test of this theory and accordingly the following experiment was tried: The nickel strip cathode was first "filled" with gas (on the above hypothesis) by cold-sputtering for several minutes, the cathode temperature being kept down by placing an interrupter in the circuit so that the current was flowing effectively for only half the time. A film was then sputtered (continuously) for two minutes, say. The cathode was then outgassed by heating to 1200°C for several minutes, allowed to cool, and the second film then sputtered. The third film was made like the first.

This gave three films, all deposited for the same time, same gas pressure and at the same cathode temperature—"cold" sputtering, i.e., around 300°C. For the first and third, however, the cathode was supposed to be initially gas-filled, while for the second it was reasonably gas-free. A great many tests were made in this way, with the order reversed in many cases. For cathodes of nickel strip only 0.1 mm thick no systematic difference could be detected, but for 0.25 mm strip the rate of sputtering from the gas-filled cathode was appreciably greater, possibly because the thicker strip retained more gas. The initial current from the gas-filled cathode was almost always higher than the other (correction was of course made for this factor), indicating the outrush of the imprisoned gas, which would not occur, initially, when the cathode had been previously heated.

If it be admitted that this experiment gives what amounts to an exaggeration of the gas effect it must be allowed that there is some basis of fact in the explosion theory. It need not, however, cause any essential change in the fundamental sputtering theory. For whether the positive ion produces its "vaporizing" effect through the medium of a gas cushion or by more direct transference of its energy to the metal of the cathode, the phenomenon is essentially the same.[11]

Another secondary experiment which was tried serves to add a little evidence on the question of the charge on metal vapor atoms from a charged electrode. Vaporization tests, as already described, were made in a large number of cases and in many of these a potential of two or three hundred volts—just short of sufficient to produce a discharge—was applied between cathode and anode. In no case was the amount of deposit changed by this potential. While a little evidence has been obtained in this laboratory to the effect that metal vapors contain a small percentage of ionized atoms, this fraction must, as usually supposed, be very small.

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[11] This statement perhaps requires modification in the light of v. Hippel's experiments indicating the essentially *atomic* character of the sputtering process. We are inclined to agree with v. Hippel's suggestion (loc. cit. p. 1045) that the explosion process is probably no more than an auxiliary effect, and, we should add, one more likely to come into account at the beginning of the process. He also makes the suggestion that our results might be accounted for on the basis of the decreased thermal conductivity which undoubtedly accompanies absorption of gas by a metal, and hence the longer duration of the element of time Δt during which the localized evaporation takes place.

Lastly, a start has been made on the task of comparing carefully the properties of sputtered films and of films produced by evaporation from the same cathode and under the same gas pressure. It is hoped that in this way there may be gained some further insight into the sputtering mechanism. As already remarked, the extent of distribution of the deposit was about the same in each of the two cases, indicating a fundamental similarity in the two processes. The deposits, too, were similar in appearance and the resistance curve for the single specimen (nickel) tested was not unlike that for hot-sputtered nickel as shown in Fig. 3. The evaporated film, however, although made with the same pressure of argon, seemed to be more completely initially aged, i.e. probably contained less gas, than even the hot-sputtered films.* This might be taken to indicate that the ionization or excitation incidental to the electrical discharge is an essential feature of the sputtering process and results in a greater occlusion of gas. That ionization or other "activation" increases the adsorption of gas at a surface is in line with the findings of others.[12]

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* (Note added in proof). Experiments since the above was written on (hot) sputtered and vaporized films of nickel and platinum produced in hydrogen, argon and helium (the latter furnished through the kindness of the Helium Division, U. S. Bureau of Mines), indicate clearly that this is a general law. The matter is, however, dependent on film thickness.

[12] See, e.g., R. E. Burk, Proc. Nat. Acad. Sci. **13**, 67 (1927), who concludes from experiments on the thermal decomposition of ammonia at a molybdenum surface that only activated molecules of nitrogen are condensed on such a surface so as to form a "poisoning" film.