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Theory of Cathode Sputtering in Low Voltage Gaseous Discharges

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To determine the amount of sputtering in a glow discharge three functions must be known: the number of ions of a given energy striking the cathode, the amount of cathode material released from the cathode by each ion, and the fraction of material released from the cathode which diffuses away. Expressions derived for these allow determination of the dependence of total rate of sputtering on the geometry of the discharge, pressure, cathode fall, current, and constants of the gas and cathode surface. The result is most accurate for very low voltage, high pressure discharges. Comparison with experimental data shows quantitative agreement under these conditions.

CATHODE sputtering is the process which removes material from the surface of the cathode of a gaseous discharge and deposits this material as a film on the walls of the discharge tube or on other nearby surfaces. There is experimental evidence that sputtering is due to ionic bombardment of the cathode and that the material sputtered leaves the cathode in all directions and in an uncharged state.[1] By identifying the spectral lines of atomic material from the cathode in gaseous discharges and measuring their intensities, Von Hippel[2] showed that a large part, if not all, of the sputtered material present in the region of the discharge was in an atomic state. There have also been numerous attempts to deflect the sputtered particles by electric and magnetic fields with the resultant general conclusion that they are uncharged. Baum[3] succeeded in attaching charges to sputtered particles of silver and deflecting them after they had been extracted from the discharge region. He concluded that they were atoms which had velocities corresponding approximately to a temperature of 1000 degrees C. Seeliger and Sommermeyer[4] allowed a beam of ions to strike a silver surface in very low pressure gas and measured the amount of material sputtered in various directions, obtaining the result that the sputtered particles leave the cathode according to the cosine law.

If the mechanism for sputtering indicated by these results is accepted, i.e., that positive ions bombarding the cathode dislodge atomic material, the theoretical problem of calculating the amount of sputtering may be resolved into the calculation of three functions:

1. The fraction of atoms released from the cathode surface which find their way to other surfaces in the discharge.
2. The number of ions of given energy striking the cathode.
3. The number of atoms dislodged by an ion of given energy.

Most previous work on sputtering has dealt principally with the effect of function (3) and with some justification because sputtering under high voltage low pressure conditions has been principally discussed. It will be shown, however, that under certain conditions in low voltage discharges, function (2) giving the distribution of ionic energies plays a dominating role.

DIFFUSION OF SPUTTERED MATERIAL

If the mean free path of the sputtered particles is much larger than the distances between the cathode and the surrounding surfaces, then material which leaves the cathode may never return; but if the mean free path is much smaller than these distances, a large fraction of the atoms which leave the cathode diffuses back to the cathode surface. To obtain quantitatively the fraction of material diffusing away from the cathode, let

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[1] In some cases chemical reactions take place between the gas and the cathode material, usually giving a large amount of cathode erosion. This type of sputtering will not be considered.

[2] A. Von Hippel, Ann. d. Physik **80**, 672 (1926).

[3] T. Baum, Zeits. f. Physik **40**, 686 (1926).

[4] R. Seeliger and K. Sommermeyer, Zeits. f. Physik **93**, 692 (1935).

$d\bar{s}_1$ = vector element of cathode surface S_1,
$d\bar{s}_2$ = vector element of surface S_2 surrounding cathode on which sputtered material is deposited,
J_0 = rate at which atoms leave cathode surface,
J = rate of deposition on S_2,
N = concentration of cathodic atoms between S_1 and S_2,
D, v, λ = diffusion coefficient, average velocity, and mean free path, respectively, of sputtered atoms in gas of discharge, and
C_1, C_2 = the fraction of the atoms which adhere on collision with S_1 and S_2, respectively.

Now

$$J = D\int \nabla N\cdot d\bar{s}_2$$

is the rate of deposition and

$$J_0 - J = C_1\frac{v}{4}\int N ds_1$$

gives the rate at which sputtered atoms are being returned to the cathode. If J_0 is constant so that a steady state is reached,

$$\nabla^2 N = 0$$

with the boundary conditions

$$C_2\frac{v}{4}\int_{S_2} N ds_2 = D\int_{S_2} \nabla N\cdot d\bar{s}_2$$

and

$$J_0 = \frac{C_1 v}{4}\int_{S_1} N ds_1 + D\int_{S_2} \nabla N\cdot d\bar{s}_2.$$

If $J_0 \gg J$ and if atoms are emitted uniformly over the cathode, the boundary conditions become

$$N_2 \approx 0$$

and

$$J_0 \approx \tfrac{1}{4} C_1 v N_1 S_1$$

where N_1 and N_2 are the values extant at S_1 and S_2, respectively. Then N may be written

$$N = f(x, y, z) N_1 = \frac{4J_0}{C_1 S_1 v} f(x, y, z)$$

and

$$J = \frac{4DJ_0}{C_1 S_1 v}\int_{S_2} \nabla f\cdot d\bar{s}_2,$$

where f is a solution of Laplace's equation which is zero on S_2 and unity on S_1. From kinetic theory, $D = \pi/8v\lambda$. Therefore,

$$J = \frac{\pi J_0 \lambda}{2C_1 S_1}\int_{S_2} \nabla f\cdot d\bar{s}_2. \quad (1)$$

For the case where S_1 and S_2 are two parallel planes separated by a distance d, the number of atoms deposited per second per sq. cm becomes

$$j = \frac{\pi j_0 \lambda}{2C_1 d}$$

from which it is seen that the approximation $J_0 \gg J$ is justified when $\lambda \ll d$. For a spherical cathode of radius a surrounded by a concentric sphere of radius b, the total rate of deposition

$$J = \frac{\pi J_0 \lambda b}{a(a-b)}.$$

The inverse dependence of j on d for the plane case was found experimentally by Güntherschulze[5] and by Blechschmidt,[6] and derived theoretically by von Hippel.[7] It may be seen from these formulae that for a fixed rate of evaporation of atoms at the cathode, the actual rate of disappearance of material from the cathode is inversely proportional to the gas pressure and depends as well on the distance to the nearest surfaces where deposition may take place. A large part of the evaporated atoms returns to the cathode surface and perhaps forms the powder of small crystals which is often observed there. The evaporated atoms may, of course, condense in the discharge, form large aggregates, and thus materially change the rate of deposition, but in most cases the density of sputtered material in the discharge is too small to allow appreciable condensation.

ENERGIES OF IONS STRIKING THE CATHODE

To find the energy of a typical ion in an electric field E, let the ion start from rest and have a mean free path in the gas λ. It will move in the direction of the electric field an average distance

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[5] A. Güntherschulze, Zeits. f. Physik **38**, 575 (1926).
[6] E. Blechschmidt, Ann. d. Physik **81**, 999 (1926).
[7] A. v. Hippel, Ann. d. Physik **81**, 1043 (1926).

λ, when it will have an energy $E\lambda$ electron volts, and collide with a molecule having a mass approximately equal to that of the ion. If the collision takes place as between hard spheres, the average ionic energy immediately after collision is $\frac{1}{2}E\lambda$. Since most of the velocity before the second collision is in the direction of E, the average energy just before the second collision will be approximately $E\lambda+\frac{1}{2}E\lambda$. Thus, if the field varies, we may write for the average total energy at a given collision the expression

$$\bar{\epsilon}\approx E_0\lambda+\tfrac{1}{2}E_1\lambda+\cdots(1/2)^nE_n\lambda+\cdots,$$

where E_n indicates the average value of the field between collisions n and $n+1$ before the given collision represented by the subscript 0. If E is constant over several mean free paths, then

$$\bar{\epsilon}\approx 2E\lambda.$$

This value is an upper limit for $\bar{\epsilon}$ since all of the ionic velocity is not in the direction of E.

To find the energy distribution function, consider variations in the energy contributions of only the last two free paths. This is justifiable because the average contribution of the next free path is only $\frac{1}{8}$ the total energy, and variations would be correspondingly small. The average energy contribution of all but the last two free paths is $\frac{1}{2}E\lambda$. During the last free path, there is a probability

$$\exp\left(\frac{-\epsilon_0}{E\lambda}\right)\frac{\Delta\epsilon_0}{E\lambda}$$

that an energy between ϵ_0 and $\epsilon_0+\Delta\epsilon_0$ will be contributed to the total energy. Variations in the energy contribution ϵ_1 of the next to the last free path occur both as a result of variations in the free path and of variations in the energy retained after collision. It may be shown that if f is the fraction of the precollision energy which an ion retains after collision, then all values of f from 0 to 1 are equally probable if the ion is considered a hard sphere. The number of ions having energy less than ϵ becomes, then

$$n(\epsilon)=\frac{n_0}{(E\lambda)^2}\int_0^{\epsilon-(E\lambda/2)}\int_0^1\int_0^{(\epsilon-\epsilon_0-E\lambda/2)/f}\times\exp\left(-\frac{\epsilon_0+\epsilon_1}{E\lambda}\right)d\epsilon_1 df d\epsilon_0$$

for

$$\epsilon>E\lambda/2$$

where

n_0 = total number of ions,

$$\frac{dn(\epsilon)}{d\epsilon}=\frac{n_0}{E\lambda}\exp\left(-\epsilon/E\lambda+1/2\right)\times\left(\int_0^1\frac{1-\exp\left[\frac{1-f}{f}\left(\frac{-\epsilon}{E\lambda}+1/2\right)\right]}{1-f}df\right).$$

A tractable approximation for the above integral of form

$$\int_0^1 g(f)df \text{ is } \tfrac{1}{4}g(0)+\tfrac{1}{2}g(1/2)+\tfrac{1}{4}g(1)$$

which gives

$$\frac{dn(\epsilon)}{d\epsilon}=\frac{n_0}{E\lambda}\exp\left(-\epsilon/E\lambda+1/2\right)\times\left(\frac{9}{8}+\frac{\epsilon}{4E\lambda}-\exp\left(-\epsilon/E\lambda+1/2\right)\right).\quad(2)$$

In order to determine $E\lambda$, the gaseous discharge in which the sputtering takes place must be examined. If the discharge is at very low pressure so that the cathode dark space is large, E may actually be measured, or at least the cathode potential fall and length of cathode dark space may be measured. At higher pressures the cathode dark space may be too small to permit accurate measurement or may not even be seen. Considerations here will be confined to the common case when λ is a small fraction of D, the length of the dark space, and D is much less than the radius of curvature of the cathode surface. A number of experimental and theoretical investigations[8] have shown that the electric field in the cathode dark space of a glow discharge may be represented by a linear function which becomes zero at the edge of the negative glow,

$$E=\frac{E_c(D-x)}{D},$$

where Ec is the field strength of the cathode.

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[8] M. J. Druyvesteyn and F. M. Penning, Rev. Mod. Phys. **12**, 87 (1940). L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley & Sons, New York, 1939), p. 578.

On this assumption, it may be shown that

$$E_c=2\left[\frac{\pi i V}{(1+\gamma)k}\right]^{\frac{1}{3}},$$

where i = current density at the cathode, V = cathode potential drop, γ = number of electrons released per ion impinging on the cathode, and k = ionic mobility. If

$$\lambda=\Lambda/p \quad \text{and} \quad k=K/p,$$

$$E_c\lambda=2\Lambda\left[\frac{\pi}{K(1+\gamma)}\right]^{\frac{1}{3}}\left(\frac{Vi}{p^2}\right)^{\frac{1}{3}}.$$

The behavior of K with varying average energy $\bar{\epsilon}$ is in general complicated, but for the values of E/p usually encountered in the cathode dark space, K is thought to be inversely proportional to the mean ionic velocity, or

$$K=\frac{\kappa}{\sqrt{\bar{\epsilon}}}.$$

Thus,

$$E_c\lambda=2\left[\frac{2\pi\Lambda^3}{(1+\gamma)\kappa}\right]^{2/5}[Vi/p^2]^{2/5} \qquad (3)$$

where the first bracket may be considered constant since $\gamma \ll 1$ and γ does not change rapidly. For many glow discharges the cathode fall V is very nearly equal to the total voltage across the discharge, so that the above formula gives the dependence of the energy with which ions strike the cathode on the voltage, current, and pressure. For known discharges $\bar{\epsilon}\approx 2E_c\lambda$ obtained from this expression varies from less than 1 ev to several hundred ev; for the higher voltage part of this range the approximations made in the derivation are poor.

When $E\lambda$ is only a few volts or less, it might be supposed that the work function of the cathode, or the energy acquired by the ion from its attraction to the cathode surface, is a very important part of the ionic energy. Thus if the force of attraction of an ion to the cathode surface is simply an image force and the ion approaches to 0.5A from the surface, the resulting energy is 7.2 ev. Massey[9] has shown, however, that an ion is usually neutralized before it strikes a metallic surface by capturing an electron from the surface. A rough calculation of the type made by Massey shows the probability that an electron has been captured in an nS level when a 1-volt proton approaches to within a distance b of the surface is

$$3\times10^3\frac{n}{(n!)^2}\exp\left(-2b/0.54n\times10^{-8}\right).$$

Considering capture in a $2S$ state only, the proton would be neutralized when it reaches a distance of about 4A from the surface, having acquired an energy due to image forces of 0.9 ev. While the kinetic energy acquired by the ion due to image forces is not known exactly, it is probably small and not strongly dependent on ion velocities, so that it will be neglected.

The neutralized ion, to be sure, has considerable potential energy, but this energy will not be effective in releasing atoms from the surface. Massey[10] has computed the probability per second of the neutralized ion becoming de-excited and delivering its potential energy to one of the conduction electrons of the cathode. He obtained about 10^{16}/sec., so that this process is much more likely than the emission of radiation. Although the rate of transfer of excitation energy to a lattice point is unknown, it would be less than the rate of transfer of energy to the conduction electrons because of the larger momenta or shorter wave-lengths associated with the lattice points. It is assumed therefore that the excitation energy is delivered to one or more conduction electrons. Since the conduction electrons have a mean free path of the order of 10^{-6} cm, they are able to escape from the region of a few atomic radii about the center of disturbance without delivering energy to the lattice points.

Before attempting a calculation of the third function, the number of atoms released per ion of given energy (dJ_0/dn), it is helpful to consider the expected general behavior of dJ_0/dn and its influence on the desired total rate of sputtering. For ionic energy ϵ less than ϵ_0, the energy re-

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[9] H. S. W. Massey, Proc. Camb. Phil. Soc. **26**, 386 (1930); **27**, 460 (1931).

[10] H. S. W. Massey, Proc. Camb. Phil. Soc. **26**, 386 (1930).

quired to release one atom from the cathode surface, dJ_0/dn, will be zero. From this point dJ_0/dn may be expected to rise rapidly at first and then continue to increase more slowly with increasing ϵ. If $\bar{\epsilon} \ll \epsilon_0$, then the exact shape of dJ_0/dn has little influence on J_0, and this function may be idealized as in Fig. 1(b). This is the case for very low voltage discharges and is the condition for which the present theory is most accurate. If $\bar{\epsilon} \sim \epsilon_0$, as in Fig. 2, both $dn/d\epsilon$ and dJ_0/dn must be known with some accuracy, and a quantitative treatment is difficult. For $\bar{\epsilon} \gg \epsilon_0$, the idealization of Fig. 3(b) may be made. This is the condition under which most observations on sputtering have been made, i.e., in high voltage, low pressure discharges.

An expression for dJ_0/dn may be calculated with the assumptions of von Hippel's[11] evaporation mechanism. Suppose that an ion delivers its energy ϵ almost instantaneously to a small hemispherical region of radius r_0 and that this energy is propagated just as is heat. An approximate solution for the temperature at any distance r from the center of disturbance and at time t is[12]

$$T = \frac{1.7 \times 10^{-21} \epsilon}{\rho s \left(\dfrac{ct}{\rho s} \right)^{\frac{3}{2}}} \exp\left(-r^2 \rho s / 4ct\right) + T_0 \quad \text{if} \quad \frac{ct}{\rho s} > r_0{}^2,$$

where T_0 = temperature of surface before collision, ρ, s, c = density, specific heat, and conductivity of cathodic material. This formula may be used when $t \geq t_0$ where t_0 corresponds to the time of collision and its magnitude in seconds is to be chosen about equal to $r_0{}^2$ in cm^2, to give the correct initial distribution of energy. If

$$t_0 = 4 \times 10^{-16},$$

$$\epsilon = 4 \text{ ev},$$

$$\rho s = 0.5,$$

$$c = 0.5,$$

then

$$T = 1700 \exp\left[-r^2/(1.6 \times 10^{-15})\right] + T_0.$$

There is over a region of a few atomic radii and for a time of the order of 10^{-16} a very high temperature. It may be easily shown that heat radiation during this time is negligible and that no other ion is likely to strike within this area and time.

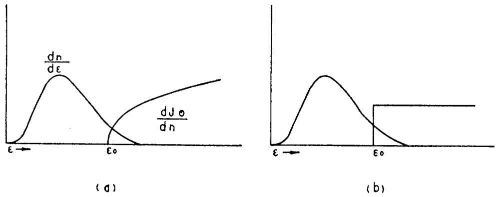
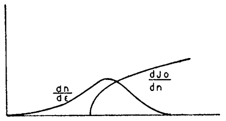


FIG. 1. $\bar{\epsilon} \ll \epsilon_0$.



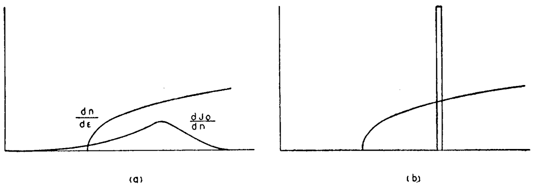


FIG. 2 (*Above*). $\bar{\epsilon} \sim \epsilon_0$.
FIG. 3 (*Below*). $\bar{\epsilon} \gg \epsilon_0$.

The rate of evaporation of the cathode material may be found if the vapor pressure is assumed to be

$$p = \exp(b - a/kT),$$

where a and b are constants characteristic of the cathode material, a being the heat of vaporization of one molecule. The number of molecules leaving unit surface area per second is

$$\nu = C_2 p / mv,$$

where m is the molecular mass, v the average velocity of molecules in the vapor state, and C_2 the fraction of molecules which stick to the surface on striking it. Hence

$$\nu = \frac{C_2 \exp(b - a/kT)}{2\left(\dfrac{2}{\pi} mkT\right)^{\frac{1}{2}}}.$$

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[11] A. v. Hippel, Ann. d. Physik **81**, 1043 (1926). E. Blechschmidt and A. v. Hippel, Ann. d. Physik **86**, 1006 (1928).

[12] H. S. Carslaw, *Mathematical Theory of the Conduction of Heat in Solids* (Macmillan Company, London, 1921), p. 149.

To find the total number of molecules evaporated by collision of a single ion with the surface, the maximum rate of evaporation per unit area will be multiplied by the length of time Δt required for the temperature to fall to such a value that the rate of evaporation is one-half its maximum, and by the area ΔS over which the rate of evaporation is not less than one-half maximum. This yields, on neglecting T_0,

$$\frac{dJ_0}{dn}=\frac{1.5\times 10^{-55}C_2\epsilon^{\frac{3}{2}}}{a^2c^{5/4}(\rho st_0)^{\frac{1}{4}}m^{\frac{1}{2}}}\times\exp\left[b-\frac{a(ct_0)^{\frac{3}{2}}}{2.3\times 10^{-37}\epsilon(\rho s)^{\frac{1}{2}}}\right]. \quad (4)$$

The usefulness of this expression is limited by an inexact knowledge of several quantities involved in addition to the assumptions under which it is derived. The thermal constants s and c may have values considerably different from those measured under ordinary conditions. The proper value of t_0 determines the radius over which the kinetic energy of the impinging ion is assumed to be distributed by the collision. Substituting reasonable values

$\rho s=1.0$ cal./degree; $c=0.5$ cal./sec. cm² degree; $t_0=3\times 10^{-16}$ sec.; $a=6\times 10^{-12}$ erg ($\epsilon_0=3.8$ ev); $b=43$; $m=10^{-22}$ g; $C_2=1$.

The above formula gives

ϵ	dJ_0/dn
4 ev	2×10^{-3} atom/ion
6	0.2
8	2

This shows that the above calculation gives a correct order of magnitude and demonstrates the rapid variation of dJ_0/dn near the energy required to remove one atom from the surface.

The total rate at which atoms leave the cathode surface may be found by integrating

$$J_0=\int_{\epsilon_0}^{\infty}\frac{dJ_0}{dn}\frac{dn}{d\epsilon}d\epsilon$$

$$\doteq\frac{IG(E\lambda)^{\frac{3}{2}}}{1+\gamma}\int_{\epsilon_0/E\lambda}^{\infty}\left(\frac{9}{8}+\frac{x}{4}-\exp\left(-x+1/2\right)\right)x^{\frac{3}{2}}\times\exp\left(-x-\frac{H}{E\lambda x}+1/2\right)dx$$

where

$$G=\frac{1.5\times 10^{-55}C_2e^b}{a^2c^{5/4}(\rho st_0)^{\frac{1}{4}}m^{\frac{1}{2}}},$$

$$H=\frac{a(ct_0)^{\frac{3}{2}}}{2.3\times 10^{-37}(\rho s)^{\frac{1}{2}}},$$

$$\frac{I}{1+\gamma}=\text{ionic current in ions/sec.}$$

This integral can be expressed in terms of error functions, but the result is complicated, and sufficient accuracy may be obtained without the complete expression. For the low pressure high voltage case where $E\lambda\gg\epsilon_0$,

$$J_0\approx\frac{21(\pi e)^{\frac{1}{2}}G}{16}\frac{I}{1+\gamma}(E\lambda)^{\frac{3}{2}}. \quad (5)$$

For the opposite case, where $E\lambda\ll\epsilon_0$,

$$J_0\approx\frac{GI\epsilon_0{}^{\frac{3}{2}}}{1+\gamma}\exp\left(-\frac{\epsilon_0}{E\lambda}-\frac{H}{\epsilon_0}+1/2\right)\left(\frac{\epsilon_0}{4E\lambda}+\frac{7}{4}\right). \quad (6)$$

As was expected, the expression for $E\lambda\gg\epsilon_0$ depends entirely on the function giving the number of atoms knocked off the cathode per impinging ion, and not on the distribution of ionic energies, whereas the rapidly varying exponential part of the expression for $E\lambda\ll\epsilon_0$ depends entirely on the energy distribution function. Since $dn(\epsilon)/d\epsilon$ is much better known than dJ_0/dn, the second expression should be correspondingly more accurate than the first.

Using (1), (3), (5), and (6), we have

if $E\lambda\gg\epsilon_0$

$$J=\frac{AI}{p}\left(\frac{Vi}{p^2}\right)^{3/5}; \quad (7)$$

if $E\lambda\ll\epsilon_0$

$$J=\frac{BI}{p}\exp\left(-c\epsilon_0\right)\left[\frac{p^2}{Vi}\right]^{2/5}\left(\frac{c\epsilon_0}{4}\left[\frac{p^2}{Vi}\right]^{2/5}+\frac{7}{4}\right), \quad (8)$$

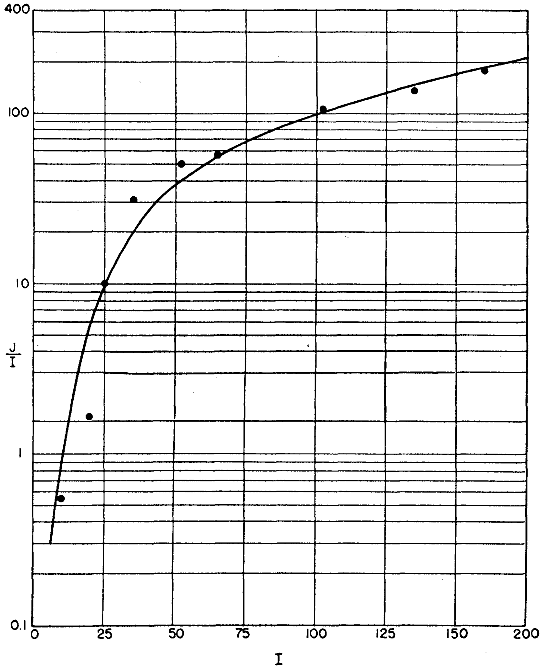

FIG. 4. Neon argon discharge. Ne, 99 percent; A, 1 percent. Rate of sputtering per unit current curve: $J/I=\text{const.}\,[7+(20.5/I^{2/5})]\exp[-(20.5/I^{2/5})]$, $I=$ total current in milliamp., $J=$ rate of sputtering measured as 1000/tube life in hours.

where A and B may be roughly determined from geometry of the discharge and from constants of the gas and cathode material,

$$c=1/2\left[\frac{(1+\gamma)K}{2\pi\Lambda^3}\right]^{2/5},$$

and I is the total discharge current. Although formula (7) agrees qualitatively with experimental results, it is formula (8) which is of particular interest here and will be compared in detail with experiment.

Sputtering measurements in the region $E\lambda\ll\epsilon_0$ have been very meager because the rate of sputtering in this case is extremely slow. Recently, however, Rockwood[13] has measured these slow rates of sputtering by measuring the rate of disappearance of the thin layer of active material on the cathodes of commercial cold cathode gas tubes. He showed that the aging of cold cathode tubes is due to sputtering of active material from the cathode, and by measuring the life of a number of tubes obtained the points in Fig. 4 for sputtering rate *vs.* current. A continuous fixed current was passed through each tube until it showed a characteristic increase in voltage drop. This increase in voltage marked the end of useful tube life and the disappearance of a large part of the cathode coating. Each point on Fig. 4 represents the mean of three tubes. These tubes contain neon gas at 60 mm Hg with a small admixture of argon and operate at 60 volts with constant cathode area (2.7 cm^2) over a range of current from about 5 to 200 milliamperes, making good the approximations involved in deriving (8). Agreement between theory and experiment is obtained as shown in Fig. 4 by properly choosing two constants to fit an expression of the form

$$J=aI^{-b/J^{2/5}}(7+b/I^{2/5})$$

to the experimental points.

Using the experimentally determined value of b and comparing its theoretical expression

$$c\epsilon_0\left[\frac{p^2}{Vi}\right]^{2/5},$$

we may evaluate ϵ_0. Since it is thought that most of the ions striking the cathode are argon,[14] moving in a gas which is essentially neon, we estimate from Table I, the values

TABLE I. Value of constants Λ and K where $\Lambda=\lambda p$ ($\lambda=$ mean free path in cm), $p=$ pressure in mm Hg, and $K=kp\sqrt{\epsilon}$ ($k=$ mobility of potassium ion in electrostatic units, $\epsilon=$ ionic energy in electron stat-volts).

	Λ*	K**
H_2		1.8×10^5
He	1.42×10^{-2}	
Ne	1.01×10^{-2}	
N_2	4.77×10^{-3}	
A	5.07×10^{-3}	3.1×10^4

* E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York. 1938).
** A. V. Hershey, Phys. Rev. **56**, 908 (1939).

$$\Lambda=7.0\times10^{-3},$$

and

$$K=7.0\times10^4,$$

so that

$$c=8.3\times10^3$$

if p is measured in mm of Hg, V and i in static units. This gives $\epsilon_0=0.013$ electron stat-volts or

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[13] G. H. Rockwood, A.I.E.E. Technical Paper (May, 1941), pp. 4–117.

[14] M. J. Druyvesteyn and F. M. Penning, Rev. Mod. Phys. **12**, 87 (1940).

TABLE II. Sputtering data.

Discharge pressure p mm Hg	Discharge current I milliamperes	Rate of sputtering J arbitrary units	I/p^2	J/p
5	2.6	<4.0	0.104	<0.8
10	11.5	5.8	0.115	0.58
15	27	14.2	0.120	0.95
20	47	20	0.118	1.0

3.9 electron volts which is in agreement with the observed values of ϵ_0 for metals varying from about 1 to 10 ev, and in particular with 2.1 ev given for pure Ba or Sr.[15] The cathode material is a mixture of Ba, Sr, and their oxides.

The second constant which is determined by the experimental data may be expressed in terms of the average number of atoms released by each ion of energy greater than ϵ_0. A tube operating at 25 milliamperes has a lifetime of 400 hours, during which time 1.8×10^{23} ions will have struck the cathode, and of these ions 3.6×10^{21} will have energy greater than 3.9 ev [Eq. (2)]. The cathode coating consists of about 1.0 mg of material of average atomic weight 100, and if we suppose that $\frac{1}{4}$ of this must be sputtered off to end the useful life of the tube, the number of sputtered atoms is found to be 1.5×10^{18}. The shape of the cathode and tube walls allows no simple evaluation of the fraction of atoms released from the cathode which are deposited on the tube walls, but a rough calculation from formula (1) gives 10^{-3}, so that about 1.5×10^{21} atoms are evaporated by the cathode or 0.4 atom per ion of energy greater than 3.9 ev. The fraction 0.4 seems physically reasonable and also agrees with the values found above from expression (4) for dJ_0/dn.

Rockwood also made measurements on a series of tubes containing pure argon at different pressures and operating at currents which were nearly proportional to the square of the pressure, so that the expression (p^2/Vi) would remain constant.[16] In this case, it is easily seen that according to Eq. (8), the rate of sputtering will be simply proportional to pressure. Table II shows that this is true within experimental error. This fact is not a test of the specific form of Eq. (8), for by making p^2/Vi constant, equivalent discharge conditions are obtained with the same ionic energies, so that it is only a test of fundamental assumptions and of Eq. (1) for the fraction of evaporated material which escapes from the cathode.

The rate of sputtering in a pure gas is complicated by the fact that ions exchange their charges rapidly in the neutral atoms of their own kind. This phenomenon probably does not occur in the mixture of gases cited above because the argon ions carry a large part of the discharge current, and argon is present in such small quantities that exchange of charge between an argon ion and an argon atom may be shown to be quite improbable. The effect of such an exchange would be to decrease the ionic mean free path and to make it strongly dependent on ionic velocity. Kallman and Rosen[17] show that the mean free path is decreased by a factor of two by the exchange of charge in He. The results quoted above for pure argon with varying pressures would not be affected because (p^2/Vi) and hence the ionic energies and free paths were kept constant. However, since the free path probably changes rapidly with change in ionic

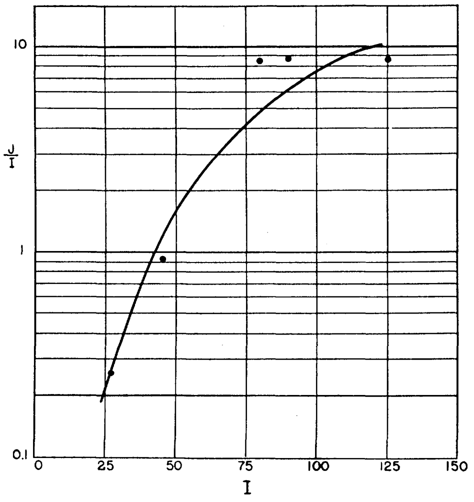

FIG. 5. Pure argon discharge. 100 percent A. Rate of sputtering per unit current curve: $J/I=\text{const.}\,[7+(30.6/I^{2/5})]\times\exp[-(30.6/I^{2/5})]$, $I=$ total current in milliamp., $J=$ rate of sputtering measured as 1000/tube life in hours.

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[16] Private communication.

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energy, formula (8) will not be accurate under more general conditions.

With this reservation, it is interesting to compare measurements made by Rockwood[18] on variation of sputtering with current for argon-filled tubes. His points are fitted to Eq. (8) in Fig. 5. Treating the experimentally determined constants as before, and assuming that the ionic mean free path is just half the atomic mean free path because of electron exchange and that consequently the mobility of an argon ion in argon gas is half that of a potassium ion in argon we obtain $\epsilon_0=3.1$ ev and $dJ_0/dn=0.27$. These quantities agree as well as can be expected with their more accurate determination from the neon-argon discharge.

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[18] Private communication.

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On the Extraction of Electrons from a Metal Surface by Ions and Metastable Atoms*

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An elementary theory is developed for the process by which a helium ion or a 2^3S metastable helium atom may extract an electron from a metal surface. The helium ion after collision may become a neutral atom although sometimes an excited or even a metastable atom. In the case of the metastable atom the collision involves an exchange of electrons between the metal and the atom, the excess energy being carried away by the ejected L shell electron. The average distance of transition $\bar{s}$ for He^+ and for the 2^3S metastable helium atom is calculated for different velocities. For $v=10^5$ cm/sec., $\bar{s}_{\text{met}}=2a_0$ and $\bar{s}_{\text{ion}}=11.5a_0$ where $a_0=0.528\times10^{-8}$ cm. For $v=3\times10^7$ cm/sec., $\bar{s}_{\text{met}}$ comes out less than $0.1a_0$ and $\bar{s}_{\text{ion}}=6.0a_0$. These values are different from the values obtained by Massey in a similar computation. The theory accounts for some but not all of the experimental evidence. The probable shape of the potential that the metal surface offers to a metastable atom is found.

I. INTRODUCTION

A POSITIVE ion or a metastable atom colliding with a metal surface may undergo a collision of the second kind with the aid of one of the metallic electrons. In the case of a metastable atom whose radiative transition to the ground state is forbidden by the spin conservation selection rule $\Delta S=0$, the collision can involve an exchange of electrons between the metal and the atom which leaves the atom in a state of different multiplicity—let us say, the ground state. The positive ion simply captures the metallic electron, thereby becoming a neutral atom, although sometimes an excited or even a metastable atom. In the latter case, the metastable atom may decay with secondary electron emission.

The electron emission due to impact of mercury metastable atoms on a nickel surface was first definitely proved by Webb.[1] This was followed up by the work of Messenger[2] and Coulliette.[3] Sonkin[4] studied this electron emission using a tungsten surface under various conditions. Oliphant[5] also studied the emission of electrons from metal surfaces as a result of impact by helium metastable atoms. Besides the above-

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