PHYSICAL REVIEW VOLUME 97, NUMBER 6 MARCH 15, 1955

Measurements and Collision—Radiation Damage Theory of High-Vacuum Sputtering*†

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(Received October 18, 1954; revised manuscript received December 8, 1954)

A brief summary of some of the important experimental and theoretical work related to the subject of metallic sputtering is presented. The need for measurements in high vacuum is indicated and an ion beam which utilized a Philips Ion Gauge discharge ion source to make high-vacuum sputtering ratio measurements is described. Absolute sputtering ratio data for the gas-metal combinations Ag-Kr, Ag-A, Ag-Ne, Ag-He, Cu-Kr, Cu-A, Pb-A, and Pb-He are presented in terms of the number of atoms sputtered per incident ion, n_a, *versus* incident ion energy, E_0, for ion energies varying between 400–6100 ev. The data are interpreted by treating the incident ion as a hard sphere which "cools" in a manner similar to a neutron losing energy by collisions in a lattice, each collision producing recoil atoms and atomic displacements near the surface. The number of atoms escaping, or "sputtering," from the metallic surface is reduced from the number displaced by absorption within the metal which is accounted for by a parameter α. By use of elementary neutron cooling theory and the Seitz formula for displacements produced by a recoil atom within a solid, the formula for the number of atoms sputtered per incident ion is given by

$$n_a=\left(\frac{\epsilon E_0}{E_d}\right)^{\frac{1}{2}}\sum_{n=1}^{n_c} e^{-\alpha\sqrt{n}}e^{-(n-1)\xi/2},\quad n_c=\frac{1}{\xi}\ln\left(\frac{\epsilon E_0}{E_d}\right),$$

for the case of ions more massive than the metallic atoms. The effect of ions rebounding from the surface after the first collision is considered to produce effectively two types of incident current particles; (1) incident gas ions and (2) recoil metal atoms. These considerations lead to a modified sputtering ratio formula, which reduces to the above equation when $M_1 \geqq M_2$. The displacement energy for the process, E_d, is calculated by use of G. K. Wehner's data on sputtering thresholds and the relation $E_t=E_d/\epsilon$. A fair fit to the experimental data is obtained by suitable choice of α in the modified formula for the cases studied.

The use of "hard" collisions is justified and an equivalent ion energy shift defined by equal average energy transfer on the first ion-atom collision is applied to the data. The subject of sputtering thresholds is treated by an attempt to bracket observed thresholds, E_t, between limits defined by the atomic heat of vaporization, the displacement energy, and the average energy transfer per collision.

INTRODUCTION

THE breakdown of a metallic surface due to positive ion bombardment is a phenomenon which has been observed since the earliest investigations in the field of gaseous electronics. Because of its basic nature and relative ease of attainment, this effect, termed "sputtering," has subsequently been the basis of many experiments which have been reported in the literature. In most of these experiments, the glow discharge served as a source of ions and the rate of sputtering was measured by indirect means because of experimental difficulties. In order to make a direct measurement of the number of atoms sputtered per incident ion it is necessary to: (1) have a sufficiently large mean free path near the metallic surface to allow escape of all sputtered atoms, (2) return secondary electrons to the target, (3) have a source of ions with sharply defined energy, and (4) directly measure weight loss of the material sputtered. The glow discharge did not serve as an ion source which could satisfy any of the above requirements until the gas pressure was reduced to a lower limit of about ten microns.

The experiments of Penning and Moubis,[1] Güntherschulze and Meyer,[2] and Güntherschulze[3] are representative of reliable studies which, by careful design, utilized the glow discharge as an ion source. Penning and Moubis were able to obtain measurements by use of a discharge employing an axial magnetic field parallel to a cylindrical cathode. The field aided in returning secondary electrons to the cathode and in reducing the operating pressure of the glow discharge. The amount of material sputtered was measured by the gain in weight of mica disks placed in a strategic position opposite to the cathode. Güntherschulze and Meyer[2] were able to make reliable measurements by running a glow discharge between a heated filament and a cathode with a hole in it to permit some of the ions to pass through. These ions struck a target which was suspended directly above the cathode by a spring at a negative potential of 200 to 1200 volts. As the target lost weight, it would rise slightly, the amount of rise being a measure of the weight loss. The measured sputtering rates were independent of pressure at pressures less than 0.010 mm Hg.

Güntherschulze[3] eliminated the effect of back diffusion by use of a cylindrical cathode surrounding a wire anode. Assuming the pressure of sputtered material to be constant throughout the vessel, the rate of deposition on the anode was identical with the rate of removal from the cathode. Measurement of the weight gained by the wire anode gave information on the sputtering rate which agreed closely with that of Penning and Moubis.

The General Electric Company, Ltd., London, England,[4] measured sputtering rates by use of a pure tungsten wire mounted in a tube with additional elec-

* Abstracted from a thesis presented to the University of Southern California in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

† Part of this work was sponsored by the U. S. Office of Naval Research.

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[1] F. M. Penning and J. H. A. Moubis, Proc. Acad. Sci. Amsterdam 43, 41 (1940).

[2] A. Güntherschulze and K. Meyer, Z. Physik 62, 607 (1930).

[3] A. Güntherschulze, Z. Physik 110, 149 (1941).

[4] General Electric Company, Ltd., Phil. Mag. 45, 98 (1923).

trodes for operating a glow discharge. Application of a negative potential to the wire while the discharge was operating caused the resistance of the wire to increase due to surface sputtering and consequent reduced cross-sectional area. Thus, the change in resistance of the wire afforded a measure of the amount of material sputtered from the sample. This method was suited for measuring sputtering thresholds and values were found ranging from 25–80 volts for argon to 700 volts for hydrogen.

Wehner[5] has recently performed notable experiments to determine the sputtering threshold of a large number of metals bombarded by mercury ions accelerated from a plasma at low pressure surrounding the metal target under study. He has developed an empirical formula for the sputtering threshold which involves the velocity of sound in the metal, the average energy transfer per collision between ion and metal atom and the heat of sublimation. In addition, by collecting the sputtered deposits from a metal strip in a plasma, Wehner[6] has been able to show that Hg^+ ions incident near the edge of the strip, i.e., at an oblique angle, will require less energy to begin sputtering than those which are normally incident near the center of the strip.

Bareiss[7] measured the resistance of gold-foil anodes bombarded by electrons of energy 200–500 ev. If there had been any removal of gold by sputtering at these anodes, the subsequent resistance change could have been easily detected; however, in no case was he able to find any indication of sputtering due to electrons at these energies.

Numerous theories of cathode sputtering have been proposed,[8–14] the generally accepted ones being those of von Hippel[11] and Kingdon and Langmuir.[12] The evaporation theory proposed by von Hippel, although not completely satisfactory, has been considered the most plausible explanation of the sputtering phenomenon and is more widely accepted than the latter, which is based upon momentum interchange and surface condition. According to von Hippel, an ion striking a point on a cathode surface will distribute its energy in the form of heat over a localized "hot spot" of atomic dimensions. The resultant extreme temperature will cause vaporization from a surface element, ΔF, for a short time interval, Δt, the rate of vaporization being dependent upon the incident ion energy and the physical properties of the cathode. Sputtering rates were expected to rise exponentially to a maximum at ion energies of about one thousand volts. The decrease at higher energy was attributed to ion penetration of the surface with subsequent increase in the number of atoms affected at the "hot spot" resulting in reduced average temperature over the area ΔF. Von Hippel's theory showed correlation between certain sputtering series observed in a glow discharge and the latent heat of vaporization of the metal sputtered. The mass dependence of the phenomenon was inferred from the assumption that heavier ions would not penetrate the surface as much as lighter ions of equal energy. Townes[10] has applied the above theory to describe sputtering in a gas at high pressure in which case the diffusion of sputtered material from the cathode is a dominant factor. Kingdon and Langmuir[12] proposed a description of the sputtering phenomenon which was suggested by their observations on the removal of thorium from a thoriated tungsten filament by positive ion bombardment. The emission *vs* time characteristic of the filaments showed an unexpected behavior, since, instead of an immediate reduction in emission with onset of the discharge, in some cases, the current remained steady for a short period and then began to decrease monotonically to a value near that for a pure tungsten filament. In order to explain these results, Kingdon and Langmuir hypothesized a "crevice" theory which was assumed to occur in two steps. The first step was the formation of a dent or "crevice" at the point of ion impact, the incident ion recoiling in the backward direction; sputtering could then result when a second ion struck this crevice and knocked out thorium atoms from around its edge. The steady period of emission was then considered to be during the time ions were forming crevices on the thoriated tungsten surface. Seeliger and Sommermeyer[15] performed an experiment which was designed to make a comparison of the momentum exchange theory and the evaporation theory. They drew ions from a glow discharge into an evacuated region and accelerated these canal rays to strike a molten gallium target at varying angles of incidence. The angular distribution of sputtered material collected on a cylinder surrounding the target indicated that Knudsen's cosine law described the density variation with respect to the normal. This was considered evidence in favor of the evaporation theory since the momentum exchange theory appeared to predict a preferred direction for the sputtered atoms. However, the evaporation theory has also been considered to have shortcomings since it does not satisfactorily explain (1) the dependence of sputtering on ion mass (2) sputtering thresholds being many times greater than the atomic heat of sublimation (3) secondary emission due to ion bombardment being considerably less than would occur if there were heating and consequent thermionic emission at the surface (4) the lack of marked temperature dependence of sputtering rates.

[5] G. K. Wehner, Phys. Rev. **93**, 633 (1954).
[6] G. K. Wehner, J. Appl. Phys. **25**, 270 (1954).
[7] Max Bareiss, Z. Physik **68**, 585 (1931).
[8] U. K. Bose, Indian J. Phys. **12**, 95 (1938).
[9] V. Bush and C. G. Smith, Trans. Am. Inst. Elec. Engrs. **41**, 402 (1922).
[10] C. H. Townes, Phys. Rev. **65**, 319 (1944).
[11] A. von Hippel, Ann. Physik **81**, 1043 (1926).
[12] K. H. Kingdon and I. Langmuir, Phys. Rev. **22**, 148 (1923).
[13] J. J. Thomson, *Rays of Positive Electricity* (Longmans Green and Company, London, 1921).
[14] C. Starr, Phys. Rev. **56**, 216 (1939).
[15] R. Seeliger and K. Sommermeyer, Z. Physik **93**, 692 (1935).

It is generally recognized that, despite the considerable amount of work which has been devoted to its study, the phenomenon of sputtering has not been explained to any full degree of confidence. This may be largely attributed to the difficulty in making sputtering measurements in terms of the number of atoms sputtered per incident ion. Timoshenko[16] performed an experiment which utilized a capillary arc ion source to measure absolute sputtering ratios for argon ions incident on silver. His experiment was conducted under apparently ideal conditions since the ions from the source were accelerated through a known potential difference into a sputtering chamber at high vacuum; secondary electrons at the target were returned and there was no back diffusion of sputtered atoms. These measurements indicated a sharp rise in the sputtering ratio when the ion energy was increased above 2800 volts. This writer[17] has essentially repeated Timoshenko's experiment by use of a Philips Ion Gauge discharge ion source and has observed that sputtering rates decrease gradually with decreasing ion energy. Moreover, it was stated in the previous letter that the sputtering ratios for argon ions incident on silver could be closely fitted to the number of collisions made by the ion in a process similar to neutron cooling with the silver lattice acting as a moderator. This led to a logarithmic form for the curve of sputtering ratio *vs* incident ion energy. The purpose of this paper will be to present additional data and to give a description of the sputtering process which includes the elementary concepts of neutron cooling and radiation damage theory to a metallic surface. For the sake of clarity, the experimental method will be described in greater detail than in the previous letter and some arguments in favor of the radiation damage concept of high-vacuum sputtering will be considered.

EXPERIMENTAL

A. Experimental Equipment

A Philips Ionization Gauge (P.I.G.) discharge has been used as a source of ions in this investigation because of its ability to supply ion currents the order of 30 000 microamperes per cm^2 at a gas pressure of a few microns. The method of forming a beam of ions was similar to that of Keller[18] who used the P.I.G. discharge for high-energy bombardment by alpha particles. Operation and characteristic behavior of this type discharge have been described by Penning[19] and Backus.[20] The discharge geometry in this study consisted of a pair of water-cooled copper cathodes separated by two plane grounded plates with one-half inch apertures for defining the discharge plasma. The discharge electrodes were supported in a vacuum chamber (inside dimensions $11\frac{1}{4}$ in.$\times 11\frac{1}{4}$ in.$\times 9$ in.) which was fixed between the poles of a 13 in. pole-face electromagnet. A ballast resistor of 30 000 ohms was placed in the cathode line to reduce discharge currents to about five milliamperes; this stabilized the discharge and prolonged the life of cathodes to the order of 15 hours. Dependent upon the gas in use, the discharge operated with approximately 1600 volts on the cathodes at a pressure of one-half to four microns in a magnetic field of 1000 gauss. All gases used were commercially available tank gas of 99.2 percent purity which was adequate to meet the requirements of this experiment. Currents and voltages were measured by calibrated standard commercial meters. Base pressure of 0.05 micron was maintained by use of a DPI, model 201, oil diffusion pump and pressure was measured by an RCA 1949 ion gauge.

B. Ion Beam

The P.I.G. discharge was used to supply a beam of ions with uniform energy by means of a 0.115-in. hole in one of the cathodes; the ions issuing from this hole were accelerated through the 0.250-in. aperture of a cylindrical target shield. The target to be sputtered was aligned with the beam and supported on an insulated wire which passed through the top of the shield. The shield performed the function of returning secondary electrons to the target by being biased 150 volts negative with respect to the sample being bombarded. Return of secondary electrons to the target could be observed as variations in the target current by varying the potential between shield and target from plus to minus polarity. The biasing voltage between shield and target was assuredly sufficient to prevent escape of

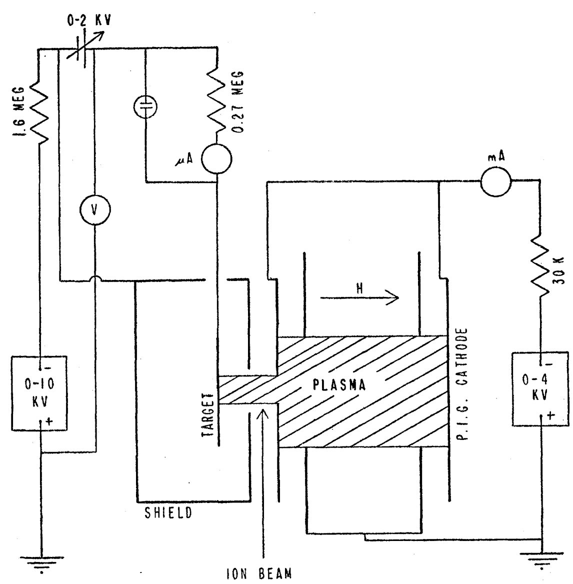

FIG. 1. The ion beam electrical circuit.

[16] G. Timoshenko, J. Appl. Phys. **12**, 69 (1940).
[17] F. Keywell, Phys. Rev. **87**, 160 (1952).
[18] R. Keller, Helv. Phys. Acta **21**, 170 (1948).
[19] F. M. Penning and J. H. A. Moubis, Physica **4**, 71 (1937).
[20] J. Backus, in *Gaseous Electrical Discharges in Magnetic Fields*, edited by A. Guthrie and R. K. Wakerling (McGraw-Hill Book Company, Inc., New York, 1949), Chap. 11, p. 345, National Nuclear Energy Series, Plutonium Project Record, Vol. 5, Div. I.

TABLE I. Some ion beam operating conditions.

Gas	Pressure (microns)	P.I.G. voltage (volts)	P.I.G. current (ma)	Target voltage (volts)	Target current (μa)
He	4.0	1800	6.0	5700	240
Ne	2.0	1500	6.0	4000	250
A	0.9	1850	6.0	2400	125
Kr	0.5	1850	5.0	4200	108

secondary electrons from the target surface. The targets were polished, cleaned in alcohol, then ether and finally cleaned by sputtering. The electrical circuit associated with the ion source is shown in Fig. 1.

The above relatively simple arrangement of electrodes has provided an ion source capable of supplying 100–220 microamperes of positive-ion current, dependent upon the gas under study. A few typical sets of operating conditions are indicated in Table I. Gas pressure in the vacuum chamber was low enough to allow gaseous mean free paths of two to nine cm.

C. Method of Measurement

Absolute sputtering ratios have been measured for a number of gas-metal combinations by essentially counting the number of ions which have struck the target and the number of atoms which have been sputtered. This was accomplished by measuring (1) weight loss of the bombarded sample, (2) true positive ion current to the sample, (3) time of bombardment for ions of known initial energy. The absolute sputtering ratio for a metal bombarded by ions of known energy, E_0, was given by

$$n_a = 96\,500 \Delta W / A I_+ t,$$

where I_+ = positive ion current to the target (microamperes), t = time of bombardment (sec), ΔW = weight loss of target (micrograms), and A = atomic weight of material. Gas pressure in the vacuum chamber was metered during each test to maintain the ion current steady to within five percent. Weight losses of the sputtered samples ranged from 500–4500 micrograms and were measured by means of a microbalance. The data recorded for a series of tests with silver metal bombarded by krypton ions is given in Table II as an illustration of the method of measurement. Absolute sputtering ratio data similar to those in Table II have been obtained for the gas-metal combinations: Kr-Ag, A-Ag, Ne-Ag, He-Ag, A-Pb, He-Pb, Kr-Cu, A-Cu.

TABLE II. Sputtering ratio data for silver bombarded by krypton ions.

Target voltage (volts)	Target current (μa)	Time of bombardment (seconds)	ΔW (μg)	No. of Ag atoms sputtered $\times 10^{-18}$	No. of ions $\times 10^{-18}$	n_a (No. of atoms/ion)
1075	100	900	646	3.60	0.56	6.4
2075	96	900	658	3.67	0.54	6.8
2475	88	1800	1275	7.11	0.99	7.2
3470	123	900	1306	7.27	0.69	10.6
4465	133	900	1346	7.50	0.75	10.1
5160	139	900	1605	8.95	0.78	11.5

A summary of the experimental data is shown in Figs. 2, 3, and 4; the curves fitted to the experimental points will be explained in the following section. The upper limit of ion energy was determined for each gas by the onset of intense arcing parallel to the magnetic field when high voltage was applied to the accelerating shield. The lower limit of ion energy was caused by space charge formation within the shield and occurred at higher energy for more massive ions such as krypton and argon. The concentration of doubly charged ions in the beam is believed large enough to introduce an error of about four percent. Error in measurement of the ion current due to ions rebounding from the target surface as ions or metastable atoms is estimated the order of two percent or less.[21,22] The estimated independent probable errors are (1) ion current, eight percent, (2) ion energy, five percent, (3) weight loss, two percent, (4) bombardment time, nil. Although there is

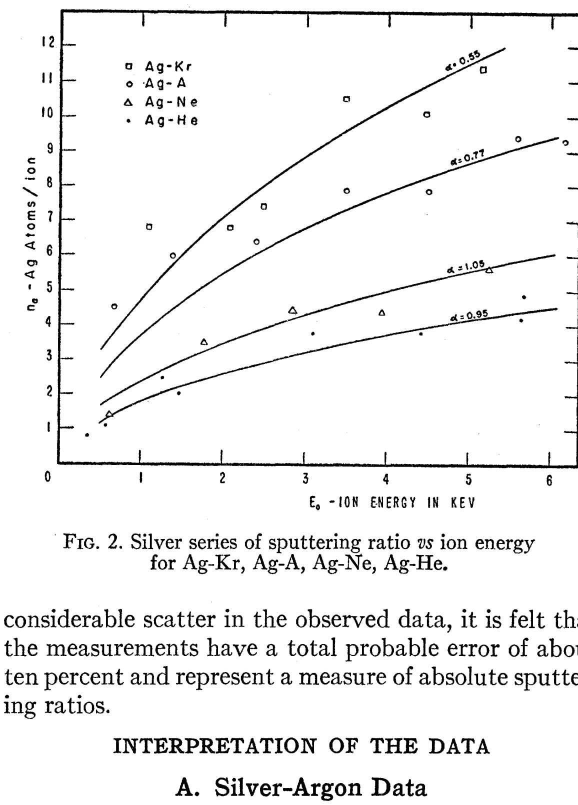

FIG. 2. Silver series of sputtering ratio *vs* ion energy for Ag-Kr, Ag-A, Ag-Ne, Ag-He.

considerable scatter in the observed data, it is felt that the measurements have a total probable error of about ten percent and represent a measure of absolute sputtering ratios.

INTERPRETATION OF THE DATA

A. Silver-Argon Data

Sputtering of silver metal by argon ions was initially studied to compare results with those of Timoshenko.[16]

[21] H. D. Hagstrum has described an instrument capable of measuring the net secondary and tertiary currents which arise due to reflection of ions and metastable atoms of the noble gases from a clean tungsten surface. In private conversation, Dr. Hagstrum has kindly given this writer data which indicate that the currents due to rebounding ions would be small in the present case. His measurements for 1000-volt ions of He^+, Ne^+, A^+, and Kr^+ on clean tungsten show the loss of ion current caused by reflected ions to be the order of one percent for He^+ decreasing to 0.06 percent for Kr^+.

[22] H. D. Hagstrum, Rev. Sci. Instr. 24, 1122 (1953).

As stated in the previous communication, both sets of data were in agreement at high energy but it was observed in this investigation that sputtering ratios decreased more gradually with decreasing ion energy than was previously reported. Furthermore, it was noted that the number of atoms sputtered per incident ion was considerably less than energetically possible.[23] For the silver-argon case, however, the sputtering ratios observed were more nearly the number of collisions required by the ion to "cool" to about 40 ev where the silver lattice acts as a moderator and the argon atom loses energy by a diffusion-collision process. When elementary neutron cooling theory[24] is applied to such a process, an ion of atomic weight M_1 which is being cooled by a moderator of atoms of atomic weight M_2 will have energy after n collisions given by

$$E_n = E_0 e^{-n\xi}, \tag{1}$$

where

$$\xi = 1 - \frac{(M_2 - M_1)^2}{2M_1M_2} \ln\left(\frac{M_1+M_2}{M_1-M_2}\right).$$

The silver-argon data were fitted by assuming the argon ion cannot cause sputtering when its energy is less than 39 ev; this gives, for the number of ion collisions,

$$n_c = (1/0.59)\ln(E_0/39),$$

which agrees closely with the observed number of silver atoms sputtered per incident argon ion.

B. Radiation Damage

It would not be expected to find the above method to apply in the case of sputtering by light ions since the trends of collision number and sputtering ratio are inverse with decreasing ion mass. Thus, the application of neutron cooling theory is not enough to explain the observed data but the success attained in the silver-argon case indicated a collision mechanism is involved. A more realistic description would surely be attained by recognizing that an ion can transfer a considerable fraction of its energy to a metallic atom in one collision,[25] thus forming an energetic recoil atom which can then strike other atoms in the lattice to produce secondary, tertiary, etc., recoil atoms. A process of this nature leads one to consider the effect as being a radiation damage phenomenon; consequently, it would appear possible to apply the theory of radiation damage, as developed by Seitz,[26] to the subject of high-vacuum sputtering. Seitz has given a method for calculating the

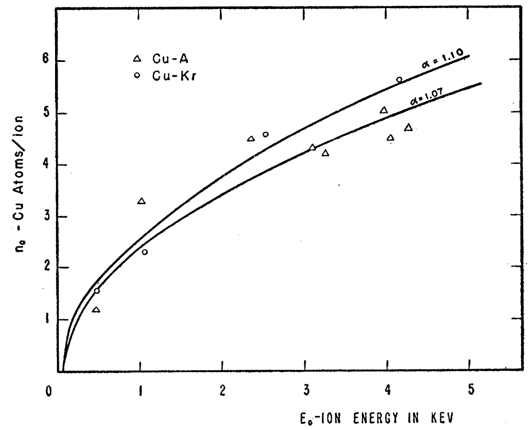

FIG. 3. Copper-krypton and copper-argon sputtering ratios *vs* ion energy.

number of displaced atoms produced in a solid due to passage of an energetic particle (alpha, proton, neutron) of high initial energy. The effect of energy transfer to electrons was considered as well as energy loss due to "knock-on" collisions. At lower energies, however, the chief process of loss is energy transfer by "hard" collisions. Therefore, in the case of ions at least as massive as helium ions and of energy less than 6000 ev, it is felt that ion-atom collisions in a conductor can be considered hard-sphere collisions. Employing the assumption of hard-sphere collisions, we can calculate the number of atoms displaced at a metallic surface due to an incident gas ion. This number should be related to the number of atoms sputtered when account is taken of the absorption of displaced atoms which were formed a few atomic layers beneath the surface.

In the immediately following treatment, it will be assumed that the ion is more massive than the metallic atom and will continue in the forward direction into the lattice to remain beneath the surface after the first collision, i.e., no rebounding ions or gas atoms are present at the surface.

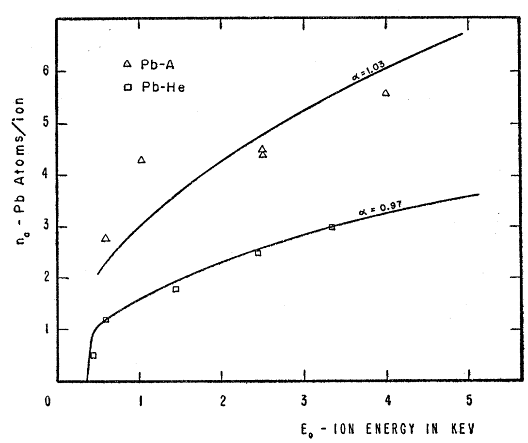

FIG. 4. Lead-argon and lead-helium sputtering ratios *vs* ion energy.

[23] Since the atomic heat of sublimation at a metallic surface is the order of 3–5 ev, a 4000-volt ion possesses sufficient energy to remove the order of 1000 atoms as compared to actual sputtering ratios of less than 10 atoms per ion.

[24] E. Fermi, *Nuclear Physics*, notes compiled by Orear, Rosenfeld, and Schluter (University of Chicago Press, Chicago, 1950), p. 181.

[25] For example, a 4000-ev argon ion will transfer, on the average, 1580 ev to a silver atom; this energy is considerably greater than the displacement energy of about 21 ev.

[26] F. Seitz, Discussions Faraday Soc. 5, 271 (1949).

If we apply the neutron cooling formula, the ion energy at the nth collision will be

$$E_n = E_0 e^{-n\xi},$$

and the average fraction of energy transferred to the metallic atom will be

$$\epsilon = 2M_1M_2/(M_1+M_2)^2, \tag{2}$$

giving

$$\bar{E}_{n+1} = \epsilon E_0 e^{-n\xi} \tag{3}$$

for the average energy of the $(n+1)$th metallic recoil atom. Using Seitz' formula for the number of displaced atoms, n_s, produced by a recoil atom of energy $\bar{E}$ in a metal of atomic displacement energy E_d,

$$n_s = (\bar{E}/E_d)^{\frac{1}{2}} \tag{4}$$

the number of displaced atoms at the nth collision will be $n_s = (\bar{E}_n/E_d)^{\frac{1}{2}}$, or

$$n_s = \left(\frac{\epsilon E_0}{E_d}\right)^{\frac{1}{2}} e^{-(n-1)\xi/2}. \tag{5}$$

The total number of displaced atoms is

$$N = \sum_s n_s = \left(\frac{\epsilon E_0}{E_d}\right)^{\frac{1}{2}} \sum_{n=1}^{n_c} e^{-(n-1)\xi/2}, \tag{6}$$

$$n_c = (1/\xi)\ln(\epsilon E_0/E_d).$$

We treat absorption of displaced atoms within the metal by assuming that of n_s displaced atoms formed at a depth x below the surface, the number escaping from the surface will be

$$n_e = e^{-\beta x} n_s. \tag{7}$$

The depth x will be related, on the average, to the number of collisions the ion has made by assuming the ion to progress by a random walk, in which case

$$x = k\sqrt{n}. \tag{8}$$

Then

$$n_e = \left(\frac{\epsilon E_0}{E_d}\right)^{\frac{1}{2}} e^{-\alpha\sqrt{n}} e^{-(n-1)\xi/2}, \tag{9}$$

where $\alpha = k\beta$, and the number of atoms sputtered is given by

$$n_a = \left(\frac{\epsilon E_0}{E_d}\right)^{\frac{1}{2}} \sum_{n=1}^{n_c} e^{-\alpha\sqrt{n}} e^{-(n-1)\xi/2}. \tag{10}$$

As previously stated, Eq. (10) does not include the effect of ions which rebound from the surface on the first collision as neutral atoms, retaining a considerable fraction of their energy and producing only one recoil atom (the surface atom which reversed the ion's direction). Energetic recoil ions have been observed previously[27] and this effect has been studied in the case of light ions such as Li^+.[28,29] In considering the effect of ions or atoms rebounding at the surface, the following assumptions will be made as a first approximation to the case which may exist in nature: (1) The ion or gas atom penetrates into the volume of the metal if its deflection in the laboratory frame after the first collision is less than 90°. (2) The ion or gas atom rebounds from the surface if its deflection in the laboratory frame after the first collision is greater than 90°.

If the mass of the incident ion, M_1, is less than the mass of the metal atom, M_2, there will be an angle of deflection θ_0, in the c.m. system such that angles less than θ_0 are penetrating cases and angles greater than θ_0 give rise to rebounding ions. It is seen by the accompanying diagram (Fig. 5) that

$$\cos\theta_0 = M_1/M_2,$$

and the probability of a penetrating type collision is

$$f_p = \theta_0/\pi.$$

The probability of the ion rebounding on the first collision is

$$f_r = 1 - f_p,$$

since we consider the ion to either rebound or penetrate the surface on the first collision. The surface is also, in effect, considered to be both clean and smooth, thus the first collision will be an ion-metal atom collision and a rebound atom will not strike a crevice but will, with certainty, escape from the surface.

For Ag-Kr, $f_r = 0.22$ and for Ag-He, $f_r = 0.49$; hence, the percentage of rebounding cases is comparable to that of the penetrating cases for lighter rare gas ions

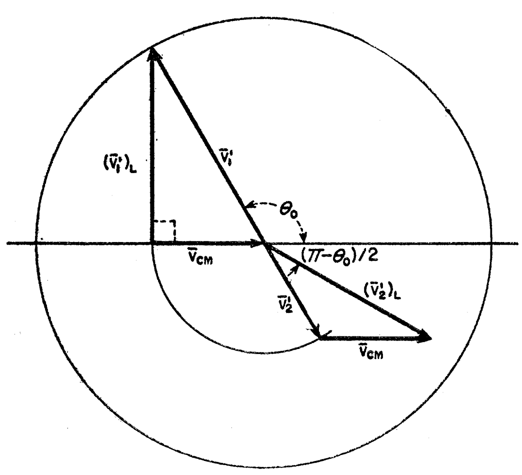

FIG. 5. Collision diagram. Subscript L denotes velocity in the laboratory frame. Primes denote velocity after collision. Subscript 1 or 2 denotes gas or metal atom velocity.

[27] Longacre (see reference 28) reflected Li^+ ions from a nickel surface and found that the fraction of energy retained by the ions was less with increasing angle of deviation. By analysis of his data, he concluded the scattering was due to elastic impacts at a roughened surface with small coefficient of restitution.

[28] A. Longacre, Phys. Rev. **46**, 407 (1934).

[29] R. W. Gurney, Phys. Rev. **32**, 467 (1928).

incident on silver, a typical series of gas-metal combinations.

Figure 5 indicates that each rebounding collision will result in a metallic recoil atom directed toward the volume of the metal. If the current of ions to the metal is I at energy E_0, there will be a fraction, f_pI, of the current which penetrates the surface; these ions will be considered to cause sputtering according to Eq. (10). In addition, there will be a fraction, f_rI, of ions which produce metallic recoil atoms at a new average energy $\bar{E}_r$ which is essentially a second type of particle incident at the surface. Therefore, the current at the surface can be considered to consist of two components; (1) incident ions in a parallel beam at energy E_0 and (2) recoil metal atoms incident within a cone of semivertical angle $(\pi-\theta_0)/2$ and with average energy $\bar{E}_r$. The energy $\bar{E}_r$ is calculated by averaging the maximum recoil energy $2\epsilon E_0$, and the recoil energy for ion deflection at θ_0, $\Delta E=2\epsilon\sin^2(\theta_0/2)$, which gives

$$\bar{E}_r=\epsilon E_0\left(1+\frac{1+M_1/M_2}{2}\right). \tag{11}$$

If n_a = average number of atoms sputtered per ion, $n_a{}^p$ = average number of atoms sputtered per ion which penetrates the surface, $n_a{}^r$ = average number of atoms sputtered per recoil metal atom at the surface, and with $I=f_pI+f_rI$ (ions per second), we have

$$n_a=f_pn_a{}^p+f_rn_a{}^r. \tag{12}$$

By Eq. (10),

$$n_a{}^p=\left(\frac{\epsilon E_0}{E_d}\right)^{\frac{1}{2}}\sum_{n=1}^{n_c}e^{-\alpha\sqrt{n}}e^{-(n-1)\xi/2}.$$

By Eqs. (4) and (9),

$$n_a{}^r=(\bar{E}_r/E_d)^{\frac{1}{2}}e^{-\alpha} \tag{13}$$

as we consider the escape of displaced atoms due to one recoil metallic atom.

Since the magnitude of $\bar{E}_r$ is between $1.5\epsilon E_0$ and $2\epsilon E_0$, we have the relation

$$1.22\sqrt{(\epsilon E_0)}\leqslant\sqrt{\bar{E}_r}\leqslant 1.42\sqrt{(\epsilon E_0)}$$

and

$$\sqrt{\bar{E}_r}\simeq 1.32\sqrt{(\epsilon E_0)},$$

which is accurate to at least seven percent for all gas-metal combinations.

Thus by Eq. (13) and the approximate value for $\sqrt{\bar{E}_r}$,

$$n_a{}^r\simeq 1.32(\epsilon E_0/E_d)^{\frac{1}{2}}e^{-\alpha}; \tag{14}$$

and by (12) and (14),

$$n_a=\left(\frac{\epsilon E_0}{E_d}\right)^{\frac{1}{2}}\sum_{n=1}^{n_c}(f_p+1.32\delta_{n1}f_r)e^{-\alpha\sqrt{n}}e^{-(n-1)\xi/2}$$

$$n_c=(1/\xi)\ln(\epsilon E_0/E_d),\quad \delta_{n1}=\begin{cases}0 & n\neq 1\\ 1 & n=1.\end{cases} \tag{15}$$

Equation (15) reduces to Eq. (10) if $M_1\geqslant M_2$.

TABLE III. Parameters for sputtering ratio formula.

Gas-metal combination	ξ	ϵ	α
Ag-Kr	0.93	0.49	0.55
Ag-A	0.59	0.39	0.77
Ag-Ne	0.33	0.27	1.05
Ag-He	0.073	0.069	0.95
Cu-Kr	0.92	0.49	1.10
Cu-A	0.84	0.47	1.07
Pb-A	0.34	0.27	1.03
Pb-He	0.038	0.037	0.97

In order to test Eq. (15), one should be able to fit the curve of n_a *vs* E_0 calculated by this equation to the observed experimental data by a suitable choice of the parameter α. E_d, ϵ and ξ are constants characteristic of each gas-metal combination. The displacement energy for silver and copper is reported 20–25 ev but it has not been measured for lead. Fortunately, the uncertainty in the displacement energy for the sputtering process can be removed by means of sputtering threshold data for silver, copper, and lead bombarded by mercury ions due to the work of Wehner.[5] The sputtering threshold, according to formula (10), is $E_t=E_d/\epsilon$; using Wehner's threshold data E_t(Ag-Hg) = 40–50 ev, E_t(Cu-Hg) = 50–70 ev, E_t(Pb-Hg) = 20–40 ev and values of ϵ calculated by Eq. (2), the displacement energies for silver, copper, and lead are about 21, 21, and 15 ev respectively. A fair fit to the experimental data has been obtained in the cases of sputtering for the gas-metal combinations and parameters, α (Table III), as shown in Figs. 2, 3, and 4. The plot of n_a *vs* E_0 according to Eq. (15) is shaped over most of the energy range by the term $\sqrt{\epsilon E_0}$ which is proportional to the average recoil momentum of the first metal atom struck at the surface. The summation factor serves to scale the curves by means of the parameter α. It is to be noted that all of the quantities involved in Eq. (15) are consistent, as we have: (1) ϵ, ξ, f_p, f_r, and n_c (rounded off to the nearest integer) are calculated by classical collision theory. (2) E_d as calculated by $E_d=E_t\times\epsilon$ using Wehner's sputtering threshold data for Ag and Cu bombarded by Hg^+ ions is in agreement with previous direct measurements of this constant. (3) Values of α the order of one indicate that about one-third of the atoms displaced at the surface on the first collision escape as sputtered atoms (the equation would be exceedingly questionable if the α's were an order of magnitude lower or higher).

One consequence of a description of sputtering based on a collision mechanism is the possibility of relating "equivalent ion energies" for a pair of ions on a common metal. Since the number of atoms sputtered is determined largely by the energy of the first few metallic recoil atoms, it would seem, when the average energy transferred on the first collision to a metal atom, type 1, by an ion, type 2, at energy E_2 is the same as the energy transferred by an ion, type 3, at energy E_3, the sputter-

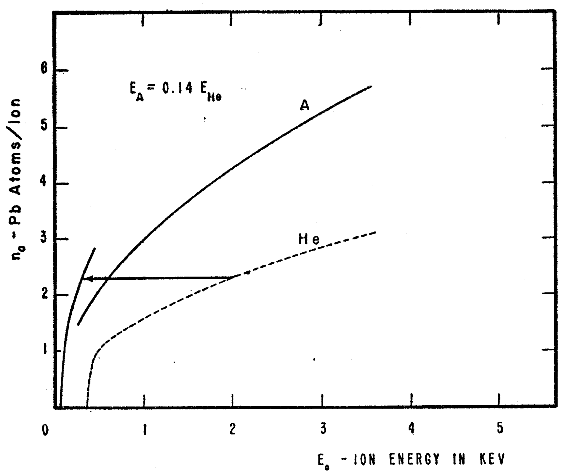

FIG. 6. Equivalent energy shift of helium sputtering ratio curve relative to argon on lead.

ing ratios should be approximately equal for the two ions. That is, sputtering of a metal by two types of ions should tend to be the same if the ion energies are related by

$$\epsilon_{12}E_2 = \epsilon_{13}E_3, \tag{11}$$

where ϵ_{12}, ϵ_{13} are given by Eq. (2). Application of Eq. (11) to the Pb-He, Pb-A curves is shown in Fig. 6 and the curves for He^+, Ne^+, and A^+ ions shifted relative to krypton on silver metal are shown in Fig. 7. The curves indicate the expected tendency of merging under equivalent energy shifts, consequently, for a given sputtering ratio, the energy differences observed experimentally are considerably reduced by this transformation. It is to be noted that the observed sputtering ratios in the copper-argon and copper-krypton cases have a common trend which is expected in view of the similarity of the collision parameters ϵ, and ξ, for these two cases.

DISCUSSION

A. "Hard" Collisions

It is generally recognized that ions will not transfer appreciable energy to the atomic electrons of a solid or a gas if the velocity of the ion is small compared with the velocity of the electrons. Thus, at low ion energy, the chief mechanism of energy loss for an ion will be nuclear or "hard" collisions which will produce recoil atoms in the stopping material. At energy less than 5000 ev, a helium ion will have velocity small compared to a five-volt electron, therefore, it appears safe to assume that energy transfer to bound electrons by ions of He^+, Ne^+, A^+, or Kr^+ will be negligible at ion energies considered in this study. Transfer of energy to conduction electrons within a solid, however, is possible at all ion energies ranging from zero to ϵ_0, the Fermi energy. Nevertheless, such transfer of energy to conduction electrons is similarly an unlikely process because: (1) Transfer of energy to electrons at the lower levels of the Fermi sea is forbidden by a combination of the exclusion principle and the small energy transfer which is allowed on a classical basis for an ion-electron collision. (2) By (1), the only electrons which can receive energy from ions are those near the top of the Fermi sea and these will have velocity large compared with that of the ions. In the case of He^+, however, conditions are marginal and a calculation by Seitz' method, for helium incident on silver indicates that energy transfer to conduction electrons may become effective at about 4000 ev. This effect may cause sputtering ratios, at higher energies than those considered in this experiment, to show a maximum with increasing ion energy which would be detectable at the lowest energies for ions of helium or hydrogen.

B. Sputtering Thresholds

It was not possible to measure sputtering threshold energy by means of the apparatus used in this experiment. Nevertheless, it is of interest to speculate on this aspect of the problem in light of the previous considerations related to a collision process. Equation (10) predicts $n_a = 0$ at energy $E_t = E_d/\epsilon$ which should be an upper limit to the sputtering threshold, E_t, since an ion with sufficient energy to produce displacements at the surface should also be capable of releasing sputtered atoms. A lower bound would be $E_L/2\epsilon$, where E_L = atomic heat of vaporization. Then E_t, for normal incidence, satisfies the relation

$$E_L/2\epsilon \leqslant E_t \leqslant E_d/\epsilon. \tag{12}$$

A comparison between $E_L/2\epsilon$, E_d/ϵ and sputtering thresholds observed by Kingdon and Langmuir and the General Electric Company, Ltd., is shown in Table IV. This table indicates the tendency of observed sputtering thresholds to lie within the bounds esti-

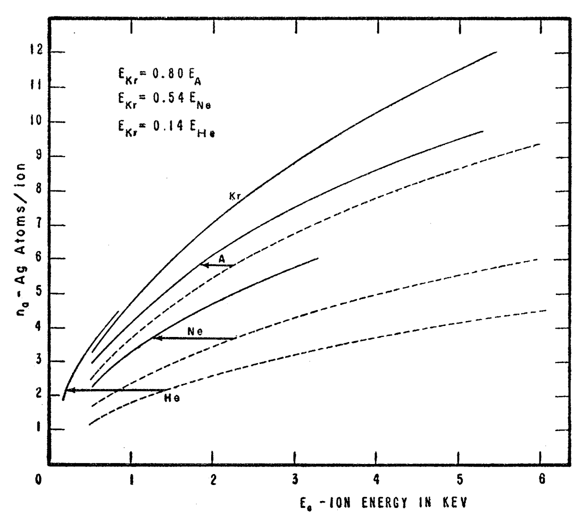

FIG. 7. Equivalent energy shift of helium, neon and argon sputtering ratio curves relative to krypton on silver.

mated by a collision process. The case is more likely described by a tendency for the sputtering ratio curve, n_a, *vs* E_0, to break away from Eq. (10) at energy near E_d/ϵ and to continue until it intersects the ion energy axis at some intermediate threshold energy.

C. Theory and Observation

The application of radiation damage theory to the problem of sputtering leads to considerations which justify its use in agreement with many of the results reported by previous investigators in the field. There has been some doubt as to the nature of the sputtered material, some opinion being in favor of an atomic process and others believing the sputtered material to be in the form of "chunks" or globules. This writer has detected globules of material to be removed from the cathode of a P.I.G. discharge when the operation of the discharge (cathode voltage = 2500 v, pressure = 0.75 micron in air) was such that it was in a transitory state between self-sustaining glow and cut off with a frequency of about two per second. However, when the discharge was running in the steady glow condition, with ample supply of gas, it was always observed that the sputtered material was vaporous and deposited as an even film on a collector plate facing one cathode. It is felt by this writer that an atomic basis for sputtering has been established in view of the following evidence: (1) Sputtering ratios are small numbers the same order of magnitude for all gas-metal combinations and, in many cases can be fitted by the sputtering ratio formula of Eq. (15). (2) The equivalent ion shift indicates an additional relation between atomic masses. (3) Sputtered films have the same general properties as evaporated films. (4) Many observers report spectral lines of the cathode material at the cathode of a glow discharge. (5) The time an ion is effective over a volume at a particular region of the cathode surface is extremely small compared to the time interval between collisions at the region.

The results of Seeliger and Sommermeyer are consistent with the radiation damage concept since a directed beam of atoms would not be expected to produce sputtering in a "preferred" direction due to the multiple collisions occurring at the surface. Electrons, of course, would not be expected to cause sputtering at low energy since (1) they transfer a major portion of their energy to conduction electrons and bound electrons (as evidenced by heating and production of secondary electrons) and (2) their mass is too small to transfer appreciable energy to a metallic atom in one collision. The only temperature dependence of sputtering should be derived from a possible reduction in the energy required to remove an atom from the surface of the metal. This may cause a slight temperature dependence, but, as has been frequently observed, the temperature dependence, allowing for vaporization, should not be very strong.

It is believed the concepts of radiation damage at a metallic surface due to high-energy ion bombardment have been useful in explaining the form of absolute sputtering ratio curves and are in agreement with many of the known observations regarding sputtering. If the views expressed in this paper are correct, it is hoped that future work will continue to support these concepts and lead to a better understanding of the sputtering phenomenon.

TABLE IV. Sputtering thresholds.

A. For tungsten observed by General Electric Company, Ltd.

Gas	E_t (observed)		$E_L/2\epsilon$[a] (ev)	E_d/ϵ[b] (ev)
A	85	25	15	153
Hg	50	50	8.8	90
H_2	begins ~700		206	2112
He	begins ~350		106	1081

B. For thoriated tungsten observed by Kingdon and Langmuir.

Gas	E_t (observed) (ev)	E_t (calculated by Kingdon and Langmuir)	$E_L/2\epsilon$[a] (ev)	E_d/ϵ[c] (ev)
H_2	600	527	260	2664
Ne	45	40	30.0	306
A	47	35	17.5	180
Cs	52	129	9.5	97.1
Hg	55	1600	8.9	90.5
He	35	142	132	1350

[a] $E_L = 8.8$ ev.
[b] $E_d = 45$ ev (from Wehner's data, using E_t(W-Hg) = 90 v).
[c] $E_d = 45$ ev (assumed the same as tungsten).

ACKNOWLEDGMENTS

I wish to express my gratitude to Professor John Backus for his assistance and for use of the 13-in. pole-face magnet. I also wish to thank the Chemistry Department of the University of Southern California for use of their microweighing facilities.