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Sputtering Yields for Normally Incident Hg^+-Ion Bombardment at Low Ion Energy*

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Sputtering yields for 26 metals under normally incident Hg^+-ion bombardment were measured in the energy range 30 ev to 400 ev. The targets were immersed like large negative Langmuir probes in a low-pressure ($1\,\mu$) Hg plasma of high density (ion current densities up to 15 ma/cm^2). Absolute yield values were obtained by measuring the weight loss from the target; relative values by measuring the speed with which sputtered material is deposited on a movable glass-ribbon collector.

The yields (atoms/ion) are essentially independent of gas pressure, target temperature (above 300°C) and ion current density and rise proportionally with the ion energy. The highest yields were obtained with Cu, Ag, and Au; the lowest with V, Zr, Nb, Si, and C.

Metals within one crystal system behave similarly in every respect (same atom-ejection patterns, same etch features) when they are bombarded with such energies that the yield becomes equal. These comparable ion energies turn out to be proportional (with the crystal system determining the proportionality factor) to H/μ_m where H = heat of sublimation and μ_m the momentum transfer factor $m_2/(m_1+m_2)$.

I. INTRODUCTION

ALTHOUGH much effort has been directed toward a better understanding of the basic nature of the sputtering process, the correlation of sputtering yields with the properties of the ions, atoms, and target lattice has not been established; and it is not yet possible to predict with any degree of accuracy how fast certain metals will disintegrate when bombarded with certain ions of a certain energy and under a certain angle of incidence.

Our lack of knowledge is, in a large part, due to a lack of reliable quantitative yield data measured under well-controlled, simple, and interpretable experimental conditions:

1. The gas pressure should be low enough to prevent back diffusion of sputtered atoms.
2. The gas pressure should be low enough to prevent most of the ions from colliding with gas atoms during their fall to the target. This is necessary in order to have a well-defined kinetic energy of the bombarding ions.
3. One should be able to control the kinetic energy of the ions down to low ion energy independent of gas pressure and ion current density. This can be achieved by immersing the target as a third electrode (like a Langmuir probe) in a plasma maintained between a separate independent cathode and an anode.
4. The voltage drop of the discharge should be low enough so that the formation of multiply-charged ions, which would cause an undetermined ion energy is negligibly small.
5. The target should be large compared to the thickness of the ion sheath, and sharp edges and corners should be avoided. This establishes the proper conditions for normal incidence.
6. The density of the bombarding ion current should be large. This is not only desirable in reducing the time for sputtering measurable amounts, but important in studies of certain materials (e.g., Al, Zr, etc.) in order to overcome the formation of chemisorbed impurity layers at the target surface.

A survey of the published literature as recently summarized by the author[1] shows that in the majority of studies in this field one or more of these conditions were violated. Among those studies violating one or more of these conditions were all those performed in the normal glow discharge at pressures above $100\,\mu$. The remaining few which can be considered reliable are mostly confined to the region of higher ion energies. The region of lower ion energy (below 500 ev) with yields of less than one atom per ion, is of particular interest, on the other hand, since it was shown[2–4] that sputtering at those energies is more a process of direct momentum transfer rather than evaporation. Evaporation seems to apply better for high ion energies. Approximately 25 metals available with properties suitable for these studies (low vapor pressure, not too low an electronic work function, melting point above 400°C, in sheet or rod form), paired with 5 rare gases plus Hg^+, would yield about 150 combinations which might be investigated. Only some single yield values are known and for only one combination (Hg^+-Pt) has the whole yield curve been measured. Hence, our goal in this study was to measure the sputtering yield of polycrystalline metals under normally incident ion bombardment, primarily as a function of the ion energy in the energy range 30 to 400 ev. So far, our measurements have been confined to Hg^+-ion bombardment. We are presently extending these measurements to noble gases.

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* This work was performed under contract with the Office of Naval Research.

[1] G. Wehner, *Advances in Electronics and Electron Physics* (Academic Press, Inc., 1955, New York), Vol. 7, p. 239.
[2] H. Fetz, Z. Physik **119**, 590 (1942).
[3] G. Wehner, J. Appl. Phys. **25**, 270 (1954).
[4] G. Wehner, Phys. Rev. **102**, 690 (1956).

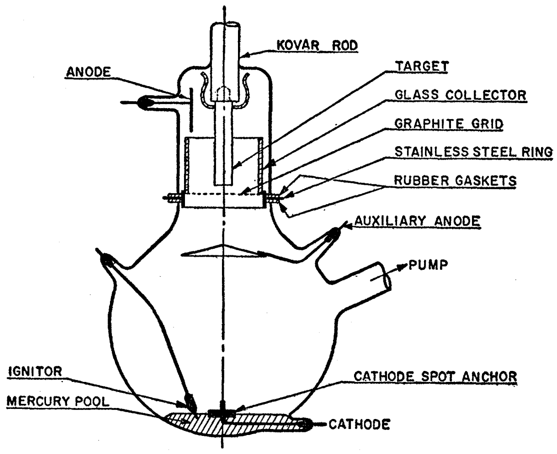

FIG. 1. The discharge tube.

II. METHODS AND APPARATUS

The six conditions for obtaining reliable results mentioned above can be met by inserting the target like a large Langmuir probe in a Hg vacuum-arc plasma of high density. The demountable Hg-pool discharge tube used in these studies (previously used for this purpose by Fetz and later, with some modification, by Wehner) is shown in Fig. 1. The igniter, the cathode spot anchor, and an auxiliary anode are mounted in the lower part of the tube. The auxiliary discharge with 3-amp discharge current is necessary to maintain a stably anchored cathode spot. The igniter (a SiC rod permanently immersed in the Hg pool) is connected to an automatic firing device such that a 4-μf condenser is discharged through the igniter every time the cathode spot extinguishes or the auxiliary anode voltage jumps to the (now unloaded) power-supply voltage. The cathode spot becomes anchored to a Mo strip partly immersed in the Hg pool. A stainless steel ring with rubber O-rings on both sides separates the upper part of the tube from the lower. In this ring is mounted a grid (graphite disk with 36 holes per cm^2, hole diameter 1.2 mm) which serves to increase the plasma density in the upper (anode) space and to stabilize the main discharge. The action and purpose of this grid is described in more detail elsewhere.[4,5] The upper part of the tube contains the main anode (2.5 amp, 30-volts voltage drop) and the target. The voltage to the anode is supplied over a load resistor from a 300 vdc power supply. A scope connected between anode and cathode helps to monitor for unwanted oscillations. The targets are in rod form (about 3 cm long, 0.6 cm in diameter, with rounded corners), and are screwed in a heavy Kovar lead (2-cm diameter) which is protected against sputtering by a glass sleeve. The negative target voltage is applied and measured against the anode which has about the same potential as the plasma surrounding the target. This voltage determines and is equal to the kinetic energy of the bombarding ions. The ion current density at the target is of the order of 5 ma/cm^2. It can be increased to 15 ma/cm^2 by means of a magnetic field arranged in the vicinity of the target. This field causes the beam electrons entering through the grid holes into the anode space to spiral, thus lengthening their over-all path to the anode and giving them a better chance for ionizing collisions. This leads to an increase in plasma density and consequently in ion current density. The thickness of the ion sheath (visible as a dark sheath covering the target) at -200 volts target potential is of the order of 0.5 mm. The tube is immersed, up to and including the stainless steel ring, in water kept at a temperature of 18°C. This determines the Hg vapor pressure in the tube ($\sim 1\ \mu$). The discharge tube is connected directly (no cooling trap) to a Hg diffusion pump.

Conditions in this discharge in relation to the six reliability requirements stated above are as follows:

1. At a gas pressure of 1 μ the mean free path of sputtered atoms is of the order of 3 cm (gas kinetic mean free path), i.e., of the order of the tube dimensions. The formation of clear shadows in the deposits behind structures which are arranged in the path of sputtered atoms shows that the major part of sputtered atoms reaches a collector or the tube wall without any gas collisions.
2. At a mean free path of 3 cm and an ion-sheath thickness of the order of 1 mm, collisions of ions within their fall region are negligibly small.
3. The main discharge current and voltage, together with the magnetic field, determine the plasma density and thus ion current density. The target voltage determines the energy of the bombarding ions. Both can be selected independently—the ion energy down to very low values.
4. At a main discharge voltage drop of 30 volts the ratio of multiply-charged to singly-ionized Hg atoms[6] becomes negligibly small.
5. With the ion sheath of the order of 1 mm thick and the target of much larger size, the incidence of ions is essentially normal to the surface.
6. The impurity background pressure in this discharge tube is probably not much better than 10^{-6} mm Hg. At this pressure, if every impurity atom stuck to the surface, a monolayer would form in about 1 second. On the other hand, an ion current density of 10 ma/cm^2 is equivalent to 60 monolayers per second. Under these circumstances one may safely assume that sputtering overcomes the formation of impurity layers unless either the ion energies are extremely low or the binding energy of impurities to the surface is extremely high.

Fortunately, one has a convenient check if the last condition is fulfilled. The frequency of ion impacts at

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[5] H. Fetz, Ann. Physik **37**, 1 (1940).

[6] A. von Engel and M. Steenbeck, *Elektrische Gasentladungen* (Verlag Julius Springer, Berlin, 1932), Vol. 1, p. 37.

the target surface is so small in space or in time that it would be difficult to understand how several ions could act together in sputtering an atom. Hence, one should expect the yield, if measured in atoms/ion, to be independent of the ion current density. If, however, sputtering must compete with the formation of impurity layers, one would expect the yield to increase with the current density. The same consideration applies if the surface would become covered with a protecting Hg film. It was found necessary to keep the target at a temperature above 300°C; otherwise, yields decrease markedly with lower target temperature and increase with ion current density. Above 300°C, probably enhanced by the high-density ion bombardment, Hg seems to evaporate so rapidly that no difficulties arise with a protecting Hg film and in this region the yields become essentially independent of target temperature and current density.

Yields are measured in two ways:

1. Rather conventionally, the number of sputtered atoms is determined after opening the tube by measuring the weight loss of the target. The number of sputtered atoms N_s is related to the loss of weight W (in grams) by

$$N_s = W/(1.7\times10^{-24}A),$$

where A is the atomic weight. The number of ions N_i which have bombarded the surface is related to the ion current I^+ (amp) by $N_i = (I^+t)/(1.6\times10^{-19})$, where t is the time of bombardment in seconds. The yield $S = N_s/N_i$ then equals

$$S = 10^5 W/(AI^+t).$$

Two errors are inherent in this method:

(a) The current to the target is not exactly equivalent to the ion current but contains a component of electrons released from the target under the ion bombardment, the plasma radiation and other secondary effects. Fortunately, Hagstrum's[7] measurements show that the γ coefficient at clean target surfaces with heavy singly ionized ions of energies below 1000 ev rarely exceeds 20% and is, in first approximation, independent of the ion energy. We follow the suggestions of Penning and Moubis[8] to present all yield data in $S/(1+\gamma)$, leaving γ (of the order of 0.1 to 0.2) open for discussion.

In a recent paper Strachan and Harris[9] claim to have found, under experimental conditions similar to our own, γ to be as high as 2 (at 400-ev Hg-ion bombardment). These authors consequently conclude that the actual sputtering yield data differ from those obtained when the electron-current part is neglected by as much as 300%. γ coefficients of the order of 2 for 400-ev Hg^+-ion bombardment of clean metal surfaces are not only in disagreement with the much lower values reported by others, but one can easily disprove such high values under our actual conditions as follows. Two small probes of exactly equal size, one made from a high electronic work-function material such as graphite, the other from a low electronic work-function material such as Th, are immersed in close proximity in the plasma. Equal plasma density in the vicinity of the probes and equal probe size manifest themselves in roughly equal electron currents collected by the probes in the saturated region above the plasma potential knee. At negative probe potentials with only positive ions being collected, the probe currents should differ according to the number of electrons released per ion. This number should be markedly higher in the case of the low work-function material. Actually, it was found that these currents differ up to 400 ev even in the case of C—Th by not more than 15% even when the probes were sputtered for such a long time that we can assume the surfaces were free of oxides. Strachan and Harris found for C—Hg at 400 ev a γ of 0.1, for Fe—Hg a ratio of 2. We found the negative currents of an Fe probe to differ from that of a graphite probe up to 400 ev by not more than 4%. We therefore think that the indirect method of Strachan and Harris of deriving the ratio of electron to ion currents from a measurement of the thickness of the dark ion sheath is highly questionable.

(b) Initial surface layers of some metals (Al, Th, Ta, Zr, Ti, etc.) are very resistant to sputtering and protect the underlying bulk material. In order to minimize the error which can arise from this effect one has three possibilities: (1) subtract the time between "switch on" of the target and the appearance of a visible deposit from the total bombarding time; (2) handle the target in between the weight measurements in such a way that the formation of thick oxide layers is prevented; or, (3) sputter enough material, i.e., for a long enough time so that the time for the removal of the initial surface layer becomes negligibly small compared to the over-all sputtering time.

2. The second method is based on a measurement of the speed with which sputtered deposits are built up at a transparent collector. The experimental arrangement is shown in Fig. 2. Part of the material sputtered from the target rod passes through a slit in an opaque shade and is deposited on a glass ribbon. This glass ribbon can be manipulated by magnets from the outside so that many (about 30) measurements can be made without opening the tube. Originally, we tried to check the thickness of the deposits by measuring the absorption of the radiation emitted from the plasma, transmitted through the sputtered deposits and received by a light meter arranged outside the tube. The reliability and reproducibility was improved considerably by inserting a more constant separate light source in the form of a W filament and filtering the plasma

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[7] H. D. Hagstrum, Phys. Rev. **89**, 244 (1953); **96**, 325 (1954); **96**, 336 (1954). This work is summarized in reference 11, p. 777.

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

[9] J. F. Strachan and N. L. Harris, Proc. Roy. Soc. (London) **B69**, 1148 (1956).

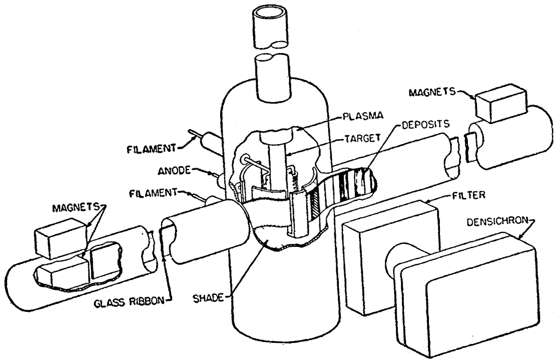

FIG. 2. Arrangement for measuring the speed with which sputtered material is deposited on a glass ribbon.

radiation out (interference filter 660 mμ). The reliability of this method rests on the assumption that every sputtered atom which reaches the exposed part of the ribbon sticks to its surface. In the case of high-vacuum evaporation one knows that difficulties with nucleation may arise at a low density of the arriving atoms. These difficulties seem to be less pronounced in the presence of a plasma. Ditchburn[10] was able to show that nucleation was readily achieved when the collector surface is under a slight ion bombardment. An insulated surface immersed in a low-pressure plasma (as the glass ribbon here) always acquires a negative net charge, hence is always under low-energy positive-ion bombardment. Nevertheless, a delay in nucleation was observed in some of our experiments. By recording the whole curve of transmitted light *vs* time and measuring the slope of the steepest part in this curve (see sample curve, Fig. 3), nucleation difficulties have been eliminated. The measurement procedure is roughly as follows: After a stable and clean discharge, in temperature equilibrium, has been established, normally requiring a burn-in period of about 1 hour, the densichron is set at zero position. A negative target voltage of 300 volts is then applied to clean the target surface until a heavy deposit appears on the ribbon. At time zero the target voltage and current are set at the selected values and the ribbon is shifted to a new position. The speed with which sputtered material collects on the ribbon is recorded by densichron readings in 5 second intervals. The procedure is then repeated for other ion energies. The slope of the steepest part of these curves is taken as a measure of the yield in arbitrary units. The results so obtained are then matched in some points to values obtained with the absolute method. At very low ion energy, i.e., very low sputtering rates, difficulties arise with materials which oxidize readily to more transparent deposits. This was especially pronounced for Ta and Th. In some cases the deposits obtained with a high sputtering rate seem to differ in structure and absorption properties from the deposits obtained with a low rate. For this reason it can generally be assumed that the reliability of this method is less than that of the absolute method.

In order to determine the actual ion energy more exactly, it was necessary to determine the voltage drop between the anode and the plasma surrounding the target. This was done by recording the voltage-current characteristic of a small probe arranged in the vicinity of the target. The procedure for measuring gas-discharge data, e.g., the plasma potential, by means of probes has been described in sufficient detail elsewhere,[11] and we shall report in the next section only the results of those measurements.

A third approach for measuring yields, especially in the low-energy region, looked very promising at first. This method is based on measuring the change of the electronic work function or the shift of the probe characteristics when it becomes covered with sputtered material from the probe material. This method had been used successfully for sputtering studies by Wehner and Medicus in a very clean Xe discharge.[12] Here, in the presence of Hg vapor and a rather large background pressure, it developed that the work function changes in a rather complex manner after cleaning the probe and after deposition of sputtered material. The resulting complex "creep" of the probe characteristics made it impossible to rely on these measurements.

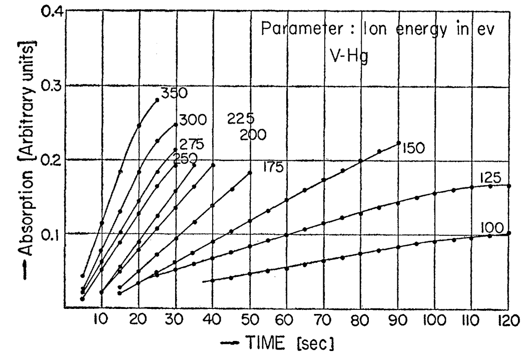

FIG. 3. The buildup of sputtered deposits in the case of $V-Hg^+$. Parameter: ion energy.

III. EXPERIMENTAL RESULTS

(a) Secondary Parameters

Prior to and during the course of the actual yield measurements, attention was given to the possible influence of parameters which supposedly play only a secondary role in the sputtering process.

Of primary interest here is the influence of the target temperature. Unpublished results of Fetz and Schieffer (University of Wuerzburg) indicate a marked tempera-

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[10] R. W. Ditchburn, Proc. Roy. Soc. (London) **A141**, 169 (1933).

[11] L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, 1955).

[12] G. Wehner and G. Medicus, J. Appl. Phys. **25**, 698 (1954).

ture influence on the yields in the case of Hg-ion bombardment (most pronounced with Pt, where the yield increased by a factor of 4 between 300°C and 800°C), but very little influence in the case of A^+-ion bombardment. Fetz ascribed this to a protecting Hg film at the target surface.

In our work, which differs from that of Fetz in that current densities are higher by a factor of 100, only a minor target-temperature influence was noticeable even in the case of Pt, provided the target temperature was maintained at a value above 300°C (see Fig. 4). At lower target temperatures the yields become markedly lower and we agree with Fetz that this is due at least in part to a Hg film at the target surface. Another independent indication of such a Hg film is the fact that the deposit patterns from single-crystal targets are obtained only when the target is at a temperature above 300°C. Above 300°C, probably enhanced by the high current density, the surface seems to remain essentially clean and Hg atoms deposited from the Hg vapor are evaporated and sputtered rapidly enough not to interfere.

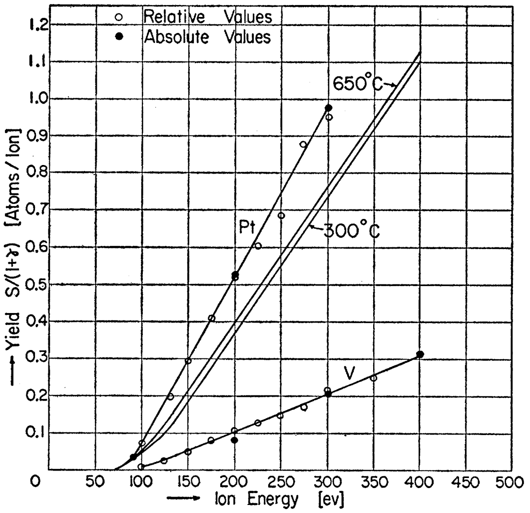

FIG. 4. Sputtering yields of Pt and V. Curves marked 300°C and 650° show results previously obtained for Pt by the author.[4]

The target temperature could have entered into sputtering from other influences. It largely determines the processes of chemisorption of impurities at the surface, of the diffusion of impurities from the bulk to the surface or the reverse, of the rate of migration of surface atoms and of the annealing of lattice defects. The temperature, furthermore, has some influence on the elastic constants of the target material. The fact that the yields change with temperature in the range 300°C to 700°C by not more than 15%, which is generally within the possible errors, proves that these effects cannot play a major role here.

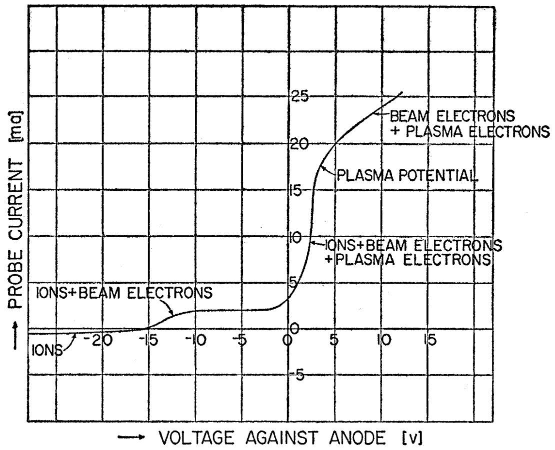

FIG. 5. Characteristic of a small probe arranged in the vicinity of the target.

Some influence on yields results from the degree of roughness of the target surface. Surfaces under sputtering become etched (as in chemical etching) and consequently the surface roughness of a polished target increases during sputtering. There is simultaneously a decrease in yield because many of the sputtered atoms are now unable to clear the surface and become trapped on surface protrusions. This effect is more pronounced at lower ion energy because a larger proportion of sputtered atoms tends in this case to leave the surface in tangential direction.[3] Reasonable care has to be taken, therefore, in starting an experiment, especially in the case of the absolute yield determination, to insure as smooth a target surface as possible. We estimate the error due to varying surface roughness not to exceed 10%.

No conclusive evidence could be found concerning the influence of the purity or the density of dislocations of the target material. Microscopic inspection of the targets after sputtering shows that dislocations and grain boundaries are more easily attacked than the perfect surface and appear respectively as pits or grooves. Differently oriented crystal grains are attacked at different rates and appear at different elevations. Hence, one should bear in mind that yield data of polycrystalline materials are actually composites of

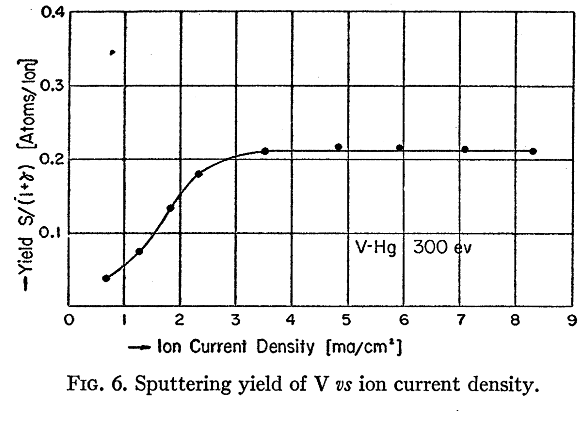

FIG. 6. Sputtering yield of V *vs* ion current density.

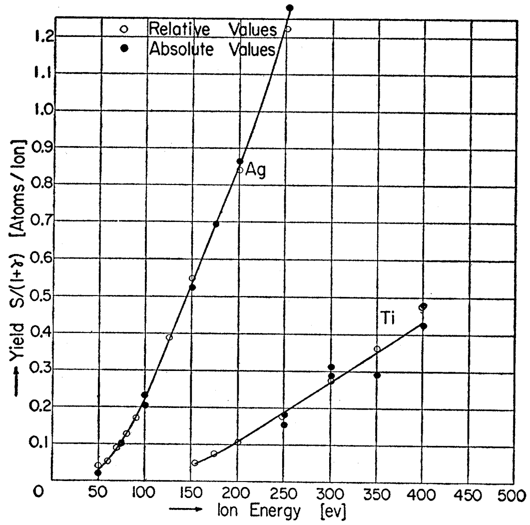

FIG. 7. Sputtering yields of Ag and Ti.

many different values, just as the electronic work function is an average of many different values characteristic of the many differently oriented single crystallites.

(b) Plasma Potential

The kinetic energy of the bombarding ions is equivalent to the potential difference between the plasma surrounding the target and the target proper. The target potential, however, is measured with respect to anode potential. Hence, in order to determine the actual bombarding energy it is necessary to know the potential difference between anode and the plasma surrounding the target. This potential difference was determined by means of probe measurements. Figure 5 shows the current-voltage characteristics obtained from a small cylindrical probe (1 mm in diameter, 2 mm long) which was arranged 4 mm away from the target. The curve has to be interpreted as follows: At large negative potentials (measured against anode) only the positive ions can reach the probe. The probe is covered with a dark (electron-free) sheath which represents the ion-accelerating region. The ion current is saturated because it is limited by the number of ions arriving at the sheath edge. As the probe potential reaches a value in the vicinity of the potential of the cathode side of the grid (−16 volt), a decrease in ion current or increase in electron current becomes noticeable. This is caused by the beam electrons which have been accelerated in the grid region and which can reach the probe as soon as its potential is slightly above the potential of the plasma at the cathode side of the grid. This current again becomes saturated because it is limited by the number of beam electrons formed in the grid region. Near anode (zero) potential, the fastest plasma electrons can reach the probe and another rise in electron current superimposed on the ion current and beam-electron current sets in. The probe potential is now approaching plasma potential and more and more plasma electrons can reach the probe. Finally, the plasma potential is indicated by a knee and from there on the current is carried only by beam and plasma electrons and becomes saturated again at still more positive potentials. In an exact determination of the plasma potential from the position of the knee one would have to take into account the difference of the electronic work functions of the probe and anode. Here, it is justified to neglect this small correction and to state that the plasma potential, even with application of a magnetic field, was never found to differ by more than about 4 volts from the anode potential. Under

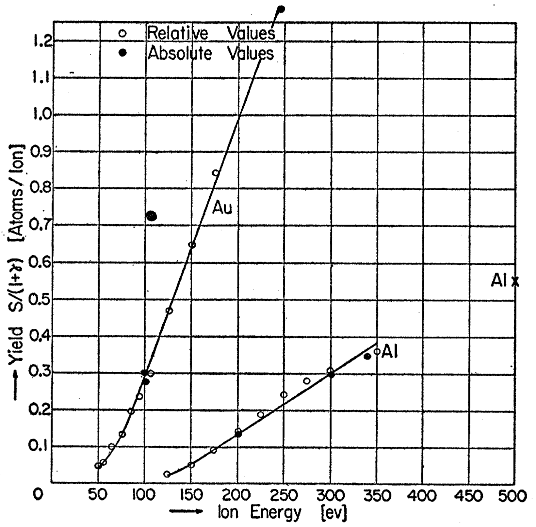

FIG. 8. Sputtering yields of Au and Al. Cross point indicates value of Meyer and Guentherschulze.[13]

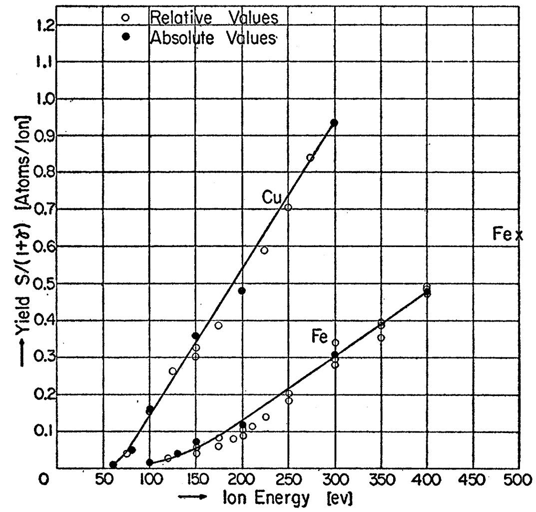

FIG. 9. Sputtering yields of Cu and Fe. Cross point indicates value of Meyer and Guentherschulze.[13]

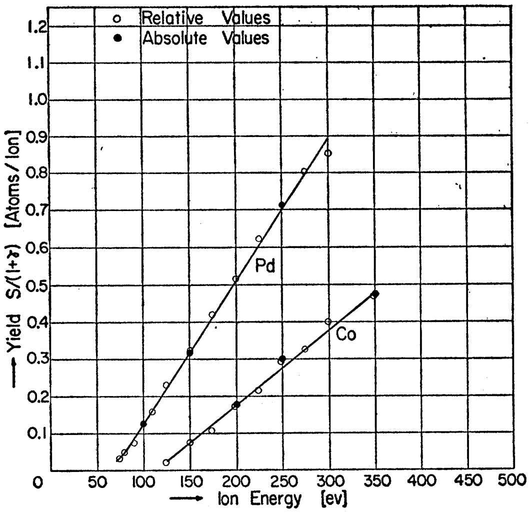

FIG. 10. Sputtering yields of Co and Pd.

these circumstances it was found unnecessary to correct the voltage scale in the following yield curves.

(c) Sputtering Yields

Sputtering yield curves for different metals are presented in Fig. 4 and Figs. 6 to 19. Shaded circles indicate absolute values obtained with the weight method; values indicated by plain circles have been measured with the (relative) deposit method.

Figure 4.—Pt sheet was wrapped around a Cu core to form a cylindrical target. The two other curves were previously obtained by the author under similar experimental conditions at two different target temperatures.[4] The yield of V is one of the lowest found in 27 metals. The metal behaves well and the scattering of the yield points is smaller than with most other metals.

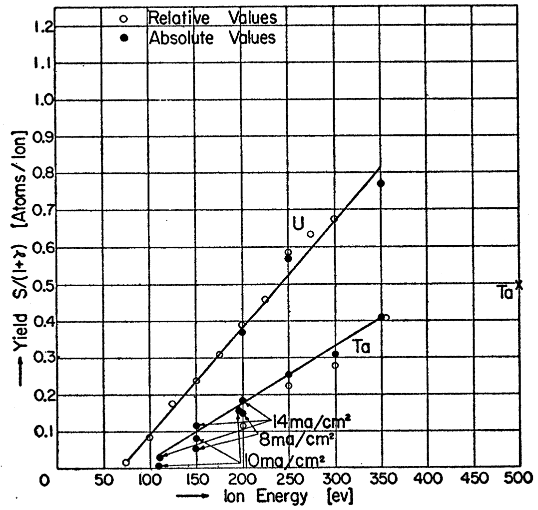

FIG. 11. Sputtering yields of U and Ta. Cross point indicates value of Meyer and Guentherschulze.[13]

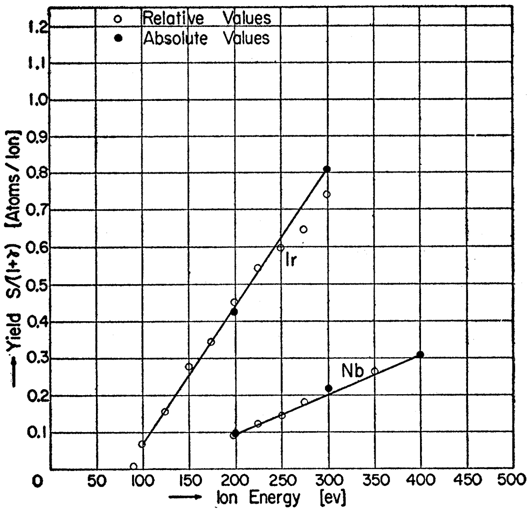

FIG. 12. Sputtering yields of Nb and Ir.

Figure 6.—This graph shows the yield *vs* ion current density (0.5 to 9 ma/cm^2) for the case of V. Above 3.5 ma/cm^2 (at 300-ev ion energy) the yield becomes independent of the ion current density.

Figure 7.—The preparation of the Ag-target rod surface is of importance. Ag is so soft that in grinding or polishing small insulating particles become imbedded in the surface. In sputtering, these particles protect the underlying bulk material and the surface becomes covered with a pelt of fine needles all of equal height, the height of the original surface. This increase in surface roughness goes hand in hand with a decrease in sputtering yield. The best way to prepare the surface and to avoid these difficulties was found to be electropolishing. The deposit method is probably less reliable in the case of Ag. It was observed that the light absorption of the silver deposits changed somewhat with time. Microscopic inspection of the collector ribbon during sputtering showed at low sputtering rates that the material is not evenly distributed but seems to surface-migrate to preferred nucleation points. Ti belongs to the group of metals which tend to form oxide surface layers with a high bond strength. These oxide

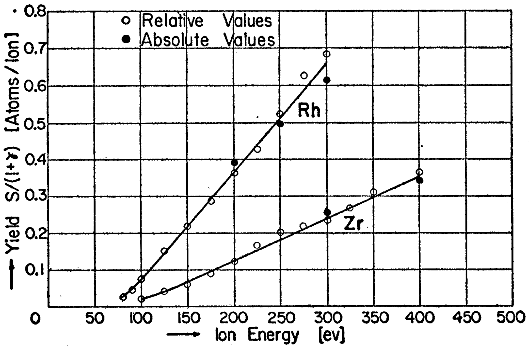

FIG. 13. Sputtering yields of Zr and Rh.

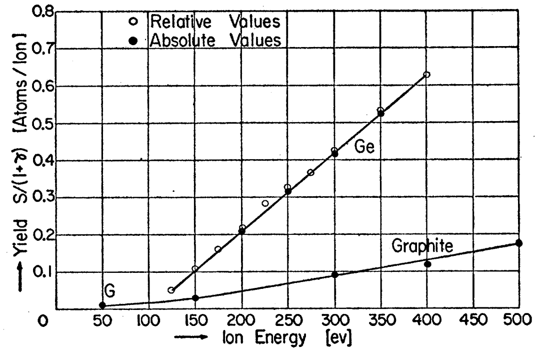

FIG. 14. Sputtering yields of Ge and graphite.

layers cause difficulties at low ion energy where sputtering cannot overcome their formation from the background pressure. Thus, it was not possible in this case, even after lengthy pumping and comparatively clean conditions, to collect reliable absolute yield data below 250 ev. The deposit method permits, to some degree, the collection of points at lower ion energy because in this case the surface can be cleaned with higher ion energy immediately before the measurement is made.

Figure 8.—Difficulties similar to those experienced with Ag arose in the case of Au. We did not succeed in electropolishing Au very well; in this case, therefore, the gold rod surface was turned in the lathe with a diamond tool before sputtering. With Al it developed that the difficulty was not so much the formation of oxide layers in the discharge during sputtering as, primarily, the removal of the original oxide layer formed at the target surface after exposure to air. For the absolute measurements it was necessary to deduct the time between the moment when the negative target voltage is connected and the appearance of the first deposits from the total sputtering time. Guentherschulze's[13] value for Al (cross) collected at 500 ev checks well with our results.

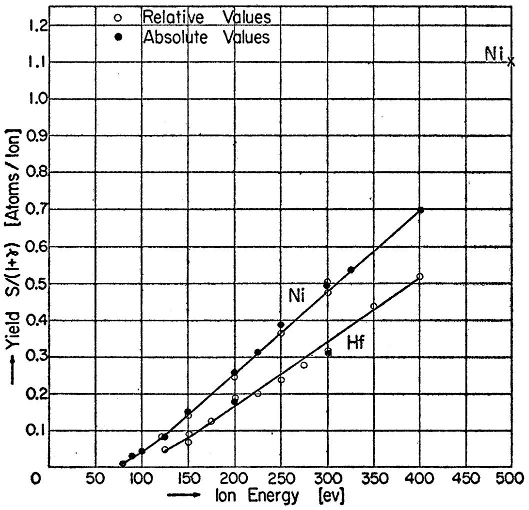

FIG. 15. Sputtering yields of Hf and Ni. Cross point indicates value of Meyer and Guentherschulze.[13]

Figure 9.—Cu in the form of an OFHC copper rod caused no difficulties after electropolishing. A polycrystalline Armco iron rod gave practically the same yield as an iron single crystal. One set of yield values was found to be out of line and much lower. It was found that the tube in this measurement had developed a small leak. A value from Guentherschulze[13] for Fe at 500 ev is included.

Figure 10.—No difficulties with Co and Pd; these metals were available in sheet form and were wrapped around a Cu-core.

Figure 11.—U available in sheet form and wrapped around a Cu-core forms oxides with a high bond strength; the lowest reliable absolute value was collected at 200 ev. Ta behaves similar to Ti; a value of Guentherschulze[13] at 500 ev is included.

The region of reliable absolute measurements can be extended down to lower ion energies by increasing the current density. This is shown for Ta in the three branches in the lower part of the curve.

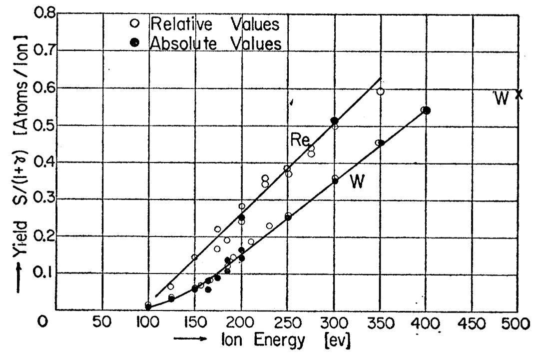

FIG. 16. Sputtering yields of Re and W. Cross point indicates value of Meyer and Guentherschulze.[13]

Figure 12.—Nb is another material with strongly bonded oxide layers. It has one of the lowest yields. Ir caused no difficulties.

Figure 13.—Zr behaves in much the same manner as Ti. The sputtering period had to be timed after the initial oxide was removed and visible sputtered deposits appeared. Rh, available in rod form, caused no difficulties.

Figure 14.—Ge was available as a rod of very high purity material with rather large crystallites. Graphite behaves unusually, in that sputtering seems to proceed down to very low ion energy. We suspect that chemical or reactive sputtering, as described by Guentherschulze[14] and Holland,[15] with traces of hydrogen possibly playing an active role, is superimposed on the physical sputtering.

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[13] K. Meyer and A. Guentherschulze, Z. Physik **71**, 279 (1931).

[14] A. Guentherschulze, Ann. Physik **36**, 563 (1926).

[15] L. Holland and G. Siddall, Vacuum **3**, 245 (1953).

Sputtering yields may be somewhat too low as a result of the high surface roughness inherent in graphite.

Figure 15.—Hf, known to form strongly bonded oxides, behaved in much the same manner as Zr. No difficulties were experienced with Ni. The yield changed only slightly when the target temperature was raised from 250 to 800°C. Guentherschulze's[13] value at 500 ev is included.

Figure 16.—Re gave very consistent results with no difficulties. In the case of W, we measured in greater detail with very high current densities (20 ma/cm^2) the absolute yield values at very low ion energy. Results below 100 ev are shown in an expanded ordinate in Fig. 17.

Figure 18.—With Th the formation of a protecting oxide layer is again very pronounced. Reliable absolute values have been obtained only above 300-ev ion energy thus far. Surface layers showed remarkable insulating properties, even at high target temperature.

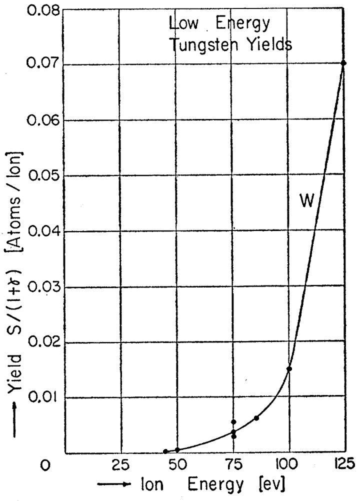

FIG. 17. Sputtering yields of W in the region of low ion energies.

Mo caused no difficulties. Included is one value at 150 ev from Fetz[2] and another value by Guentherschulze[13] at 500 ev.

Figure 19.—Si was available in the form of a rod of optical-grade single-crystal material. It showed the lowest yield measured so far. Different samples of Cr did not give very consistent results.

No reliable results could be obtained with Ce or Sr. The low electronic work function of these materials (~2.7 ev) causes such a high secondary-electron yield that this part of the current can no longer be neglected. On those spots where the oxide has been removed the secondary electron emission becomes so high that little secondary spark discharges appear at the target surface. Their appearance is connected with a breakdown of the target voltage and the current is then limited by the resistor in the target circuit.

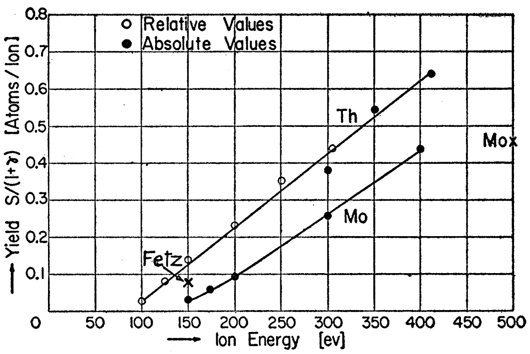

FIG. 18. Sputtering yields of Th and Mo. Cross point indicates value of Meyer and Guentherschulze.[13]

IV. DISCUSSION OF RESULTS

The yield curves show a region where the yield rises approximately proportionally with the ion energy. Hence, this part can be described by a "cut-in" energy and a slope.

The lower end of the curves always show a more or less pronounced tail which makes it difficult to establish a well-defined threshold. Hence, different authors, depending on the sensitivity with which they were able to detect sputtered atoms, arrive at different apparent threshold values. From Fig. 16, for instance (W−Hg^+), one could expect a threshold in the vicinity of 90 ev; from Fig. 17, however, for the same case one could derive a threshold of 40 ev. With still more sensitive methods such as those used by Bradley[16] (surface ionization) or Morgulis[17] (radioactive tracer), one can detect atoms being sputtered at energies in the vicinity of the heat of sublimation of the target material, i.e., only several ev. The nonexistence of a pronounced absolute threshold is not so surprising in that there are always atoms in positions or atoms which have been lifted in a previous impact to positions with least near neighbors or a higher surface energy. Such atoms could

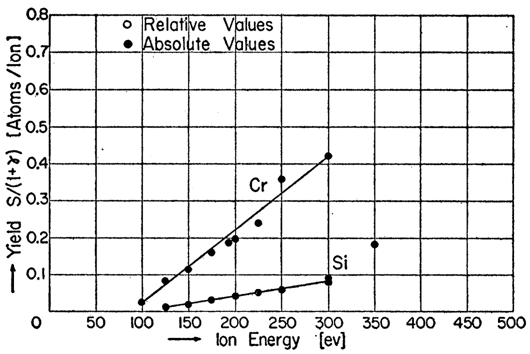

FIG. 19. Sputtering yields of Si and Cr.

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[16] R. C. Bradley, Phys. Rev. **93**, 719 (1954).

[17] N. D. Morgulis and V. D. Tishchenko, J. Exptl. Theoret. Phys. U.S.S.R. **30**, 54 (1956) [translation: Soviet Phys. JEPT **3**, 52 (1956)], and News Acad. Sci. U.S.S.R., Phys. Ser. **20**, 10 (1956).

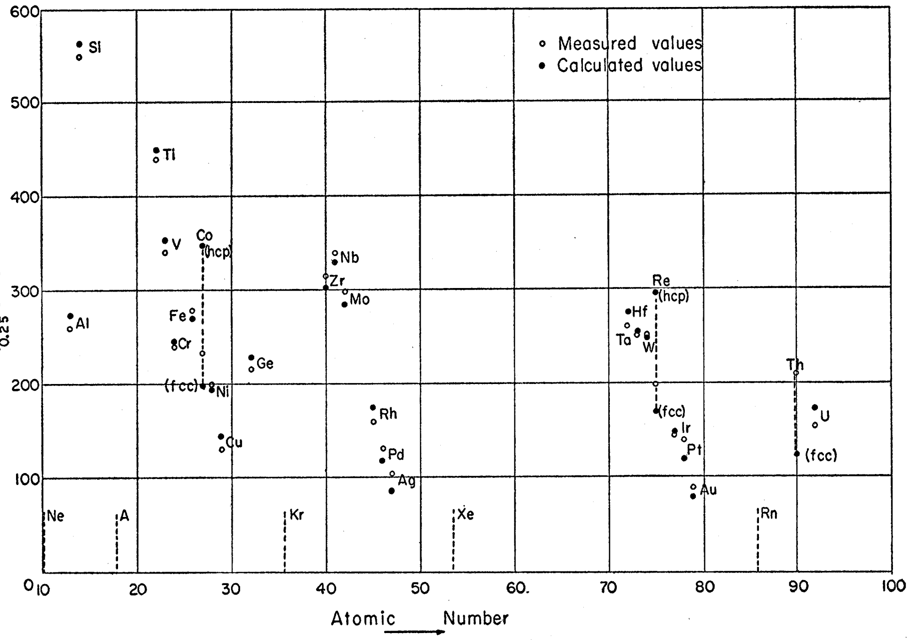

FIG. 20. Ion energies $V_{0.25}$ necessary to obtain a yield of 0.25 atom/ion. Experimental (open circles) and calculated values (solid circles) *vs* atomic number.

be sputtered at much lower energy than those coming from within a filled plane. Finally, even though relatively rare, sputtering may take place wherein two impacts simultaneously help in lifting an atom out of its place.

The "thresholds" which had been determined previously in a very preliminary way (measurement of the appearance of deposits) by the author[18] can be roughly identified with the "cut-in" energies. A comparison of the earlier values with the present values shows that the former values are too low for Mo, Ge, Fe, Si, and too high for Ta, Th, Hf, Zr. In the latter case the error was due to the formation of oxides at the target surface which at low ion energies could not be overcome by sputtering. Furthermore, the sputtered metal deposits may have changed to their more transparent oxides. In the measuring procedure which was employed, this seemed to indicate a lower apparent yield or a higher "cut-in" energy.

Parameters which in large part determine the sputtering yield are (on the gas-discharge side) the atomic weight of the ions (m_1) and their angle of incidence and (on the target side) the atomic weight of the target atoms (m_2), the crystal structure, the crystal orientation and the heat of sublimation of the target material. Possibly still other parameters such as size of atoms, elastic constants, etc., may enter into the picture.

The physical process in sputtering is probably analogous to the model wherein a hard sphere representing the neutralized ion is dropped in a box filled with hard spheres representing the metal atoms. The momentum directed to the inside of the material must be reversed in direction in order to account for sputtering. This process takes place within the lattice and brings the crystal structure and orientation into play. Finally, a surface atom in the neighborhood of the point of impact receives sufficient energy from one of its nearest neighbors underneath to separate it from the surface. In many cases, just as in evaporation, the process may proceed stepwise in an energetically more favorable manner. For example, atoms from within a filled plane may first be lifted to a position on top of a filled plane and then by a subsequent impact separated from the surface.

From a more detailed study of the ejection pattern[19] when low index planes of single crystals are sputtered (these results will be published later), as well as from the study of the etch patterns which develop during sputtering at the target surface, we obtain a significant result: Different metals of the same crystal structure behave similarly in every respect at the same yield value. In other words every metal within one crystal system requires a certain bombarding energy in order to obtain the same yield, the same ejection pattern and the same etch features. Consequently, different metals can be compared and described by those ion energies which are necessary to give a certain fixed yield value. A yield S of 0.25 covers our range of studies well and lies for all metals in the proportional region; hence, it was taken as the reference value. Results for a yield of 0.5 would not be basically different except for a proportionality factor. In Fig. 20 we plotted these ion energies V_S for $S=0.25$ for different metals *vs* their atomic number. The $V_{0.25}$ values are roughly proportional to H, the heat of sublimation. When comparing

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[18] G. Wehner, Phys. Rev. **93**, 633 (1954).

[19] G. Wehner, J. Appl. Phys. **26**, 1056 (1955).

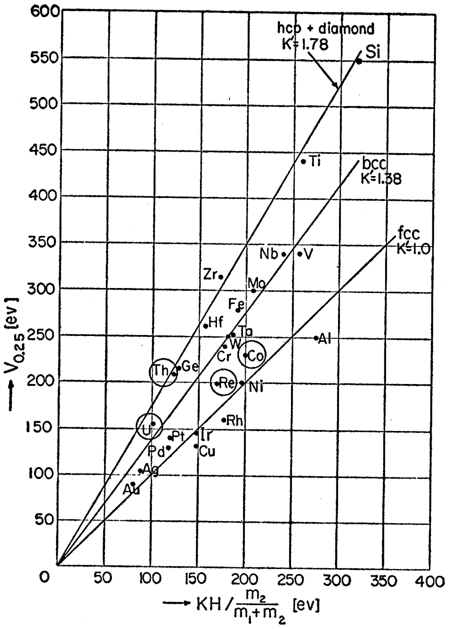

FIG. 21. $V_{0.25}$ *vs* KH/μ_m where $\mu_m = m_2/(m_1+m_2)$.

the $V_{0.25}$ values of metals with the same crystal structure and similar heats of sublimation such as Au, Pd, and Ni, one finds that the atomic weights of ion and target atom enter with the momentum transfer factor $\mu_m = m_2/(m_1+m_2)$ and not with the energy transfer factor $E = m_1m_2/(m_1+m_2)^2$. A plot of $V_{0.25}$ *vs* H/μ_m (Fig. 21) shows that the face-centered cubic (f.c.c.) metals line up along one slope, the body-centered cubic (b.c.c.) metals along another, and the hexagonal close-packed (h.c.p.) and diamond-lattice materials again at a still higher slope. U, which has a rhombohedric structure, that is a somewhat distorted h.c.p. crystal system, appears at the h.c.p. slope.

We have thus far found three exceptions (Co, Re, Th) to this relationship: Co is known to change from h.c.p. to f.c.c. quite readily, that is at a transformation temperature of ~450°C. A study of the atom ejection pattern from a Co crystal showed that under our operating conditions the crystal had at least in major part changed from h.c.p. to f.c.c. Hence, it is not suprising that we find this material in between the h.c.p. and closer to the f.c.c. slope line. The same situation may exist for rhenium although no crystal system changes have been reported in the literature. The change from h.c.p. to f.c.c. may well be caused or enhanced in the outermost surface layers by the ion bombardment. Unfortunately, no Re single crystal has been available to check this point. In the case of Th we suspect that the unusually large lattice constant may favor a deeper penetration of the (neutralized) Hg ion into the metal lattice such that the yield is lower and $V_{0.25}$ higher than in other comparable cases. At very high ratios of m_1/m_2, as in the case of C–Hg, we cannot expect this relation to hold too well because the impinging ion has sufficient momentum and energy left after the first impact in a favorable collision to cause additional atoms to be dislodged. The remarkable correlation of the other experimental values with the calculated values is shown in Fig. 20 where the full circles indicate the $V_{0.25}$ values obtained with the following relation:

$$V_{0.25} = KK'H/\mu_m,$$

where K is a proportionality factor, $\mu_m = m_2/(m_1+m_2)$, and $K' = 1$ for f.c.c., $K' = 1.38$ for b.c.c., and $K' = 1.78$ for h.c.p. and diamond-lattice metals and materials.

It remains to be seen if this law holds as well for sputtering by the much larger noble-gas ions.

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