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Sputtering of Alkali Atoms by Inert Gas Ions of Low Energy

RICHARD C. BRADLEY
Department of Physics, University of California, Berkeley, California

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Direct measurements of sputtering have been made using alkali metal targets bombarded by inert gas ions in high vacuum, the sputtered atoms being counted by a surface ionization detector. Measurements were made in the range 0–1800 ev ion energy for the ions He^+, Ne^+, A^+, and Xe^+ incident upon Na and K target surfaces. Secondary electron coefficients γ were measured simultaneously. It was found that over most of the energy range covered, the measured sputtering coefficient θ' (number of sputtered atoms reaching the detector per positive ion incident on the target) was linear in $\ln E$ for He^+ and Ne^+ and in $\sqrt{E}$ for A^+ and Xe^+, where E is the ion energy. At energies less than about 150 volts the sputtering rate appeared to be controlled by the amount of kinetic energy which could, on the average, be transferred to a single surface atom in a direct two-body collision. Thus at low energies Ne^+ produced the most sputtering from a Na surface, whereas A^+ produced the most from a K surface. At high energies, the sputtering rate was in the same order as (but not proportional to) the mass of the ion. The effect of surface contamination was also studied. An old surface showed a lower sputtering coefficient than a fresh surface and a higher and more erratic secondary electron coefficient, the effect being most pronounced for the light ions. The absolute sputtering coefficient θ (total number of sputtered atoms per incident ion) could not be measured directly, but it was estimated from the geometry that for 1000-volt ions the value of the coefficient ranged from about 1.0 for Xe^+ on K to 0.05 for He^+ on Na.

INTRODUCTION

SPUTTERING, the phenomenon of the disintegration of metal surfaces under the impact of gaseous positive ions, has been known for nearly a century. However, even though a great many investigations of the phenomenon have been conducted, relatively little is known concerning the mechanism involved. The trouble is that most of the early experiments were conducted in glow discharges where the uncertainties inherent in the method make quantitative interpretation of the data difficult. The early studies have been well summarized by Massey and Burhop.[1]

With the improvement in vacuum techniques and the development of good positive ion sources, it is now possible to study sputtering in vacuums with monoenergetic ion beams. Such studies have been made by Timoshenko[2] and Keywell[3] for several ion-target combinations. The target weight loss method used by them gives absolute sputter rates θ (number of sputtered atoms per incident ion) and is applicable whenever the rate is reasonably high—that is, for ion beams of hundreds or thousands of electron volts energy and tens or hundreds of microamperes intensity. It is not, however, a sufficiently sensitive method for low-energy measurements. Evidence of sputtering due to ions of very low energy ($\sim$10 ev) has been reported by Loeb,[4] Wehner and Medicus,[5] and others, but under conditions not suitable for an accurate evaluation of the sputtering rate.

Several theories on sputtering exist,[3,6–8] but the evidence thus far is not conclusive in favor of any of them. Actually, the process is probably sufficiently complicated so that no single theory would be applicable under all conditions.

The purpose of the present experiment was to apply the ion-beam vacuum technique to a study of sputtering at low energy. In order to have sufficient sensitivity, an electrical method of counting the sputtered atoms was used. The apparatus consisted of an ion source and gun, an alkali metal target, and a surface ionization detector to measure the sputtered alkali atoms. Aside from its sensitivity, the method has also the advantage of giving direct measurements of the sputtering rate θ' (number of sputtered atoms reaching the detector per positive ion incident on the target). With a given target, one can rapidly run through the available energy range for several different types of ions without ever having to expose the system to air; reproducibility checks are possible at any time to see if the surface has changed its characteristics. If at the end of a run the initial measurements were repeated and found to be unchanged, it was assumed that the surface maintained constant characteristics throughout the run.

The disadvantages of the method are: (1) it is limited to the alkali metals; hence there is no opportunity for a direct comparison with other studies. (2) It does not give absolute sputtering rates, since only those atoms which strike the detector are counted. On the other hand, unless one has reason to think that the angular distribution of sputtered atoms may change, relative values can give as much insight into the sputtering mechanism as absolute values. (3) There is no way of

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* This research was supported under a grant from the U. S. Office of Naval Research.

[1] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952).

[2] Gregory Timoshenko, J. Appl. Phys. **12**, 69 (1941).

[3] Frank Keywell, Phys. Rev. **87**, 161 (1952).

[4] Loeb, Kip, and Hudson, Phys. Rev. **60**, 714 (1941).

[5] G. Wehner and G. Medicus, Phys. Rev. **89**, 339 (1953).

[6] K. H. Kingdon and I. Langmuir, Phys. Rev. **20**, 108 (1922).

[7] A. V. von Hippel and E. Blechschmidt, Ann. Physik **81**, 1043 (1926).

[8] E. S. Lamar and K. T. Compton, Science **80**, 541 (1934).

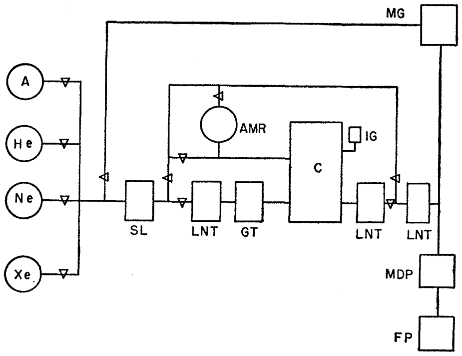

Fig. 1. Schematic diagram of the vacuum system. *C*, chamber; *AMR*, alkali metal reservoir; *IG*, ionization gauge; *MG*, MacLeod gauge; *SL*, variable slow leak; *LNT*, liquid nitrogen trap; *GT*, gold trap; *MDP*, mercury diffusion pump; *FP*, mechanical fore pump.

ensuring a really clean surface since it is not possible to "flash" the surface to a high temperature before each measurement. With a possible background pressure of oxygen of 1×10^{-8} mm of Hg, an oxide monolayer would form on a fresh alkali surface in a matter of minutes, whereas the time required to make a complete series of measurements was several hours.

The effect on sputtering of an aging surface was studied at some length, and it was found possible to slow up the aging process sufficiently so that reproducibility could be maintained over the period required to make a complete series of measurements.

DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

A. The Vacuum System

The experimental chamber, which is shown as *C* in Fig. 1, was evacuated by a mercury diffusion pump *MDP* backed by a mechanical pump *FP*. Liquid nitrogen traps *LNT* were installed between the chamber and the rest of the system so that during actual operation there were no stopcocks directly exposed to the chamber.

The outgassing procedure consisted of baking the chamber in an oven at 400°C for forty-eight hours, induction heating the electrodes to a cherry-red temperature for several hours, running all filaments at a higher-than-operating temperature for several days, and thoroughly torching all the glass tubing of the vacuum system. All this was done, of course, before any alkali metal was admitted to the chamber. The vacuum obtained was such that with all filaments at their operating temperatures the pressure in the chamber was about 5×10^{-8} mm of Hg as read by an ionization gauge.

Spectroscopically pure inert gases He, Ne, A, or Xe could be admitted to the system through a mercury-ceramic variable slow leak *SL*.[9] The normal operating pressure in the chamber ranged from 2×10^{-5} mm for Xe to 3×10^{-4} mm for He. Aside from furnishing ions for the beam, the inert gases could also be used to move the liquid alkali metals into the chamber.

B. The Alkali Metals

The two target metals used in this experiment were sodium and potassium. While in principle any alkali metal would have served, these two were chosen because of their low vapor pressures at room temperature and because they can readily be distilled in Pyrex vessels.

Several ounces of each metal were distilled through six stages under high vacuum. A vacuum breakoff seal between the fifth and sixth stages *D* and *R* of Fig. 2 made it possible to distill through the first five stages, using an auxiliary vacuum system and thus without exposing the chamber to the distillation products. In the sixth distillation the alkali metal was allowed to flow down into the horizontal intake tube and, while still liquid, pushed into the chamber. When the alkali appeared in the mouth of the intake tube it was allowed to solidify, and the solid surface formed the first target. Subsequent fresh targets could be obtained by reliquefying the metal, overflowing the old surface using pressure from behind, and allowing the new surface to freeze.

The liquid alkalis were pushed either by a magnetic slug *MS* sealed in a quartz envelope which could slide in the intake tube and be moved by a magnet outside the system or else by a slight pressure of inert gas. The magnetic slug technique was used whenever possible as it afforded better control. Greater force was possible using gas pressure, but the flow tended to be more erratic. The difficulty lies in the strong adhesion between the alkali metals and Pyrex glass.

C. The Electrode System of the Chamber

A schematic diagram of the electrode system of the chamber is shown in Fig. 3. The essential elements are (1) the ion source and gun, (2) the target and secondary

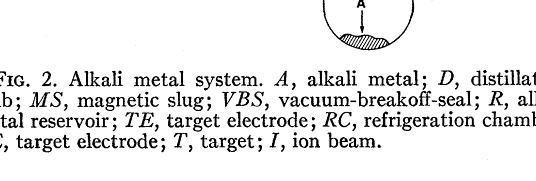

Fig. 2. Alkali metal system. *A*, alkali metal; *D*, distillation bulb; *MS*, magnetic slug; *VBS*, vacuum-breakoff-seal; *R*, alkali metal reservoir; *TE*, target electrode; *RC*, refrigeration chamber; *TE*, target electrode; *T*, target; *I*, ion beam.

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[9] H. D. Hagstrum and H. W. Weihart, Rev. Sci. Instr. **21**, 394 (1950).

electron collector, and (3) the surface ionization detector. Except for the target and the filaments all electrodes were of tantalum.

1. *The Ion Source and Gun*

The ion source was of the Finkelstein type.[10] Such a source was well suited for this study since (a) it gives an ion beam of low-energy spread, (b) it can be operated at pressures so low (10^4–10^5 mm of Hg) that the kinetic mean free paths of the ions and sputtered atoms are long compared to interelectrode distances, thus obviating any need for differential pumping, and (c) it can be operated at source voltages so low that the ionizing electrons have insufficient energy to produce doubly charged ions—thus giving assurance that there are only singly charged atomic ions in the beam. (Singly charged molecular ions are ruled out by the low pressures.)

The operation of the source was roughly as follows: electrons emitted by the hot tungsten cathode C were attracted by the anode cylinder A and repelled by the electrodes RP and L_1. An axial magnetic field H of about 200 gauss caused the electrons to follow tight helical trajectories back and forth along the axis between C and L_1, giving them long free paths in a small volume, accounting for the high efficiency of the source. Eventually, as a result of inelastic impacts, space charge fields, or otherwise, the electrons were collected by A.

In the meantime a fraction of the positive ions, which were created in this region by electron collisions with gas atoms, were drawn out by the extraction electrode L_1 into the gun. The voltages used on the various electrodes L_1-L_4 of the gun to give best operation were determined experimentally. Best extraction was obtained when L_1 and L_2 were maintained at the same potential, approximately 350 volts negative with respect to the anode A. L_4 and T were kept at the same potential (aside from a contact potential difference) so that electrons from the target could be separately collected. Highest beam intensity was achieved when L_3 was highly negative ($\sim$2 kv) but this led to difficulties, for at low ion energies secondary electrons produced at the walls of the gun were being accelerated by the high field between L_3 and L_4 and were reaching the target in appreciable numbers. This difficulty was largely removed if L_3 were maintained at the same potential as L_4 and T, even though this meant an over-all reduction of beam intensity. The extraneous electron current could only be measured when the anode-target potential was less than the cutoff potential for the ion beam, but above cutoff its effect could be inferred by noting whether γ, the secondary electron coefficient of the target, showed a reasonable behavior on the basis of the independent researches of Hagstrum,[11] Parker,[12] and others.

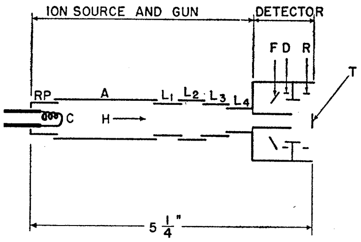

FIG. 3. Schematic diagram of electrode system. C, hot tungsten cathode; RP, electron repeller plate; A, anode; H, magnetic field; L_1-L_4, ion lenses; F, hot platinum filament; D, alkali ion collector; R, secondary electron collector; T, target.

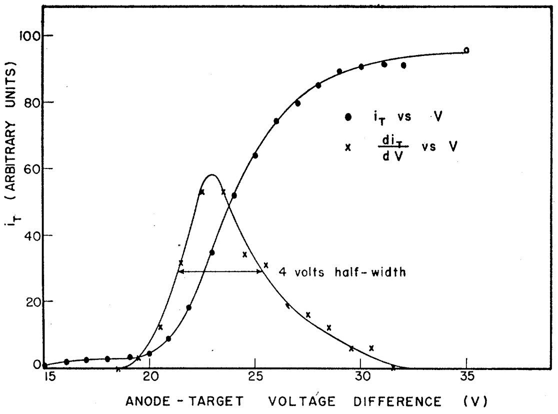

FIG. 4. Typical retarding potential measurement to determine energy spread of primary beam.

The ion energy as well as the energy spread of the beam was determined by retarding potential measurements. Figure 4 is a typical curve. Although the apparent half-width of the beam was 4 volts, there are two reasons for believing that the actual half-width was less than this. In the first place it is seen that the geometry of the electrode system was unsuitable for accurate retarding potential measurements; an isolated potential hill produced by a target of this shape would deflect the ions to the side unless they were approaching the hill normally to the equipotentials. Thus, even a perfectly monoenergetic ion beam would show an apparent energy spread. The second reason for believing that the measured energy spread was exaggerated lies in the work of Parker,[12] who, using a similar source and gun, but having better geometry, found the half-width not to exceed two volts. On this basis, then, it was assumed that the actual half-width of the beam was two volts and that the peak of the distribution was one volt from the high-energy limit. Aside from this one-volt correction, the ion energy was assumed to be the difference in potential between the target potential and the cutoff potential (Fig. 5).

From the cutoff potential one could infer the energy of the electrons which produced the ions V_e. This is the difference between the cutoff potential (corrected for contact potential) and the cathode potential. In order that only singly charged ions be produced, this potential was adjusted for each gas to lie between the first and second ionization potentials of that gas. It was

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[10] A. Theodore Finkelstein, Rev. Sci. Instr. **11**, 94 (1940).

[11] Homer D. Hagstrum, Phys. Rev. **89**, 244 (1953).

[12] J. H. Parker, Phys. Rev. **92**, 536 (1953).

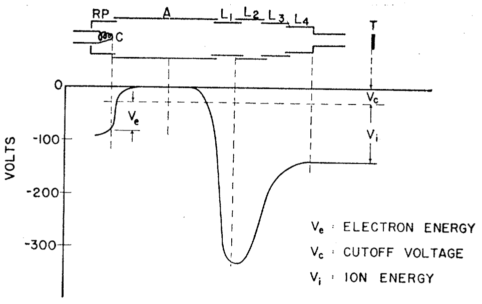

FIG. 5. Typical axial voltage distribution of ion source and gun neglecting space-change effects.

found in a preliminary test that the effect of an unknown admixture of doubly charged ions (which were created when the anode-cathode voltage was sufficiently high) was to cause a decrease in the apparent sputtering coefficient and an increase in the apparent secondary electron coefficient (Fig. 6). This is understandable when one considers the relative importance of the following factors in contributing to sputtering and secondary electron emission: (a) the doubly charged ions arrive with half the mass-to-charge ratio of the singly charged ions, and, therefore, for a given ion current to the target there are fewer incident ions; (b) they arrive with twice the kinetic energy and will hence produce more sputtering per ion but in general not twice as much; (c) they arrive with nearly three times the potential energy and will accordingly produce more secondary electrons. The apparent sputtering rate would be lower with the mixed beam because the effect of (a) overshadows the effect of (b), but the apparent secondary electron emission would be higher because the effect of (c) more than cancels out the effect of (a).

2. *The Target and Secondary Electron Collector*

The solidified alkali metal in the mouth of the intake tube served as a target. By magnetic control a substitute tantalum target could be swung into position between this tube and L_4 so that the ion beam could be measured in the absence of the alkali target.

L_4 and T were maintained at the same potential, and the secondary electron collector ring R was biased 40 volts positive with respect to T. The bias on the ring necessary to achieve a nearly saturated electron current was determined experimentally (Fig. 7). It was possible to read the target current (i_T), the ring current (i_R), or the combination of the two (i_{TR}). Ideally, i_{TR} is the ion current alone, i_R the secondary electron current alone, and i_T the sum of the two or $i_+(1+\gamma)$, where i_+ is the ion current and γ is the secondary electron coefficient. Admittedly the geometry was unsuitable either for 100 percent collection of the target secondaries or 100 percent removal of the extraneous secondaries produced in the gun so that i_R and hence i_{TR} were both subject to error. (Measurements of i_T below ion cutoff indicated that only a negligible number of extraneous electrons were reaching T so that i_T at least was accurately given by the above expression.) However, if a Faraday cage sort of arrangement had been used to remove this trouble, it would have been difficult to install the surface-ionization detector to measure sputtering. On the basis of the curves obtained for γ (actually the ratio i_R/i_{TR}), it was felt that above about 50 volts ion energy i_+ could be assumed to equal i_{TR} quite closely, and below 50 volts i_+ was obtained from the relation $i_T=i_+(1+\gamma)$, where γ was gotten by extrapolating the γ curves obtained above 50 volts back to zero. Justification for this extrapolation again lies in the work of Hagstrum[11] and Parker.[12]

3. *The Surface Ionization Detector*

It is known from both theory and experiment[13] that a neutral alkali atom striking a hot metal surface will lose its valence electron to the surface and will boil off as an ion provided only that the work function of the surface exceeds the ionization potential of the atom. For Na and K atoms incident on hot platinum there is effectively 100 percent ionization by the surface. The emerging positive ions can be collected by an electrode negatively biased with respect to the platinum surface.

Sputtering is a diffuse process (the angular distribution of sputtered atoms, according to Seeliger,[14] follows a cosine law) so that in applying this type of detector to a sputtering problem it is desirable that the filament subtend a fairly large solid angle with respect to the target to ensure adequate sensitivity. In this case it was achieved by using a conical-shaped annular ring (F of Fig. 3) of 0.6-mil platinum foil, 0.25 in. wide at a distance of 0.8 in. from the target. It was heated to an orange color by a conduction current of a few amperes carried by 0.060-in. tungsten leads that served also to

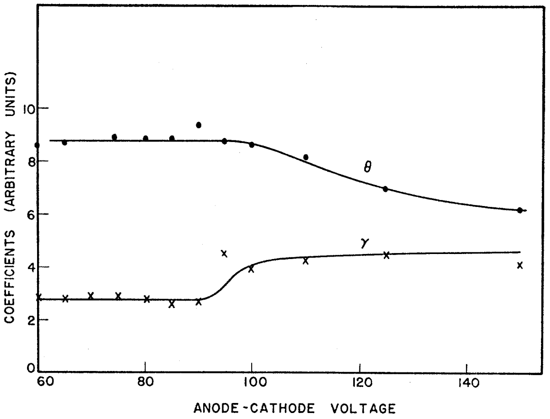

FIG. 6. The effect of the ion source voltage on the sputtering and secondary electron emission rates for He^+ on Na. The breaks in the curves correspond to the appearance potential for He^{++}, and the behavior at high source voltage is attributed to an admixture of He^{++} in the beam.

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[13] K. H. Kingdon and I. Langmuir, Phys. Rev. **21**, 380 (1923).

[14] R. Seeliger and K. Sommermeyer, Z. Physik **93**, 692 (1935).

support the electrodes of the ion gun. The collector (D of Fig. 3) was a tantalum ring placed below the foil and shielded from the ion beam. The collector current was measured by a Kiethley electronic electrometer which read the voltage drop across a Victoreen high resistor.

There were several sources of background current to the collector, the principal one being due to vapor from deposits of sputtered alkali metal in the vicinity of the filament. For the purpose of bucking out the general dc background, an opposing voltage across a low resistance potentiometer was put in series with the Victoreen high resistance, the electrometer being shunted across the combination of the two. The limit to the sensitivity of the detector was set by the "noise" level, the amplitude of which was about 10^{-11} ampere for sodium and somewhat higher for potassium.

The contribution to the collector current due to sputtering (i_D) was measured by switching the ion beam on and off. In order that temperature-dependent background currents be unaffected in the process, the switching was done on an electrode voltage (anode-cathode voltage of the ion source) rather than on the source filament.

It is to be noted that the geometry of the detector was unsuitable for 100 percent collection of the ions from the filament, but if a Faraday cage arrangement had been used it would have been difficult to shield the collector from reflected ions of the primary beam, and moreover one might expect a higher vapor pressure of alkali metal and hence a higher background current in such an enclosure.

A bias of 45 volts gave a reasonably saturated collection current (Fig. 7) and was maintained at this value throughout the experiment. Since the objective of this study was to measure relative sputtering rates, lack of total collection would introduce no serious error; but it could cause an error in any estimates of absolute sputtering rates.

One further correction was still necessary. It was found that even when the platinum filament was cold, there was a small change in the ion current to the collector when the primary beam was switched on and off. The problem was to decide whether this change was due to charged sputtered particles or whether it was due to reflected ions from the primary beam. Using a high-energy primary beam, a retarding potential was put on the detector assembly to ascertain the energy of the ions which were reaching the detector. It was found that most of the ions were of high energy. Since it might be expected that an appreciable fraction of sputtered particles would be of low energy, it was assumed that this current was due solely to reflected beam ions, and it was therefore subtracted from the measured sputtering current. Mass spectrographic analysis would be desirable to prove the point conclusively. All sputtering coefficients at ion energies larger than 150 volts are affected by this correction. At 1000 volts the correction ranged from approximately 50 percent for He$^+$ to 5 percent for Xe$^+$.

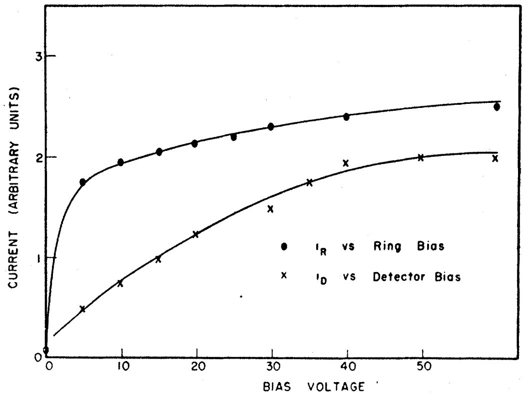

FIG. 7. Collector currents *versus* bias voltages.

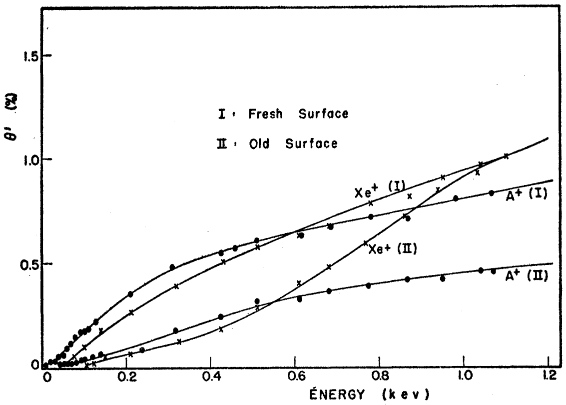

FIG. 8. The sputtering coefficients for A$^+$ and Xe$^+$ for a fresh sodium surface (I) and for a 5-day-old surface (II).

DISCUSSION OF RESULTS

A. Effect of an Aging Surface

When the first sodium surface was obtained, several runs were made over the available energy range for A$^+$ ions to determine the degree of reproducibility that might be expected. It was found that if all traps were maintained at liquid nitrogen temperatures, the morning and afternoon runs would agree within the limits of accuracy of the experiment, showing that the aging process was proceeding at a negligibly slow rate. Several hours of bombardment with the most energetic ions (1900 ev) produced no change, indicating that the rate of energy transfer to the surface was insufficient to effect any degree of "cleanup." On the other hand, if only the trap next to the mercury diffusion pump was kept cold overnight and the other traps were allowed to warm up, the result was that each day the sputtering rates were lower than the day before and the secondary electron emission rates were higher and more erratic. Thus, the effect of an aging sodium surface for A$^+$ ions was to decrease the measured sputtering coefficient θ'

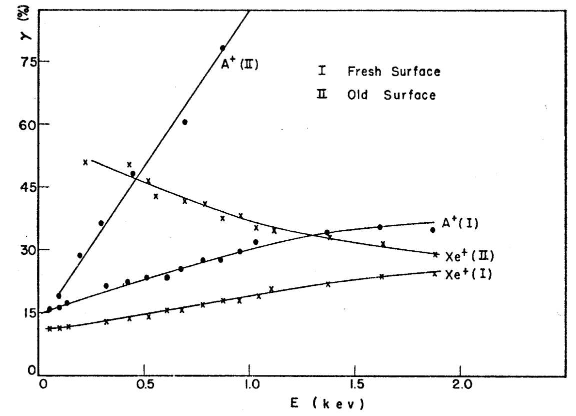

FIG. 9. The secondary electron coefficients for A^+ and Xe^+ for a fresh sodium surface (I) and for a 5-day-old surface.

and to increase the secondary electron coefficient γ. This is not surprising. It has long been known that a layer of oxide or other impurity on a surface inhibits sputtering. As for the secondary electron emission, since it is a process which depends on the nature of the metal, the surface layer, and the incident ions, various workers have observed different effects due to surface contamination. Oliphant[15] and Timoshenko[2] found lower γ's for clean surfaces, whereas Hagstrum[11] and Parker[12] found the reverse.

The effect on θ' and γ due to an aging sodium surface for He^+ and Ne^+ were similar in all respects to the effect for A^+, except that γ values were if anything even more erratic. The effect for Xe^+ seemed to be quite different. Whereas θ' for A^+ decreased over the entire energy spectrum available, θ' for Xe^+ showed a marked decrease only at the lower energies; at 1500 volts there was relatively little change, as is seen in Fig. 8. In like manner, γ was less affected at high energies than at low, as is shown in Fig. 9. A possible interpretation of this is that only the fast, heavy ions were able to blast their way through the surface layer and react with the underlying sodium metal. Of the other ions, a fraction would lose their energy in the surface layer, producing a more copious electron emission (causing a higher γ) and sputtering the surface impurity atoms or molecules which would not be detected by the detector (causing a lower θ').

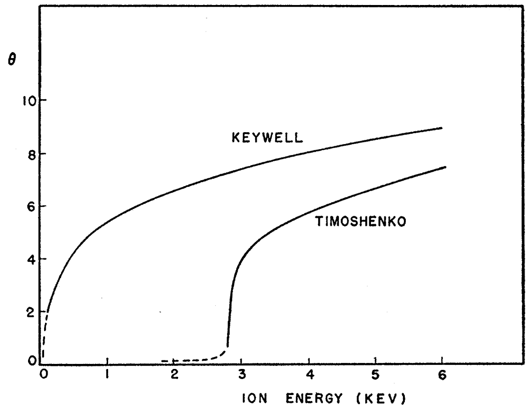

FIG. 10. The data of Timoshenko and Keywell for argon ions on silver.

There is an interesting point concerning the θ' curves for Xe^+: The difference in curves I and II is reminiscent of the difference observed by Timoshenko and Keywell for argon ions on silver, as seen in Fig. 10, suggesting that perhaps their difference can be explained by a difference in cleanliness of their target specimens. Such a conclusion may not be justified in view of the qualitative nature of the present study.

The next test was made on the reproducibility of initial values for several fresh sodium surfaces. In each case the same procedure was followed, namely: (1) flashing all filaments until the background pressure under operating conditions was 5×10^{-8} mm or less, (2) filling all liquid nitrogen traps, (3) overflowing the old surface and allowing the fresh surface to freeze, and (4) making measurements immediately. Unfortunately it was found that such measurements would not repeat themselves closely, sometimes differing with each other by as much a factor of 2. The reason for this variation is not known. It might have been due partly to lack of reproducibility of target surface shape. The frozen alkali surfaces were never flat on the one hand nor smooth on the other. They generally were convex near the edge with a dimple in the center and were always etched in some peculiar pattern. The variation might also have been the result of different degrees of purity of the sodium surfaces, caused by conditions which could not be controlled.

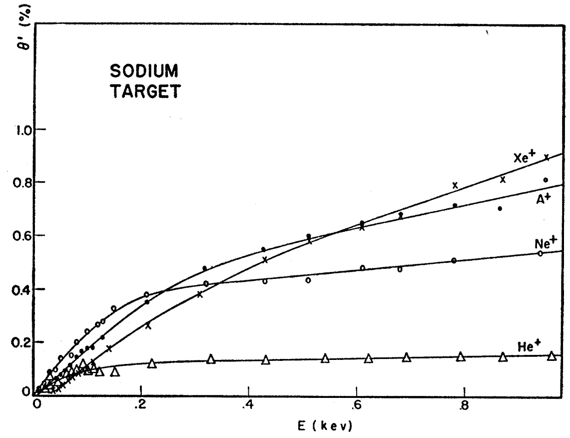

FIG. 11. Results of measurements of the sputtering coefficients for He^+, Ne^+, A^+, and Xe^+ on a fresh sodium surface.

The final test that was made was on the reproducibility of measurements for a single surface over a 24-hour period if all the traps were kept cold. This, fortunately, was successful. The change in θ' and γ for Ne^+ and He^+ was less than 5 percent in this period.

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[15] M. L. E. Oliphant, Proc. Roy. Soc. (London) **A127**, 373 (1930).

Having established, then, the conditions under which it was necessary to operate, four series of runs were made to determine the effect of ion mass and energy on relative sputtering rates. Before each series a fresh surface was obtained using the method described above. Then runs were made over the available energy range for He^+, Ne^+, A^+, and Xe^+. The time required to do this, allowing for evacuation to 5×10^{-8} mm between runs, was 18 hours. At the end of one of these runs, a check was made using the initial gas to see if the surface characteristics had changed, and again the change proved to be less than 5 percent (approximately the accuracy of the measurements). It was assumed, then, that all runs within each series were made on surfaces of constant characteristics.

As was expected, the absolute values did not check from series to series, nor were relative values always in the same ratio. However, each series showed similar characteristics which will be discussed in the next section.

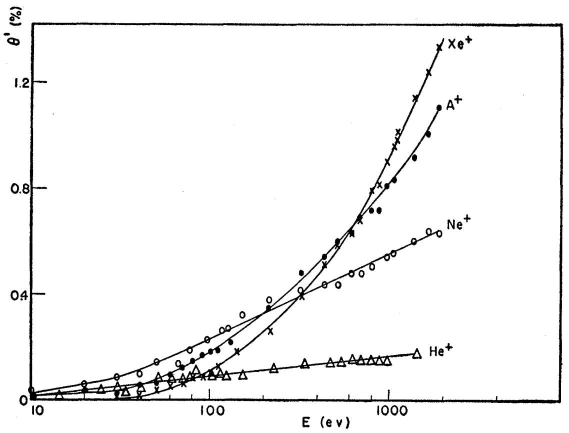

FIG. 12. The data of Fig. 11 plotted on a semilog scale.

B. Effect of Ion Mass and Energy for a Sodium Target

Figures 11, 12, 13, and 14 are plots of the sputtering data from one of the series of runs, using a sodium target. Figure 15 shows the corresponding curves for the secondary electron coefficient.

In the momentum-transfer theory, as first proposed by Kingdon and Langmuir,[6] sputtering is presumed to arise as a result of an ion rebounding from the bottom of a microscopic pit in the surface, striking from behind one of the lattice atoms on the edge of the pit and knocking it loose. The theory predicts an initial period of low sputtering rate while the surface is becoming pitted by the incoming ions. In the present experiment, no initial period of low sputtering rate was ever observed. With a fresh sodium surface the sputtering rate appeared to reach its final value immediately upon turning on the ion beam.

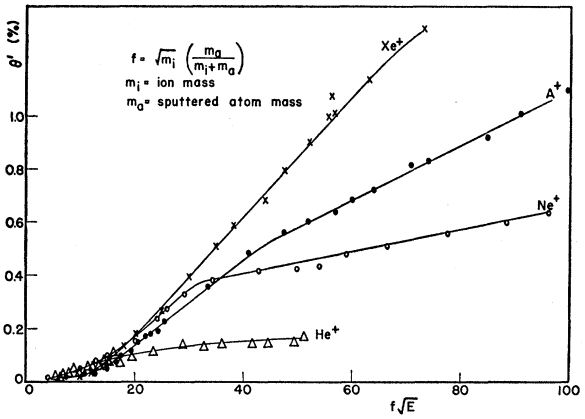

FIG. 13. The data of Fig. 11 plotted on a momentum scale.

Lamar and Compton,[8] from their work on accommodation coefficients, suggested that the same sort of mechanism could occur for the case of an ion penetrating the surface since there would then be a chance of the ion striking a surface atom from behind after colliding with subsurface lattice atoms. They predicted that this mechanism would predominate for the small, light ions whereas for the heavy ions surface penetration would be less likely and another mechanism ("local heating"[7]) would predominate.

Keywell[3] has recently proposed that the theory of neutron cooling by a moderator is applicable to the case of an ion penetrating a metal lattice. The ion loses its energy to the lattice atoms, some of which in turn are able to escape. The theory predicts a relationship of the form

$$\theta = A \ln E - B,$$

where A and B are constants characteristic of the ion-metal combination.

From the theories of Lamar and Compton and of Keywell one might expect Keywell's equation to hold for the light ions and von Hippel's "local heating" equation ($\theta = CE$, where C is a constant characteristic

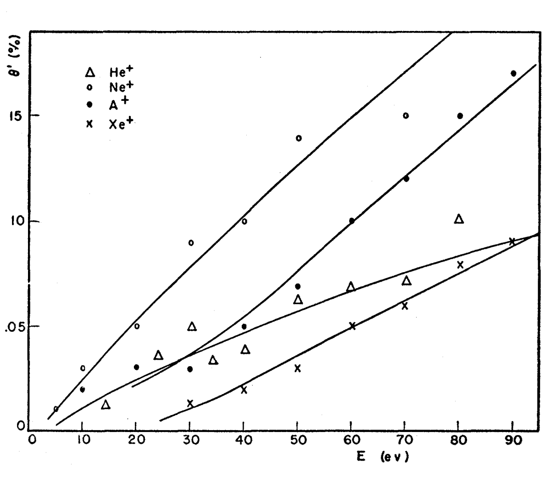

FIG. 14. The data of Fig. 11 plotted on an expanded energy scale.

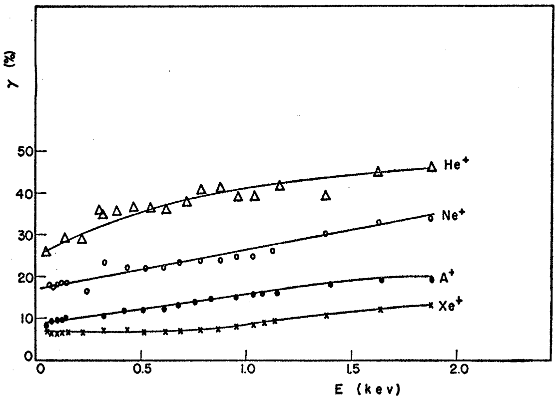

FIG. 15. Results of measurements of the secondary electron coefficients for He$^+$, Ne$^+$, A$^+$, and Xe$^+$ on a fresh sodium surface.

of the metal surface, its temperature, etc.) to hold for the heavy ions. It is seen from Fig. 12 that the sputtering rates for He$^+$ and Ne$^+$ can indeed be satisfactorily represented by straight lines on a semilog plot over most of the energy range in agreement with Keywell's equation, whereas the curves for A$^+$ and Xe$^+$ are seen to be of a different form. The form, however, for A$^+$ and Xe is not that predicted by von Hippel's theory, as can be seen from Fig. 11. In fact, the sputtering rates for these two ions, instead of being linear in E, appear to be much more nearly linear in the square root of E, as seen in Fig. 13. This suggests that the momentum of the ion is a more meaningful parameter than its energy, which theory is further borne out when one notes that at high energy and for a given energy the order of mass and, for a given energy, the order of sputtering for the four ions is the same as the order of mass and hence momentum. What actually is plotted in Fig. 13 is θ' *vs* the momentum relative to the center-of-mass system in a direct two-body collision involving a stationary sodium atom and an incident ion. (The square root of 2 factor has been omitted since it would merely change the abscissa scale by this factor but would not affect the linearity or the relative values.) The most interesting feature of the plot, apart from the linearity of the curves for Xe$^+$ and A$^+$, is the region of nearly common values at low momenta, suggesting that here perhaps there is a mechanism which is common to all the ions, the sputtering rates being controlled primarily by the amount of momentum—and hence kinetic energy—which can be transferred to a single sodium atom in a two-body collision. Since it is believed that Xe$^+$ is unable to penetrate the surface appreciably, the implication is that at these low energies the other ions also do not penetrate appreciably. In fact, the break in the curve for Ne$^+$ and A$^+$ might be interpreted as a sort of "threshold" for penetration. That is, at lower energies Ne$^+$ reacts directly with the surface atoms whereas at higher energies it buries itself in the lattice and by a "neutron cooling" process is able to transfer some of its energy back to the surface atoms.

The momentum-transfer theory also predicts a sputtering *threshold* when

$$\frac{4mm'}{(m+m')^2}E=q,$$

where m and m' are masses of the target atom and incident ion; E, the ion energy; and q, the atomic heat of sublimation. For sodium, $q=1.1$ electron volts so that the sputtering threshold for Ne$^+$, A$^+$, He$^+$, and Xe$^+$ should be 1.1, 1.2, 2.2, and 2.2 electron volts, respectively. The energy spread of the beam (apparent or real) precluded any possibility of detecting sputtering at these low voltages; for the beam intensity was so low that any sputtering currents to the detector, which would have been small even with a beam of normal intensity, were completely out of range below the noise level of the detector. Furthermore, this noise level made it impossible to make precise measurements of sputtering currents at a few volts above threshold, thus ruling out the possibility of being able to make accurate extrapolations. Sputtering could first be detected for Ne$^+$ at 5 volts, for He$^+$ and A$^+$ at 10 volts, and for Xe$^+$ at 30 volts. Up to about 200 volts, Ne$^+$ showed the highest sputtering rate, with A$^+$ next. This is consistent with the theory, since Ne$^+$, having most nearly the same mass as Na, is able to transfer the most kinetic energy in a collision with a sodium atom. Figure 14 represents the data for θ' at less than 100 volts. In consideration of the uncertainties in the measurements, it is felt that the extrapolations come reasonably close to the theoretical values for Ne$^+$ and He$^+$ but are doubtful for A$^+$ and completely unsatisfactory for Xe$^+$. Apparently below 30 volts it was impossible for Xe$^+$ to transfer its energy effectively to a sodium atom. Whether this is a significant feature in the sputtering mechanism or whether it was caused by the surface oxide layer is not

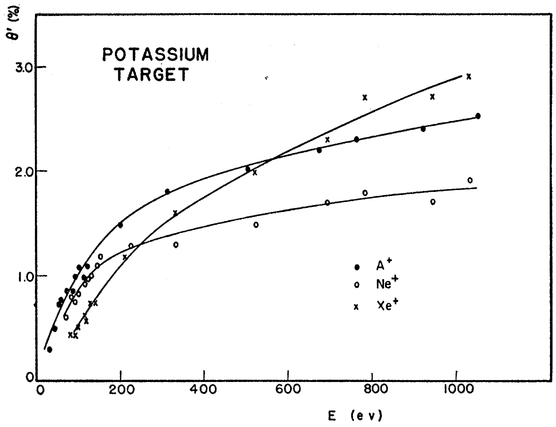

FIG. 16. Sputtering coefficients for Ne$^+$, A$^+$, and Xe$^+$ on a fresh potassium surface.

known. That it might have been the latter is suggested by Fig. 8.

C. Effect of Ion Mass and Energy for a Potassium Target

Figures 16, 17, and 18 represent the data for a potassium surface. Because of its high vapor pressure, potassium proved to be a more troublesome metal than sodium with the present experimental setup. In the first place, the general background noise level to the detector was an order of magnitude higher than for sodium so that even though the sputtering rates were somewhat higher, the over-all sensitivity was considerably lower. For this reason no measurements could be made at very low energies, and no reliable measurements could be made at all with helium. In addition, the overflow technique of obtaining successive fresh surfaces was not readily applicable, because reliquefying the metal resulted in a deposition of potassium on the insulators supporting the detector, making further measurements impossible without dismantling the apparatus. The data obtained, then, were neither as extensive nor as reliable as that obtained with sodium.

In spite of these drawbacks, however, the measurements appear to confirm the conclusions previously drawn for sodium in that (a) at low energies sputtering is greatest for the ions with mass most nearly equal to the mass of the target atoms (A^+ ions in this case), and (b) at high energies the order of sputtering is the same as (but not proportional to) the mass, and, hence, the momentum of the ion. The plot of θ' *vs* $f\sqrt{E}$ also shows a region of relatively common values at low energy, again indicating that here the sputtering rate is controlled by the amount of energy which can be transferred to a target atom in a two-body collision.

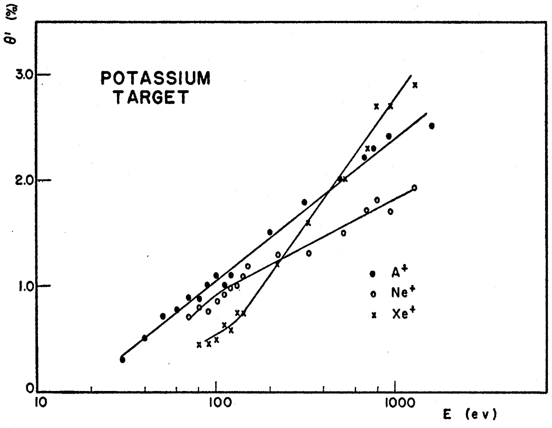

FIG. 17. The data of Fig. 16 plotted on a semilog scale.

As for the form of the sputtering curves, those for A^+ and Ne^+ seem to be reasonably linear on a semilog plot, whereas that for Xe^+ appears to be most nearly linear on a $\sqrt{E}$ plot.

D. Effect of Surface Temperature

Two attempts were made to measure sputtering with a sodium target at liquid nitrogen temperature, using the ions He^+ and Ne^+ (A^+ and Xe^+ could not be used since their boiling points are above this temperature). In both cases sputtering was observed to decrease as the surface began to cool, but before any steady low value was reached the sputtering began to increase again and eventually reached a value approximately twice the initial value. The high rate persisted after the target was allowed to return to room temperature and did not reach the initial value again until over two hours later. The initial decrease was probably a true temperature effect, but the subsequent increase may well have been due to sodium vapor coming from the region of the hot detector and condensing on the cold target as a "clean" sodium layer. It was thus not possible to get meaningful data on the temperature dependence of the sputtering rate.

E. Secondary Electron Emission

The theory of secondary electron emission has been rather completely worked out by Hagstrum[11] and others. Basically the mechanism is believed to consist of neutralization of an incoming positive ion by an electron from the metal, the energy of neutralization being carried off as kinetic energy by a second electron which may then escape. The curves of Fig. 15 seem to be consistent with this theory of potential energy ejection, in that (a) the relative values of the emission are in the same order as the relative values of the potential energy of the ions, and (b) there is apparently only a small dependence on the kinetic energy of the ions.

No attempt was made to measure the energy distribution of these electrons since the geometry was unsuitable for this.

F. Absolute Sputtering Rates

Only the roughest sort of estimate can be made for the absolute values of the sputtering rates. At least

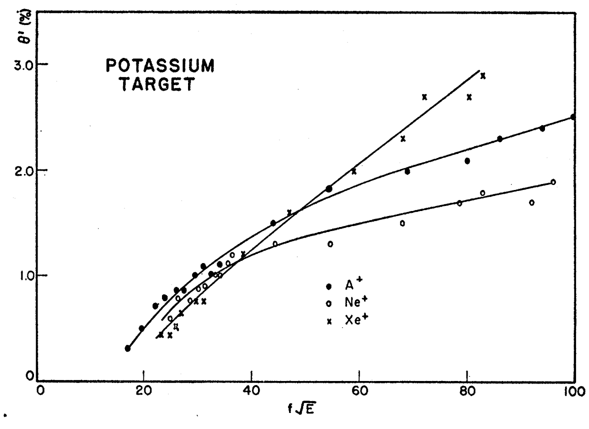

FIG. 18. The data of Fig. 16 plotted on a momentum scale.

four factors must be taken into account: the ratio of the solid angle subtended by the detector to the total solid angle available for sputtering, the angular distribution of the sputtered atoms, the ratio of the collector current to a saturated collector current (saturated with respect to both the bias and the temperature), and the degree to which sputtering has been reduced as a result of surface impurities. The effect of the last item is difficult to reckon since at no time was there ever a guarantee that the metal surface was clean. On the basis of the attempted temperature variation measurement previously discussed, it is felt that in general sputtering was diminished for He^+ and Ne^+ by at least a factor of 2 as a result of the oxide layer. There are no such data available for A^+ and Xe^+. Neglecting, then, this effect as incalculable, it is estimated from the geometry (using a cosine distribution law for the sputtered atoms) and also from the electrical characteristics of the assembly that about 3 percent of the total number of sputtered atoms were counted. Thus, absolute sputtering rates may be deduced approximately by multiplying the ordinate scales by 33.

It is seen that for 1000-ev ions, θ, the absolute sputtering coefficient, ranges from 1.0 for Xe^+ on K to 0.05 for He^+ on Na. In view of the studies of Timoshenko and Keywell, θ seems surprisingly low, especially since the alkalis, having low sublimation energies, might be expected to sputter quite easily. It is felt that the discrepancy cannot be entirely attributed to an error in the estimate of the absolute coefficient but that in fact the alkali surfaces used did indeed show a low sputtering rate. Certainly surface impurities—which were not "cleaned up" by ion bombardment in the present experiment—account for a part of it. Timoshenko and Keywell both used high energy and high intensity beams, and not only were their surfaces probably cleaner as a result of this, but also the sputtering mechanism itself might have been quite different. However, any conclusions which might be drawn would be little more than speculation until such time as the present study is repeated under conditions which have been modified to simulate those of the other authors.

SUMMARY OF CONCLUSIONS

The results may be briefly summarized as follows:

(1) It appears that no single theory for sputtering is applicable under all conditions.

(2) At low ion energy, the sputtering rate appears to depend only on the amount of energy which can on the average be transferred to a single surface atom in a two-body collision. What the sequence of events is between this collision and the emergence of a sputtered atom is a matter of conjecture.

(3) At high energy the sputtering rate is in the same order as (but not proportional to) the mass of the ions.

(4) No evidence was found in favor of the theory of local heating, at least insofar as a linear dependence of θ' on E is concerned. It appears instead that for the light ions θ' is linear in $\ln E$, and for the heavy ions in $\sqrt{E}$.

(5) Sputtering, being a surface phenomenon, is greatly effected by surface conditions, the effect of an oxide layer being to reduce the sputtering rate.

DISCUSSION OF ERRORS

The principal uncertainties in this experiment resulted from:

(1) Lack of control over the initial characteristics of a fresh surface, causing θ' to vary by as much as a factor of 2 for two different surfaces of the same metal but otherwise similar conditions.

(2) Fluctuating background currents to the detector, limiting its sensitivity, and thus making impossible accurate measurements at very low energy. The probable limit of error at ion energies less than 30 ev may well have been as high as 50 percent.

There were, of course, other sources of error (unaccountable electrons in the ion beam, the energy spread of the beam, etc.) and most of these have been mentioned, but the limit to the accuracy of the experiment was set by the two factors mentioned above. At energies greater than 100 volts, and with a given surface, measurements could be duplicated to within 5 percent over a period of several hours. It is believed, therefore, that the results have at least qualitative significance, for the general characteristics which have been discussed were present in all of the series of runs.

ACKNOWLEDGMENTS

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