For a pure quadrupole resonance of Br or I isotopes, carried out in other piezoelectric crystals at $3\text{–}5\times10^8$ cps at 4°K, the effect should be 2 or 3 orders of magnitude larger and should be readily observable. It is necessary that the crystal lacks a center of inversion symmetry. Otherwise the contributions of lattice sites related to each other by the inversion will cancel each other in the summation of Eq. (A1), because they have opposite sign of the tensor elements R.

The physical origin of this "quadrupole-electric effect" is, of course, based on the observation that the equilibrium position of the nucleus in the lattice depends on the orientation of the nuclear quadrupole moment. If the nucleus is at a site which lacks inversion symmetry and has nonvanishing third derivatives of the electrostatic potential, the force on the nucleus is

$$-Ze\nabla V-e\mathbf{rr}:\nabla\nabla\nabla V.$$

The electric field $-\nabla V$ acting on the nucleus is not exactly zero on the average. The equilibrium position of the Ga and As nuclei is not exactly at the center of the tetrahedra, but slightly displaced towards or away from one of the corners, depending on whether the nuclear quantum state has $|m_I|=\frac{3}{2}$ or $\frac{1}{2}$.

The magnitude of the displacement depends on the extent to which the electron orbitals follow the nuclear displacement. The polarization resulting from all nuclear and electronic displacements is, however, unambiguously determined by Eqs. (A1) and (A2). If the model from Sec. III of ionic displacements with an effective charge is adopted, the spatial displacement δr of a nuclear spin, while making a $|m_I|=\frac{3}{2}\rightarrow\frac{1}{2}$ transition, is given by

$$e_{\text{eff}}\delta r=2^{-1/2}R_{14}{}^{\text{ion}}eQ. \tag{A4}$$

This displacement is about 2.5×10^{-16} cm, much smaller than the zero-point vibration of an individual nucleus or even the nuclear dimension. The combined effect of all spin transitions in the ensemble of nuclear spins in the crystal leads, however, to a macroscopically observable polarization. The difference in equilibrium position of a nuclear spin in the $|m_I|=\frac{3}{2}$ or the $|m_I|=\frac{1}{2}$ is an example of a Jahn-Teller distortion to lift the fourfold degeneracy of the nuclear spin levels into two Kramers doublets. The effect is so small that, in the absence of external fields, each nucleus would "tunnel" rapidly between the four equivalent positions along the four body diagonals.

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Electron Ejection from Metals due to 1- to 10-keV Noble Gas Ion Bombardment. I. Polycrystalline Materials*

G. D. MAGNUSON AND C. E. CARLSTON
Space Science Laboratory, General Dynamics/Astronautics, San Diego, California
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A method is described which complements present techniques and enables measurements to be made of the secondary electron emission coefficient, γ, for ions on materials for which γ is difficult or impossible to measure by the "flashing" or heating technique. The method allows operation in a high-vacuum (10^{-8} Torr) system as opposed to an ultra-high vacuum ($<10^{-9}$ Torr) system. Results for the secondary electron emission coefficient, γ, are presented for Ar^+ on Zr, Cu, Mo, Ni, Ta, and Al, and for Ne^+, Kr^+, and Xe^+ on Cu and Mo in the energy range 0.5 to 10.0 keV. Comparisons with present theories and with other experimental results are made.

I. INTRODUCTION

INTEREST in the study of the secondary electron ejection from atomically clean surfaces due to positive ion bombardment has been stimulated, at least in part, by the advanced vacuum techniques now available. For example, many of the data obtained by earlier investigators are open to question because of surface contamination,[1] due in part to poor vacuum conditions. During the past decade, Hagstrum has published a great deal of significant research on the measurement of γ, the secondary electron emission coefficient, from various refractory metals[2] and semiconductors[3] subjected to noble gas ion bombardment. Hagstrum's work was done in the energy range from 10 to 1000 eV. In this energy range electron emission occurs by the potential ejection mechanism which is a result of Auger neutralization and de-excitation.[4] Hagstrum has also demonstrated the strong influence of

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[1] For a good review of the subject prior to 1956 see H. S. W. Massey and E. H. S. Burhop in, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), Chap. IX.

[2] H. D. Hagstrum, Phys. Rev. **89**, 244 (1953); **96**, 325 (1954); **104**, 672 (1956); **104**, 317 (1956).

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[4] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).

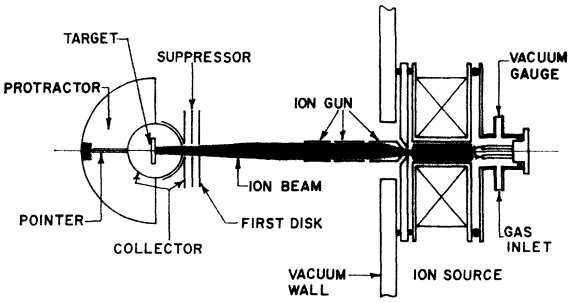

FIG. 1. Sputtering and secondary electron ejection apparatus.

adsorbed surface layers on the ejection of electrons from solids.[5]

When the energy of the bombarding ion becomes greater than roughly 1 keV, a different process seems to be primarily responsible for the ejection of electrons. This mechanism is termed the kinetic ejection mechanism. The theory of the kinetic ejection of electrons is not clearly understood at present, but it seems most probable that kinetic ejection involves excitation of the bound electrons of the solid rather than the free electrons.[6–9] In general, the measurements of various investigators working in the kinetic ejection region have not been in satisfactory agreement.[10–12] It was thought that results obtained by use of a different technique might be useful in resolving these discrepancies.

In most of the work reported to date, the surfaces have been cleaned by "flashing", i.e., heating the sample to a temperature sufficiently high to dissociate and/or vaporize surface impurities. If this heating is performed in an ultra-high vacuum system ($<10^{-9}$ Torr) the measurement of γ can be made in a time short compared to the monolayer formation time. The research reported here employs a technique different from that of flashing in that an intense ion beam is used to simultaneously clean the target and produce secondary electrons. Hence, no heating of the target is required and the need for an ultra-high vacuum system is obviated. A distinct advantage of this sputtering technique is that it allows measurements of γ to be made on materials the surfaces of which cannot readily be cleaned by the flashing method. Although the cleaning of surfaces by sputtering is not a new technique,[13,14] the application as presented here has previously not been used to any great extent or carried out with sufficient care.[15,16]

II. APPARATUS

The experiments were carried out in a vacuum chamber, 14-in. diam and 18 in. long, made of type-304 stainless steel. The chamber was evacuated by an oil diffusion pump with a rated pumping speed of 1400 liters/sec. This speed was reduced to about 700 liters/sec by a liquid nitrogen cold trap mounted between the chamber and pump. Special composition viton-type-A O-rings, which were baked prior to installation, were used throughout the system. Baking reduces the vapor pressure of the O-rings and allows the system to be baked to 175°C with O-rings installed. After a minimal bakeout (10 h at 100°C) a pressure of 8×10^{-9} Torr was achieved. Typical ambient background pressure during experimental measurements were 1 to 5×10^{-8} Torr.

The ions were extracted from a magnetically confined, oscillating electron bombardment source, the characteristics and operation of which have been previously reported.[17] A direct in-line system without magnetic separation of the ion beam was used since the beam extracted from the source was of purity $>97\%$. The total energy spread of the beam was ≤ 3 eV. Energetic neutrals or metastable atoms and ions formed in the source or along the beam trajectory were measured by retarding potential methods and were estimated to comprise less than 0.01% of the total ion beam current. Calculations of the amount of neutral atoms expected due to charge transfer indicated that for argon, target chamber operating pressures of less than 2×10^{-5} Torr must be maintained in the apparatus to keep the neutral and metastable quantities formed along the

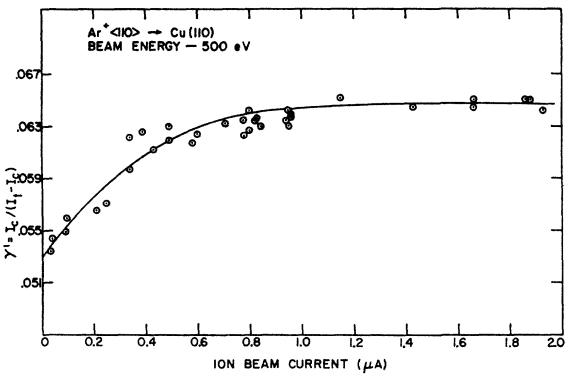

FIG. 2. Secondary electron emission coefficient γ' vs target current at constant beam spot-size. Ar^+ ions normally incident on a copper (110) single crystal at an energy of 500 eV.

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[16] G. Slodzian, Compt. Rend. **246**, 3631 (1958).
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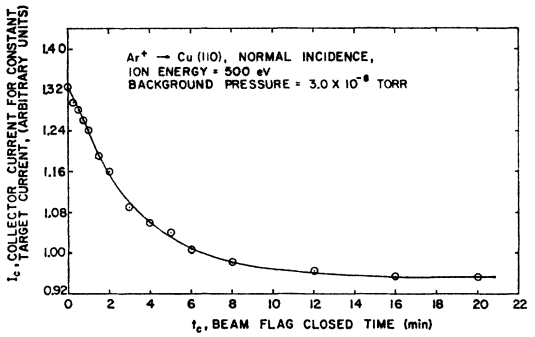

FIG. 3. Monolayer formation time curve of γ' vs t_c, beam flag closed time, for Ar^+ normally incident on a copper (110) crystal. Beam energy is 500 eV.

beam trajectory below 2% of the total ion beam current delivered to the target. In our experiments operating target chamber pressures varied from 1 to 8×10^{-6} Torr, depending on the gas used.

The ions were formed in the source at the desired potential and then accelerated to the target at ground. The beam energy was therefore the same as the source anode potential (neglecting a 6-V potential difference between the source plasma and the anode walls).

After extraction, the ion beam was focused by an einzel lens cylindrical focusing system and directed into the entrance aperture of the first of two disks prior to striking the target. See Fig. 1. The first disk was grounded and served as a collimator to prevent the ion beam from striking the second aperture. The first disk was also used as part of a shield for the secondary electron collector. The second disk was used simply as a suppressor to prevent electrons in the beam and those formed at the first disk from entering the target-collector regions, and also to prevent secondary electrons from the target from streaming back up the beam. The high current densities used in the measurements result in the beam appearing as a shallow potential well for electrons, making suppression imperative. It was found necessary to increase negatively the suppressor voltage as the beam energy was increased. An electromagnetically operated beam flag was placed in front of the first disk. This flag was closed during the source bakeout and clean-up period and when electrical leakage measurements were made. The beam flag was also used when monolayer formation times were measured.

The secondary electron collector was a sphere 3 in. in diameter with two diametrically opposite holes, one an entrance hole for the ion beam and the other to allow the target holder arm to pass into the collector. The targets used were nominally 1 in. in diameter, 0.020 in. thick, and were aligned to within $\frac{1}{4}°$ of normal incidence by using a permanently mounted protractor. The total opening angle of the incident ion beam envelope was measured to be less than 2° (1° half-angle).

The secondary electron collector and target holder were completely surrounded by a metal shield to prevent stray currents from reaching the collector and the arm supporting the target holder. Electrical leakage and stray currents were at most 0.1% of the smallest collector current measured. Calibrated electrometers were used to measure all currents. Accuracy of measurement of the current was limited by the reading uncertainty of the electrometers.

A calibrated vacuum tube voltmeter was used to measure beam energy. The reading uncertainty in energy was less than $\pm3\%$.

III. PROCEDURE

Prior to bombardment of the targets, the ion source was prepared for operation by a procedure somewhat akin to "baking-out." For this reason, the procedure is named source bakeout and involves a cleaning of the source by increasing the anode voltage to 300 V with the filament temperature somewhat higher (10–20%) than normal operating temperature. The source pressure is allowed to drop to roughly 9×10^{-6} Torr as read by an RG-75 vacuum tube. The anode voltage is then returned to the operating value (40–50 V depending upon gas used) and the gas is bled in until operating pressure is reached. The discharge is initiated and ions extracted for 20 to 30 min before the filament temperature is dropped to operating value, the beam flag opened and bombardment begun. After the complete source bakeout procedure, the source pressure (with no gas admitted) is of order 5×10^{-6} Torr.

When changing from one gas to another, the complete procedure of source preparation is somewhat more extensive. Prior to bakeout, the source pressure is increased to approximately 20 μ of Hg for several minutes to purge the source and gas feed system. The bakeout procedure previously described is then completed, followed by 20 h of ion extraction from the source before measurements are taken. The target is bombarded at several keV until clean, as evidenced by a constant value of γ with bombardment time. Generally,

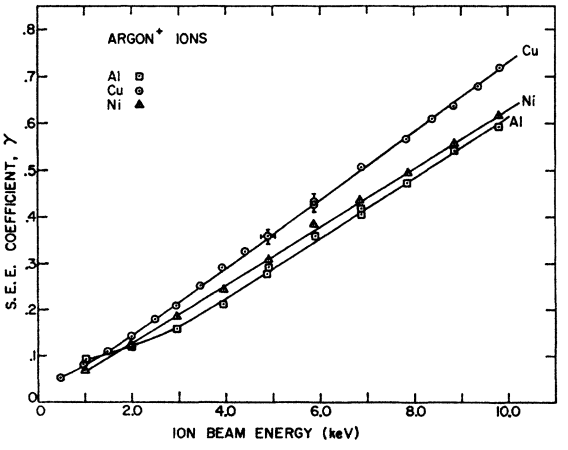

FIG. 4. Secondary electron emission coefficient for electron ejection by Ar^+ on Cu, Ni, and Al as a function of ion energy.

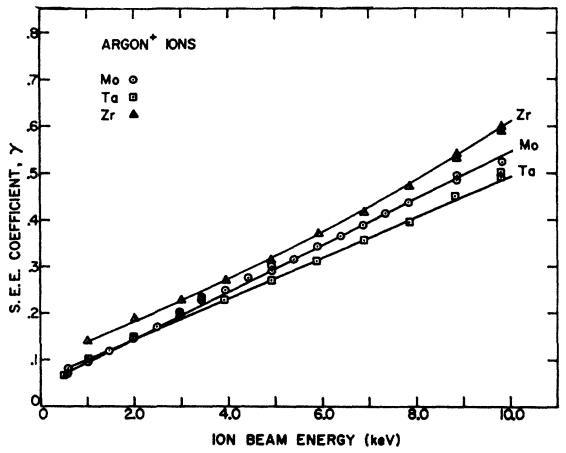

FIG. 5. Secondary electron emission coefficient for electron ejection by Ar^+ on Mo, Zr, and Ta as a function of ion energy.

only 4 h of operation is necessary to obtain a pure beam.

Secondary electron emission coefficients are not measured until the target chamber ambient pressure is less than 5×10^{-8} Torr. At this pressure it is possible to maintain a clean target at a beam energy of 500 V. In cases where it was not possible to keep a target clean (within a few percent of a monolayer) the target was bombarded at a high energy until clean at which point the beam energy was quickly lowered and the currents measured. These measurements were made usually within twenty seconds from the time the beam energy was decreased and were reproducible within $\pm3\%$. The above procedure was found to be necessary with Al and Zr but not with the other materials examined.

Target preparation included mechanical cleaning, alcohol wash, acid etch, and water wash followed by an alcohol rinse. There were deviations from the cleaning procedure for some targets. For example, Mo and Al were simply washed with Labtone and water, rinsed with alcohol, and etched by ion bombardment in the system.

The principle upon which the experiment is based is quite simple. The target is kept clean by atomic ejection (sputtering) while measurements are taken. The ion beam thus simultaneously cleans the target and produces secondary electrons. The experiment depends upon the surface layer removal rate being much larger than the surface layer deposit rate from the ambient gas. For example, at a beam energy of 1 keV the ion current density is about 13 μA/cm^2. At a background pressure of 3×10^{-8} Torr, the ratio of bombarding ion to ambient gas atom striking the target is about 8. Therefore, with a sputtering yield of 1 the number of surface layers removed is 8 times the number of surface layers that would be deposited, assuming a sticking coefficient of unity. At higher energies, the ratio is even more favorable due to the increased ion beam current density. This has been shown to be the case by plotting in Fig. 2 the secondary electron emission coefficient γ vs beam current at constant spot size and a beam energy of 500 V for Ar^+ on the (110) face of copper where the sputtering rate is relatively low.

The sputtering rate of (110) Cu single crystals due to argon ion bombardment has been measured in this laboratory and at 500-eV ion energy, is about 0.80 atom per incident ion. With a current density of 6 μA/cm^2, about 3.0×10^{13} atoms/cm^2 are removed per second. However, assuming a sticking coefficient of unity and with a background pressure of 10^{-8} Torr, about 0.6×10^{13} atoms/cm^2 are deposited on the target. Therefore, for each monolayer of gas atoms laid down on the target, there are 4.8 monolayers removed. After initial cleanup of the target, the target must be considered clean. The aforementioned case is the limiting one for our experiments. As an additional indication of surface cleanliness (i.e., lack of contaminants) γ' has been plotted versus beam flag closed time which shows the effect of a monolayer on the value of γ', in accordance with Hagstrum's[5] findings. See Fig. 3.

In order to obtain the monolayer buildup curve, the beam flag was closed for a period of time t_c after the target was initially cleaned. The beam flag was then opened and a reading of γ' was made within 2 sec after opening the flag. The results were plotted as $\gamma'=I_c/(I_t+I_c)$ whereas the results for γ were plotted as $\gamma=(I_c+I_R)/(I_t+I_c)$, where I_R is the saturation current to the collector with negative voltage applied to the collector, I_c is collector saturation current, and I_t the target current with a positive voltage applied to the collector. It is assumed that I_R is either or both high-energy reflected ions or metastable atoms formed at the target releasing electrons at the collector which return to the target. In any case, this point is still open to question and an arbitrary decision was made to report γ including the "reflected ion" component. How-

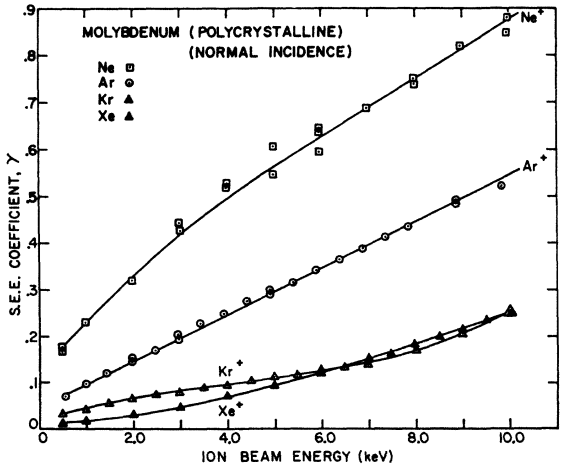

FIG. 6. Secondary electron emission coefficient for electron ejection from polycrystalline Mo by Ne^+, Ar^+, Kr^+, and Xe^+ as a function of ion energy.

ever, the correction of I_R to γ is at most 5% in the range of γ reported here.

Reproducibility of results was better than the expected uncertainty in the experiment. Reproducibility was of order $\pm 3\%$ under widely varying conditions, whereas maximum expected uncertainty was $\pm 7\%$.

IV. RESULTS AND DISCUSSION

The results we have obtained are shown in Figs. 4 to 7. Figure 4 shows γ for Ar^+ on Cu, Ni, and Al. Figure 5 shows γ for Ar^+ on Mo, Ta, and Zr. Figure 6 shows γ for Mo bombarded by ions of the four noble gases, Xe, Kr, Ar, and Ne. Figure 7 shows γ for Cu bombarded by the same noble gas ions. It can be seen that there is a great deal of dissimilarity between the sets of curves of Fig. 6 and Fig. 7. The Cu curves seem to have a crossover point for all gases but Xe. Above the crossover point the behavior of the curves are inverted from what they are in the potential ejection range. In the potential ejection region, the curves for Mo and Cu are similar. The behavior of Xe^+ and Kr^+ on Mo is curious. There seem to be two crossover points in this case. No complete explanation for this can be given at this time.

Our curves of the noble gases bombarding Mo agree quite well with those of Arifov and Rakhimov.[12] For example, the slopes of our curves are almost identical with the slopes of the curves reported by these investigators. However, for the case of Ar^+ and Kr^+, our curves are a constant value (~ 0.025) lower than their curves. In the case of Ne^+ on Mo, however, our values are slightly higher than theirs, again by roughly 0.025 electron/ion. This is within our absolute uncertainty for Ne. Our Ne^+ on Mo curve dips as the energy is decreased below 4 keV, whereas the curve of Arifov and Rakhimov[12] flattens out to a value of 0.27 electron/ion. We checked target cleanliness at 500 eV by the monolayer build-up time method. The result is shown in Fig. 8. A calculation of the removal to deposition ratio, i.e., number of monolayers removed per monolayer deposited was made. Both the monolayer time check and the calculation seem to indicate that monatomically clean surface values of γ have been measured. The shape of our Ne^+ on Mo curve has been seen previously by Petrov[10] for He^+ on W and by Ploch[6] for Li^+ and Ne^+ on Pt.

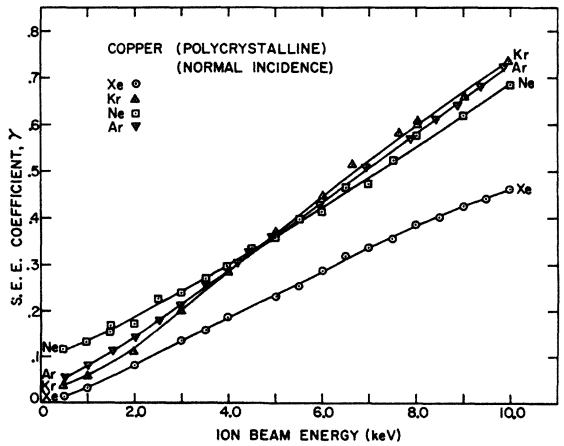

FIG. 7. Secondary electron emission coefficient for electron ejection from polycrystalline copper by Ne^+, Ar^+, Kr^+, and Xe^+ as a function of ion energy.

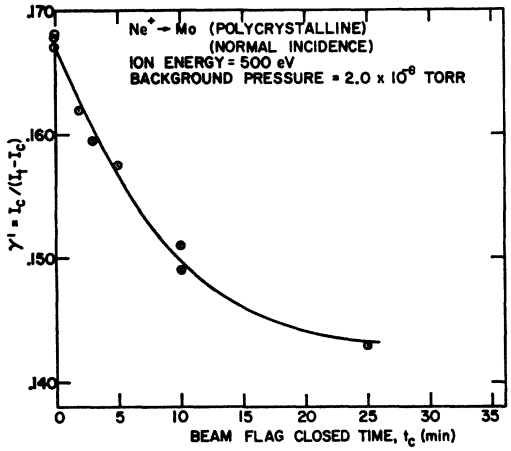

FIG. 8. Monolayer formation time curve of γ' vs t_c, beam flag closed time, for Ne^+ on Mo. Beam energy is 500 eV.

Our value of γ at 500 eV for Ar^+ on Mo was 0.076 which agrees with the value of Varney[18] at 350 V, but differs from that of Hagstrum who obtains a γ of about 0.112 at 500 eV.

The behavior of the γ of Cu and Mo from our points at 500 eV was examined as a function of the first ionization potential E_i of the bombarding ion, and the results are shown in Fig. 9. It is interesting to note that γ depends linearly upon E_i in the potential ejection region but it is not immediately obvious why this should be so. Hagstrum's data[2] on Mo when plotted in this fashion show the same linearity but with γ values somewhat higher than ours and with a greater slope.

Our values are also in excellent agreement with Mahadevan *et al.*,[19] over the energy region of overlap with their work, 500 to 2500 V. It is possible that much of the discrepancy in the measurements of γ reported by different investigators can be accounted for by differences in the past metallurgical histories of their targets. The targets used in making measurements of γ are usually rolled foils, thin enough to heat by passing current directly through the sample. It is, therefore, likely that these target foils have a great deal of preferred orientation which could make the targets used in one laboratory differ from those used in another. In the following paper[20] the results of γ measurements on single crystals are given that illustrate the strong

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[19] P. Mahadevan, J. K. Layton, and D. B. Medved, Phys. Rev. **129**, 79 (1963).
[20] G. D. Magnuson and C. E. Carlston (to be published).

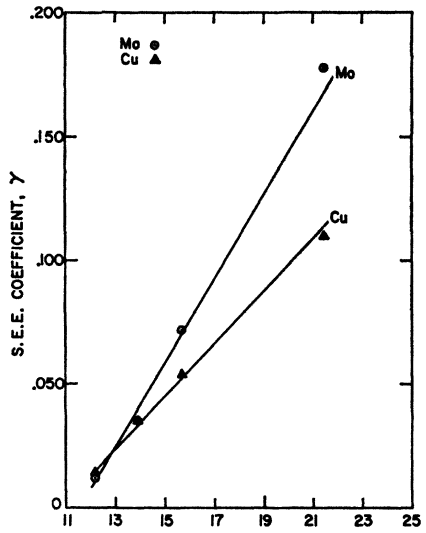

FIG. 9. Secondary electron emission coefficient at 500 eV vs the first ionization potential of the bombarding ion for Mo and Cu bombarded by Ne^+, Ar^+, Kr^+, and Xe^+.

influence of crystallographic orientation on the kinetic ejection of secondary electrons.

Parker[21] has measured γ for Ar^+ on Ta at 140 eV and obtains a value of 0.023. It is difficult to say whether his curve would extrapolate to our value of 0.08 at 500 eV. However, his background pressure and flashing technique would indicate that his values were clean surface values. Our results for Ar^+ on Ta agree well with the results of Petrov,[10] but his curve has a slightly greater slope.

Cousinié *et al.*,[15] have measured γ for Ar^+ on Mo, but the results do not agree favorably with ours. They used a technique similar to the one we employ. However, there seems to be some indication that their current densities were not large enough to keep their targets clean below 10 keV. The fact that the slope of their curve is less than ours indicates that the surface becomes progressively contaminated as the energy is decreased. Our monolayer formation time curves made at energies above 1 keV show very little drop or no drop at all with beam flag closed time, but show an essentially flat region followed by a rise after the monolayer time. Above 3 keV, the curves rise almost directly with increasing closed time from $t_c=0$. Therefore, if a target is not quite clean, a value which is larger than the clean surface value will be measured at energies above 1 keV. For this reason we believe that Cousinié's[15] high values of γ are values associated with contaminated surfaces. Cousinié's results for Al, the most difficult metal for us to keep clean and which necessitates the clean up at high energies previously mentioned, are quite at variance with ours and are another indication of the difficulty they may have had with surface cleanliness. Of the metals investigated, Al shows the largest difference between clean and contaminated values.

A direct comparison cannot be made with the results of Ploch[6] since his work was done with different ion-metal pairs than was our work. However, he finds curves which have the shape exhibited by our Ne^+ on Mo curve. Comparison with Slodzian[16] shows that at 5 keV ion energy for Ar^+ on Al, Zr, Ni, Ta, Mo, and Cu his target surfaces were most likely gas covered. His values for γ are all much higher than our values.

The theory of the kinetic ejection of secondary electrons from polycrystalline materials is not in a satisfactory state at the present time. It seems most probable that the kinetic ejection of electrons involves the bound electrons of the lattice atoms as other authors have stated.[6-9] Roos[9] derives the theoretical result that γ varies as the square of the primary ion energy. As can be seen from our curves, we find essentially a linear dependence on energy. The theoretical predictions of Parilis and Kishinevksii,[8] at least for the shape of the lower $\frac{2}{3}$ of their curves, is in general agreement with our results, with the exception of Ne^+ on Mo.

We believe that the evidence presented in this paper shows that the method of sputtering is a valid way to measure the secondary electron ejection coefficient in the kinetic ejection region. This method has the advantage that it allows measurements of γ to be made on those materials that are difficult or perhaps impossible to investigate using the flashing or heating technique. By allowing investigation of more ion-metal combinations further information can be made available which may lead to a better understanding of the mechanism of the kinetic ejection of electrons from solids.

ACKNOWLEDGMENTS

The authors would like to thank P. Mahadevan and J. K. Layton for many interesting and informative discussions about the material in this paper.

[21] J. H. Parker, Jr., Phys. Rev. 98, 1148 (1954).

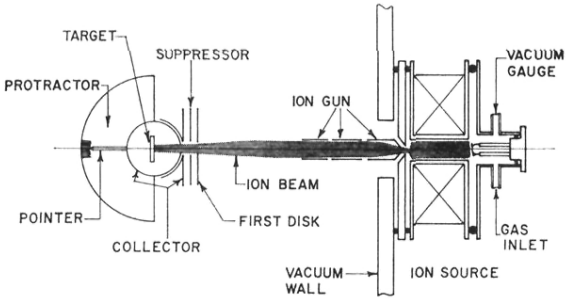

FIG. 1. Sputtering and secondary electron ejection apparatus.