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Controlled Sputtering of Metals by Low-Energy Hg Ions

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Sputtering has been studied under well controlled conditions, i.e., low gas pressure (1 micron), defined energy (up to 300 ev) and angle of incidence of the bombarding ions, and high ion-current density (10 ma/cm²), by immersing the target in a low-pressure Hg plasma of high density created in a pool-type vacuum arc.

It turned out that threshold energies (minimum ion energy for sputtering to ensue) are considerably lower under oblique than under normal incidence, and the atoms are ejected away from the direction of incidence. Thresholds were measured for twenty-three metals under normal incident Hg-ion bombardment. They follow, without exception a simple law: The product of the momentum transferred at threshold from ion to target surface atom and the sound velocity of the target material is proportional to the heat of sublimation of the target material. The threshold energies to be expected accordingly in the case of rare gas ion bombardment under normal incidence are tabulated. The yield (atoms per ion) *vs* ion energy was carefully measured for the case of polycrystalline Pt. When metal single crystals were sputtered, it was discovered that atoms are preferentially ejected in the directions of closest packing, that is [110] in fcc, [111] in bcc and diamond lattice. Deposits sputtered from plane low-index surfaces of single crystals therefore form characteristic patterns. Their study reveals more details: At low ion energy, only such atoms are sputtered which have no obstructing neighbors in the way of a close-packed direction. At higher ion energy, additional atoms are set free from positions where neighbor atoms interfere. Such atoms deviate in a characteristic way from the directions of close packing. Most atoms sputtered in close-packed directions which are parallel to the surface are trapped again, causing growth of oriented hillocks. The possibility for crystal growth by sputtering was demonstrated in another experiment. Some characteristic features of the etch effects caused by sputtering are described.

The basic process in sputtering at low ion energies is one of momentum transfer. The important parameters with respect to the gas discharge are ion energy, angle of incidence, and atomic weight of ion; on the target side they are the atomic weight, the elastic constants, crystal structure and orientation, the heat of sublimation, dislocations, and surface roughness. Many details need durther clarification, and the studies are being continued.

I. INTRODUCTION

AMONG the phenomena which arise when positively charged rare gas ions bombard a solid surface, the disintegration of the target material which is known as physical sputtering is one of the least understood. This is to a major part due to the lack of reliable quantitative data collected under well-defined and simple enough experimental conditions. Interpretation of experimental results becomes difficult and unreliable when cathode sputtering is a function of tube geometry or gas pressure, as is the case in the glow discharge. Such parameters as geometry and pressure are not of a basic nature. Besides, the functional connection of discharge current and voltage with those parameters which are of basic interest, such as energy and angle of incidence of the bombarding ions, in such cases is complicated and not well known.

These problems had been realized for quite some time, and the first important step forward was to study sputtering at pressures (1 micron or less) where the mean free path of sputtered atoms becomes comparable to or larger than the tube dimensions. All problems concerned with the diffusion of sputtered atoms, particularly the return of sputtered material back to the target, were thus eliminated. The next step was to create conditions for a well-defined energy of the bombarding ions. Sputtering then became independent of gas pressure and tube geometry. Such conditions were achieved in two principal ways: (1) Monoenergetic ion beams extracted from a highly ionized gas were accelerated in vacuo towards the target. (2) The target was immersed in a low-pressure plasma of such a high density that the thickness of the fall region was small compared to the mean free path of the ions, and collisions in the Langmuir sheath became negligibly small.

The first method has the advantage that secondary electrons released under the influence of the bombarding ions can be collected and measured, and used for determining the correct ion current, and the angle of incidence can be controlled. A basic disadvantage, however, is that ion beams in high vacuum are limited to low current densities, because of the large space-charge effects of ions. High ion-current density is not only desirable because measurable amounts should be sputtered in reasonable time, but also because sputtering has to overcome the formation of chemisorbed impurity layers on the target surface if such measurements are to yield reliable results. Unless extremely pure discharge conditions are maintained in the tube (impurity pressures of 10^{-9} mm Hg or less) and the targets are of very pure material (diffusion of impurities to the surface), the second method should be superior and more reliable.

Many experimental results must be reviewed in the light of the discovery of Fetz[1] that the angle of incidence of the bombarding ions is an important parameter in sputtering, especially at low ion energies. When the target is small compared to the thickness of the ion sheath, as is the case with targets in form of thin wires, the angle of incidence is undetermined and many ions strike the wire obliquely. The measurement of yield

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[1] H. Fetz, Z. Physik 119, 590 (1942).

or threshold under such conditions[2,3] (undetermined angle of incidence) has no great value.

Below 500-ev ion energy, the only useful quantitative yield data besides those of Fetz[1] (Mo sputtered by 150-ev Hg ions) are those of Guentherschulze and Meyer, and of Penning and Moubis. Guentherschulze and Meyer[4] immersed a large target in a low-pressure plasma of high density (normal incidence) and measured the sputtering rate of Ag and Cu bombarded by A^+ ions of 300-ev energy and Ne^+ ions of 150- and 450-ev energy, and in another paper[5] they published results on the sputtering rate of 16 metals under Hg-ion bombardment of energies as low as 500 ev. Penning and Moubis[6] measured the sputtering yield of cathode targets (Al, Cu, Ni, Ag) bombarded with A^+ ions of energies as low as 400 ev with a method in which a high plasma density at low gas pressure was achieved in an unsupported discharge by means of a magnetic field.

Even fewer data are available on another important value in sputtering, the minimum ion energy necessary for sputtering to ensue, called the threshold energy. The difficulty here is to detect the extremely small amounts of material sputtered near threshold. Sputtered atoms from clean metal surfaces are usually emitted uncharged and this eliminates the possibility of detecting these atoms directly by electrical means. Threshold measurements fortunately require only the determination of relative values of yields as function of the ion energy. Thresholds are sensitive to the angle of incidence of the bombarding ions, even more than the yield, hence measurements in glow discharges or with thin wire targets are not of much help. Bradley[7] measured sputtering thresholds of very pure K and Na under rare gas ion bombardment with an ion beam method. The surface ionization on a hot Pt surface was used in this study for detecting the extremely small amounts of sputtered material. Unfortunately, this method is limited to materials with very low ionization potentials. Wehner and Medicus[8] measured threshold and relative yield at ion energies between 30 and 200 ev for Pt sputtered by Xe ions. In this case the sputtered material was detected and measured by observing the change of the electronic work function of a tungsten probe, as it becomes covered with sputtered Pt.

With the limited number of reliable experimental data available, it becomes difficult to judge the value of any theory in this field. One aim of the studies to be described was to improve this situation, especially in the region of low ion energies.

The Hg discharge with pool cathode offers the most convenient way of creating a low-pressure plasma of high density in a demountable tube. For this reason our present measurements have been confined to Hg-ion bombardment. Conclusive evidence can be given that sputtering at low ion energies is essentially a momentum transfer process, and that thresholds are much lower under oblique than under normal incidence. The thresholds of twenty-three metals measured under normal incident Hg-ion bombardment follow an empirical law, which shows that besides the atomic weights of ion and target atoms, the heat of sublimation of the target material and its elastic constants are determining factors in sputtering. When metal single crystals were sputtered, it was discovered that the metal atoms are preferably ejected in the direction of closely packed atoms. This result provides an explanation for the fact that crystal structure and crystal orientation are important parameters in sputtering. The yield of Pt under normal incident Hg-ion bombardment was measured under carefully controlled conditions. Finally, attention was devoted to the interesting etch effects caused by low-energy ion bombardment.

Earlier results of others in the field of sputtering, as well as part of this work, are discussed by the author in a review article.[9]

II. METHODS AND APPARATUS

The most important requirements for reliable results may be once more summarized: (1) Mean free path of sputtered atoms should be larger than tube dimensions. (2) The ion energy should be well defined. (3) The angle of incidence of the ions must also be well defined. (4) The density of the bombarding ion current should be large enough so that sputtering can overcome the formation of impurity layers.

Such conditions can be achieved when the target is immersed like a large Langmuir probe in a low-pressure plasma of high density. Such a plasma can be created in a vacuum arc discharge between a thermionic or pool type cathode and an anode. The tube should be demountable so that targets can easily be exchanged, collectors for sputtered material be replaced, deposits from tube walls be removed, etc. The advantages of a Hg pool cathode discharge are striking: No difficulties with gas cleanup, gas pressure control by bath temperature, direct connection between Hg diffusion pump and tube without cooling trap, plus the advantage of being ready for operation without the necessity of processing the cathode. Some modifications of the tube previously used by Fetz[1] are advantageous: The plasma density can be considerably increased without drawing uncomfortably high discharge currents by inserting a properly designed fine mesh grid between anode and cathode. This grid completely separates an anode-space from a cathode space. The discharge reacts

[2] K. H. Kingdon and I. Langmuir, Phys. Rev. **22**, 148 (1923).
[3] The Research Staff of the General Electric Company, London, Phil. Mag. **45**, 98 (1923).
[4] A. Guentherschulze and K. Meyer, Z. Physik **62**, 607 (1930).
[5] K. Meyer and A. Guentherschulze, Z. Physik **71**, 279 (1931).
[6] F. M. Penning and J. H. Moubis, Proc. Acad. Sci. Amsterdam **43**, 41 (1940).
[7] R. Bradley, Phys. Rev. **93**, 719 (1954).
[8] G. Wehner and G. Medicus, J. Appl. Phys. **25**, 698 (1954).
[9] Gottfried K. Wehner, in *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. 7.

to the grid obstruction with a higher voltage drop. Fetz[10] showed that in this case an electrical double layer is formed in and near the grid holes, and every electron reaching this layer from the cathode side is accelerated toward the anode space. These faster "beam electrons" are more efficient in ionizing, and consequently the plasma density in the anode space is much higher than in the cathode space or than it would be in a gridless discharge with the same current. The velocity of the beam electrons, which is equivalent to the increase in voltage drop, can be controlled with the potential applied to the grid. In the present experiments this velocity usually was around 30 to 40 ev. The formation of doubly charged ions at such electron energies is still negligibly small. A further increase in plasma density can be achieved by placing the anode outside the path of the beam electrons and arranging a repeller electrode with cathode– or more negative–potential in such a manner that the beam electrons are reflected back to the plasma.[11,12] An insulating tube wall exposed to the beam electrons becomes negatively charged and performs more or less in the same way as a repeller. Repeller and grid operate at about 50 volts negative relative to anode space plasma, hence these electrodes are subject to sputtering. This however can be kept small enough as not to interfere with the measurements by selecting materials which have a low sputtering rate and a high sputtering threshold. A further increase in plasma density is possible by applying a magnetic field such that the plasma density is highest in the vicinity of the target. Plasma densities of 10^{11} to 10^{12} per cm^3 can be achieved in this way at pressures of 1 micron with discharge currents of 1 amp. The negative target inserted in the anode space plasma becomes covered with an ion sheath which represents the fall region for ions. The ion energy is equivalent to the potential applied between target and plasma. The electrical conductivity of the highly ionized plasma is so high that plasma potential and anode potential are practically identical. The ion current density is determined by the plasma density, hence can be controlled independently by the main discharge current. The ion current density $j^+=N^+ev^+$ (N^+ = density of positive ions, e = ion charge and v^+ their average random velocity), the sheath thickness d_c and the potential difference V_i between target and plasma are connected by the Langmuir-Child space-charge equation: $j^+=(2e/M_g)^{\frac{1}{2}}V_i^{\frac{3}{2}}/d_c^2$ (plane case, M_g = atomic weight of ions). When a plane target is large compared to d_c the incidence of ions is normal. The transport of sputtered material from target to collector or the tube walls in a first approximation is not disturbed by the gas. Hence the deposits can give direct information about the place of origin of the sputtered material and the angle under which this material escaped from the surface. Difficulties have sometimes been reported to arise from the influence of neutralized or positive or negative ions reflected from the target. Such particles can have sufficient kinetic energy to cause sputtering from other parts of the tube and resputtering of material from the collector. Furthermore, sputtered atoms can be reflected from the collector or other surfaces. Therefore, in these studies close attention was paid to the shadows caused by tube structures, and it was found that deposits must essentially have come from the target and from no other place, which indicates that such effects were negligibly small.

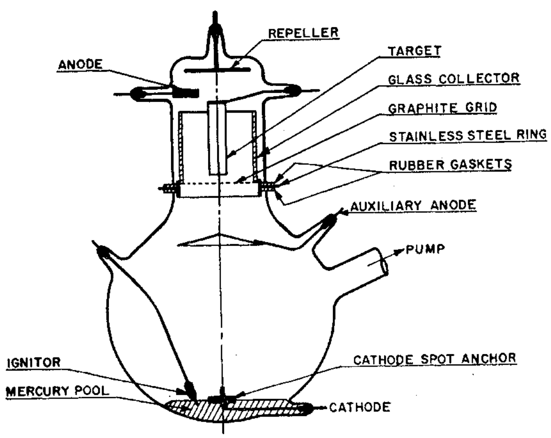


FIG. 1. Discharge tube.

Quantitative yield measurements require the correct measurement of the bombarding ion current. The target current is not equivalent to the ion current, but contains a component of electrons released under the influence of the ion bombardment, the radiation from the plasma, and thermionic action. Recent measurements by Hagstrum[13] show that the first part of this component (γ coefficient) from a clean target surface rarely exceeds 20% of the ion current and (between 10- and 1000-ev ion energy) in a first approximation is independent of ion energy and target material. The number of electrons released by plasma radiation as well as by thermionic action in the present experiments was negligibly small. The suggestion of Penning and Moubis[6] was followed to give yield data in $S/(1+\gamma)$, leaving γ, the number of electrons liberated from the target by one impinging ion (of the order 0.2), open for discussion (S = sputtered atoms per impinging ion).

Details of the tube are shown in Fig. 1. The lower half of the tube with the separating ring is immersed in a water bath of 17°C, which corresponds to a gas pressure of about 1 micron. An auxiliary discharge with a current of 3 amp maintains the anchored cathode spot. The graphite grid (0.4 mm thick, 6 holes per cm of 1.3 mm diam), with a potential in the vicinity of the cathode potential, controls the one-amp main discharge

[10] H. Fetz, Ann. Physik **37**, 1 (1940).
[11] G. Wehner, Ann. Physik **41**, 501 (1942).
[12] G. Wehner, J. Appl. Phys. **22**, 761 (1951).
[13] H. D. Hagstrum, Phys. Rev. **96**, 325 (1954).

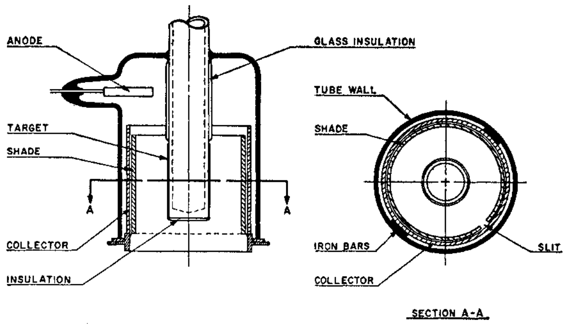


FIG. 2. Arrangement for yield measurements.

to an over-all voltage drop of around 50 volts. The repeller is connected with the cathode, and the potential of the target with respect to anode determines the energy of the bombarding ions. At ion current densities of the order 10 ma/cm^2 and ion energies of 100 ev, the thickness of the ion sheath is about 0.2 mm. The gas kinetic mean free path of Hg atoms in this discharge ($\approx$200°C gas temperature) is of the order 2 to 3 cm, the mean free path of sputtered atoms and of the bombarding ions being probably somewhat larger. Surprisingly, no difficulties were encountered with materials which are known to amalgamate. It was only necessary to bring the target and collector to a temperature of several hundred degrees Centigrade in order to evaporate the mercury so rapidly (this is probably enhanced under ion bombardment) that even on gold and silver surfaces no traces of Hg are detectable, provided these materials are removed from the tube when still at elevated temperature.

In many cases such as when low melting materials or the temperature influence on sputtering are investigated, it is desirable to control the target temperature. This was done by connecting the target with good thermal contact to a closed-end Kovar tube, the temperature of which can be controlled from the outside. Figure 2 shows an arrangement where the target cylinder is slipped over such a Kovar tube. This arrangement was used for measuring sputtering yields.

The amount of sputtered material was measured in the following ways: The cylindrical target, as shown in Fig. 2, is in the center of a cylindrical opaque shade which has a slit 3 mm wide parallel to its axis. A glass cylinder surrounding this shade collects the material sputtered through the slit. By magnetically rotating this cylinder, many successive exposures can be made without opening the tube. A photocell outside the tube receives light from the discharge through the slit and indicates the amount of material deposited in front of the slit. It was found that the discharge is not noticeably affected by changes of the target potential; hence, at least up to 200 ev, the light output is independent of the energy of the bombarding ions. The yield in arbitrary units can then be measured as a function of the ion energy by determining the time which is necessary at different ion energies to reduce the indicated light by a certain fixed amount. Initial surface layers are sputtered off before a series of measurements is started. The absolute values are determined by fitting this yield curve at some points to the absolute values, obtained in the conventional way by measuring the weight loss of the target. In order to minimize in this case the influence of surface layers it is necessary to sputter so much material that sputtering becomes proportional to the sputtering time. The same method was used for the investigation of such parameters which cause changes in the light output such as current density, target temperature, etc.

It is highly improbable that several ion impacts act together in sputtering an atom out of the surface because the density of arriving ions is much too small or the time intervals between impacts on one surface atom are much too long (at 1 ma/cm^2, a surface atom receives about 6 impacts per second). The sputtering yields (atoms per ion) should therefore be independent of the ion current density, and this fact provides an excellent possibility of checking the reliability of such measurements.

III. RESULTS

(a) Oblique and Normal Incidence

A somewhat puzzling phenomenon is observed when a target with sharp edges is subject to sputtering. Most material is removed not from the edges proper, but in a region a little more inside. When a metal sheet is sputtered in a uniform plasma, a small strip of material is finally separated from the sheet along the edges. The photograph in Fig. 3 shows how sputtering has most heavily eaten away material somewhat separate from the corner of the sheet (finally causing a hole). The grooves give the impression that the sheet has been sandblasted from all sides under grazing incidence.

The preferential attack could be due to the distribution of the ion current density near the sheet edge. The field lines in the ion sheath as sketched in Fig. 4 become curved near a sharp edge. The heavy ions cannot follow curved field lines very well and therefore become focused to a region somewhat away from the edge. The following experiment shows that in addition to this

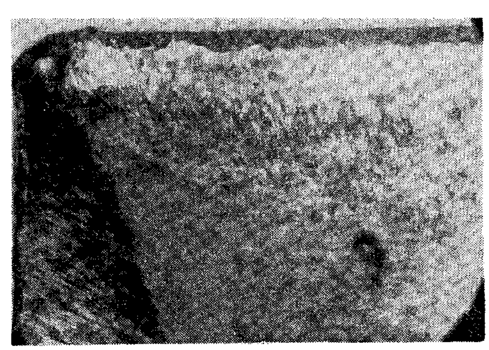


FIG. 3. Corner of metal sheet after sputtering treatment.

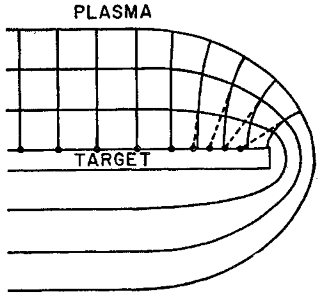


FIG. 4. Sketch of bombardment conditions near sheet edge.

effect the difference in angle of incidence between edge and flat portion of the target has a marked influence. The polycrystalline metal strip for this purpose, as shown in Fig. 1, was mounted along the axis of a glass cylinder on which the sputtered material was collected. The surprising result of this experiment—when performed at low ion energies—is, as published previously in a Letter to the Editor,[14] that four separate deposits can be distinguished and hardly any material appears opposite the flat areas of the target. In order to ascertain the areas from which these deposits were ejected, the experiment was repeated with a metal strip which was protected on one side along one edge [upper right in Fig. 5(b)] from sputtering by painting that area with aquadag. The result was that the opposite (upper left) deposit disappeared. This indicates that the deposit was ejected from a seam along the right edge in a direction inclined to the target surface. This suggests that momentum must have been transferred from the obliquely incident ions to the sputtered atoms.

Increasing the ion energy and at the same time adjusting the plasma density such that the form and thickness of the ion sheath remain the same ($j^+ \propto N^+ \propto V_i^{\frac{3}{2}}$) brings the maxima of the two deposits closer together. Finally they merge together opposite the flat sides of the target. Obviously, at low ion energy sputtering under oblique incidence is much more efficient and the large middle portion of the target, being under normal incident bombardment, contributes but little to the deposits. At higher ion energy (several hundred ev), the difference between normal and oblique incidence becomes less pronounced. The results indicate a threshold energy for sputtering which is markedly lower under oblique than under normal incidence. When the same experiment is repeated with different target materials it turns out that the ion energy necessary to fill the portion between the two deposits, i.e., to start sputtering from the middle portion i.e., to overcome the threshold for normal incidence, is different for different materials.

It should be mentioned that deviations arise when the surface grains of the target have a preferred crystal orientation. In this case, as will be described later, the material is sputtered in a direction which is determined in addition by the crystal structure and orientation. It can be assumed that the lowest possible threshold would exist in the case of grazing incidence.

Further evidence for these conditions is obtained when a fine mesh grid, adjacent on one side to a plasma, is bombarded with ions from one side only. When grid holes and wires are much smaller than the ion sheath thickness, then the ions bombard essentially in a direction normal to the grid plane, as shown in Fig. 6, and strike the grid wires partially tangentially. Under these conditions the grid wires are sputtered in a direction away from the plasma and sputtering starts at very low ion energies. Actually a Mo grid sputtered in this way showed considerable sputtering away from the plasma at ion energies as low as 20 ev, while deposits on a collector on the plasma side did not appear before the ion energy was raised to about 80 ev.

The conclusions to be drawn from these experiments may be summarized as follows: Earlier results of Fetz,[1] who found that at low ion energy, sputtering is more efficient under oblique incidence, are confirmed. In addition, it is shown that thresholds are considerably lower under oblique bombardment than under normal incidence. Momentum is transferred from ions to sputtered atoms in such a way that atoms are ejected preferably in a direction away from the direction of incidence. These results indicate that sputtering at low ion energy is definitely not an evaporation process. Conditions seem to become different at higher ion energies insofar as the difference between normal and oblique incidence becomes less pronounced. This is in agreement with results of Seeliger and Sommermeyer,[15] who found that sputtering with ion energies of 5000 to 10 000 ev is independent of the angle of incidence and that the sputtered material in this case is distributed according to the cosine law.

(b) Threshold Energies for Normal Incidence

With a cylindrical target large compared to the ion sheath thickness, the incidence of ions becomes essenti-

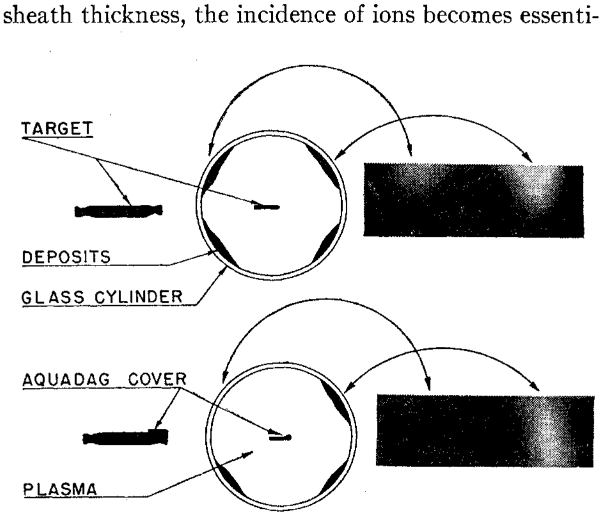


FIG. 5. Sputtering from metal strip indicating momentum transfer.

[14] G. Wehner, J. Appl. Phys. 25, 270 (1954).

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

ally normal. Thresholds under determined angle of incidence are much easier to interpret than yields because they describe only the optimum and most favorable impact conditions. Surface roughness, preferred orientation of surface grains, density of grain boundaries or dislocations on the surface, surface layers partially protecting the bulk material—all these factors are important for the yield, but not so much for the threshold. This can be demonstrated by comparing sputtering from a target which is in form of a solid sheet with a target which is prepared by cold pressing a powder of the same material. The yield in the second case is considerably lower, mostly due to the large surface roughness which causes the sputtered atoms to be trapped, but the threshold remains essentially the same. Hence, the thresholds of materials which were only available in powder form could be investigated by supporting them on a base metal with high threshold, as for instance Zr.

The thresholds for 23 metals under normal incident Hg-ion bombardment and at target temperatures around 300°C were measured with the setup of Fig. 2 in the following simplified procedure: First the surface layers were sputtered off; then, after rotating the collector by one step, the target was sputtered for 10 minutes with 200-ev ions; then for 10 minutes again with 190-ev ions, etc., so that finally a succession of deposits was obtained which showed how much material was sputtered in 10-minute intervals at ion energies which were varied in 10-ev steps. The deposits naturally became weaker at lower ion energy, but then, below a certain ion energy which varied for different metals, they disappeared completely. These experiments, repeated with 30-minute exposure time (instead of ten minutes) show essentially the same minimum ion energy. In order to secure enough nuclei for the adsorption of sputtered atoms on the collector, and to prove that this observed disappearance of deposits was not caused by a rapid decrease of the accommodation coefficient with decreasing density of arriving atoms,[16] the collector in another experiment was first uniformly covered with a thin transparent metal layer. The mini-

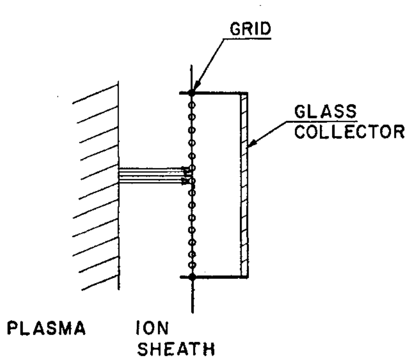


Fig. 6. Sputtering of fine mesh grid.

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

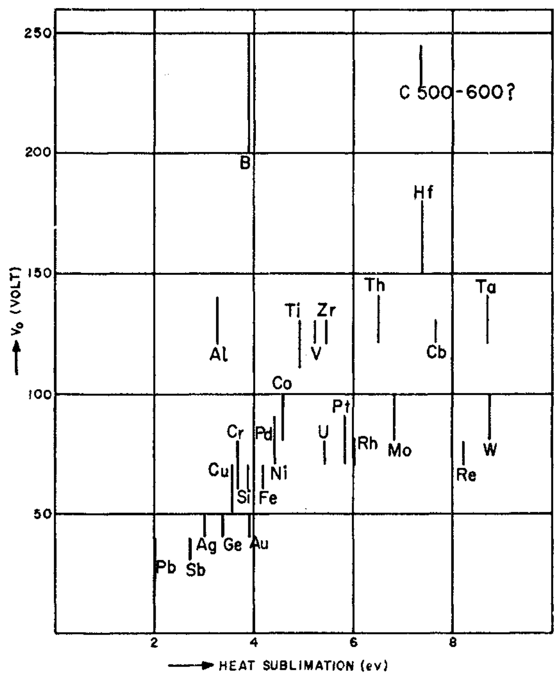


Fig. 7. Threshold energies for normal incident Hg-ion bombardment *vs* heat of sublimation.

mum ion energy still remained the same.[17] It therefore seems justifiable to identify this energy with the threshold energy for normal incidence.

These thresholds, determined to lie within the indicated limits, are plotted *vs* the heat of sublimation of these materials[18] in Fig. 7. They are consideably higher than previously determined under more oblique incidence,[2] but of the same magnitude as determined for the case $Pt-Xe^{+}$ under normal incidence.[8]

The first step in an attempt to fit these experimental values into an empirical law was to plot the energy transferred at threshold to a target atom *vs* the heat of sublimation, under the assumption of central elastic impacts between free elastic spheres. Figure 8 shows that, although some tendency for proportionality seems to exist, no simple relationship is obtained. Figure 9 shows a plot of the momentum transferred in a central elastic impact *vs* the heat of sublimation. Two things were noticed in this diagram: (1) The numerical value of the velocities with which the momentum values have to be multiplied in order to convert them into the corresponding heat of sublimation is of the order of magnitude of the sound velocity in metals. (2) Metals with a high sound velocity tend to be found at the lower

[17] Ditchburn (reference 16) has shown that the accommodation coefficient is unity and essentially independent of the density of striking atoms as soon as the collector is in a plasma and under ion bombardment.

[18] L. Brewer, in *Chemistry and Metallurgy of Miscellaneous Materials Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1950), National Nuclear Energy Series, Plutonium Project Record, Vol. 19B, Div. IV, p. 13.

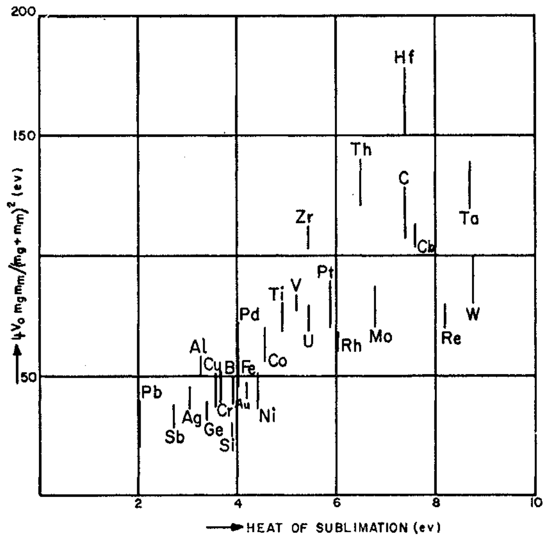


FIG. 8. Energy transferred at threshold to a target atom *vs* heat of sublimation.

right and those with small sound velocity at the upper left side of the diagram. Finally, the surprising result shown in Fig. 10 and previously reported in a Letter[19] is that all values line up nicely along a straight line when the momentum transferred at threshold is multiplied by the bulk sound velocity[20] of the metals and these values are plotted *vs* the heat of sublimation.

The significance of the sound velocity is obviously to introduce the elastic constants of the target material, which determine what part of the transferred energy with the momentum directed toward the inside arrives at the surface with the momentum vector pointing to the outside. This part has to be at least equal to the binding energy of a surface atom before sputtering ensues. With the dimensionless proportionality factor of 11.2, obtained from Fig. 10, the empirical law for thresholds V_0 under normal incidence is

$$V_0=\left(\frac{1.7\times10^5(M_g+M_m)\phi}{M_g^{\frac{1}{2}}M_m v_s}\right)^2,$$

where V_0 is in ev, M_g=atomic weight of ion, M_m=atomic weight of metal, v_s=bulk sound velocity of metal in cm/sec, and ϕ=heat of sublimation of metal in kcal/mole. The influence of the sound velocity is rather pronounced. If W, for instance, were to have the sound velocity of Pb, a threshold energy of 550 ev against a measured 90 ev would be calculated. This law applied for electrons bombarding a metal surface would yield threshold energies of 10^6 to 10^7 ev. Measurements on graphite, a material with pronounced anisotropy of the elastic constants seem to indicate that thresholds are determined by $(v_s)_{\max}$. Unfortunately measurements with graphite are somewhat obscured by a kind of chemical sputtering[21] (the origin and cause of which has not yet been determined), which is superimposed and active down to very low ion energies (10 ev). The threshold of boron (200 to 250 ev) indicates a bulk sound velocity for this material of 14×10^5 cm/sec (between Si and diamond) a value which seems not unreasonable.

These threshold measurements allow no decision if the potential energy which becomes available when the ion is neutralized can contribute under favorable conditions to sputtering. With $(V_i'-W)$ of the order 5 ev (V_i'=ionization potential of gas, W=electronic work function) this effect, if present, would be well within the measuring error. A contribution of this potential energy to sputtering would be difficult to understand because the generally accepted view is that the ion becomes neutralized before actually reaching the surface and $(V_i'-W)$ in an Auger-type transition is transferred to a conduction electron.[22]

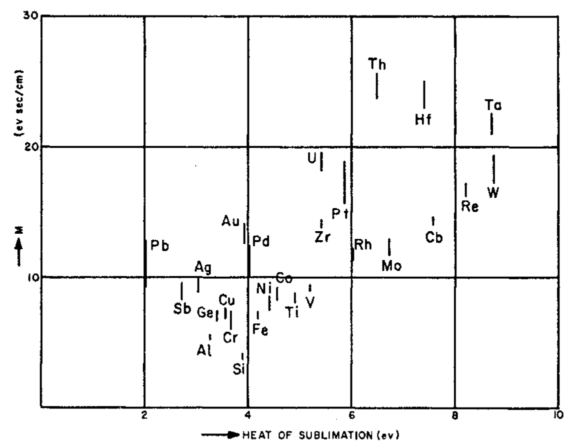


FIG. 9. Momentum transferred at threshold to a target atom *vs* heat of sublimation.

There is reason to believe that the threshold law is of a general nature and applicable to other ion-metal combinations as well. Measurements in other gases, however, have to be made before this can be considered to be established. The plots of yield *vs* ion energy [see Sec. III(c)] show that the minimum energy is not very well defined because the curves show a tendency to taper off towards the abscissa rather than cut it clearly. This is not surprising since a surface always contains many atoms which are in a condition of weaker binding or higher surface free energy, such as at dislocations, at grain boundaries, or in corner, step, or kink positions where atoms have less neighbors than in a filled plane.

Threshold energies for some common metals under normal incident rare gas ion bombardment to be expected according to this threshold law—with some

[19] G. Wehner, Phys. Rev. **93**, 633 (1954).
[20] W. Koester, FIAT Rev. Ger. Sci. 1939 **31**, 46 (1950).
[21] A. Guentherschulze, Z. Physik **36**, 563 (1926).
[22] H. D. Hagstrum, Phys. Rev. 96, 336 (1954).

arbitrariness in definition, as mentioned—are given in Table I.

An interesting consequence of the dependence on the sound velocity occurs with iron: The threshold should be higher with higher target temperature because Fe shows a pronounced decrease of the sound velocity with increasing temperature. Measurements on a heated iron target show that this indeed is the case. The threshold of 65 ev at 300°C increases to around 120 ev at 700°C. Here we have the rather unusual situation that sputtering above and near threshold decreases with increasing target temperature.

(c) Sputtering Yield

With the gas discharge part well controlled and better understood, emphasis can now be shifted more to the solid state side of the problem. The decrease in yield with increasing surface roughness (trapping of sputtered material) was demonstrated with targets which were cold pressed from powder. The microscopic inspection (see later) of sputtered polycrystalline targets shows that grain boundaries, dislocations, etc., are in general more readily attacked than undisturbed regions. The different rate of attack of different grains in a polycrystalline target shows the influence of the crystal orientation. A survey of published experimental results shows that body-centered cubic metals seem to have generally a lower sputtering rate than face-centered cubic crystals. Therefore one has to also expect the crystal structure to come into play. The lower sputtering rate of chemisorbed surface layers such as oxides, etc., is well known and can most strikingly be demonstrated with materials which are known to form strongly bound oxide layers, such as Al, Zr, Ti, Th, Ta, U, etc. Such materials may be under ion bombardment for a long time without major signs of sputtering; then quite suddenly, after the original surface layers are removed, sputtering of the bulk material sets in and heavy deposits are formed in a short time. Unless very pure discharge conditions are maintained and the deposition of impurities from the gas, as well as diffusion of impurities to the surface from inside the target, are so small that sputtering can overcome the continuous formation of such layers, a large influence of target temperature and ion current density on the yield is to be expected.

Attention should be paid to these errors which may sometimes arise: A silver surface, for instance, after sputtering treatment was found to be densely covered with a pelt of fine needles, all of equal height. It turned out that in preparing the surface by grinding and mechanical polishing, small insulating particles had become imbedded in the surface and had protected the underlying material from sputtering. Hence mechanical polishing with abrasives should be avoided, and the last step in preparing a surface should be turning with a diamond tool or electrolytical polishing. Another source of error may arise from little tinsels created when material peels off the collector, the tube walls, or other electrodes. These tinsels eventually

TABLE I. Threshold energies in ev for normal incidence as predicted from the threshold law.

Ion / Metal	He	Ne	A	Kr	Xe	Hg	Hg (measured)
Al	127	59	59	77	100	136	120–140
Si	60	27	27	35	45	61	60– 70
Ti	262	90	76	82	97	123	110–130
V	305	103	86	88	102	128	120–130
Cr	156	53	42	44	51	64	60– 80
Fe	205	66	53	53	61	75	60– 70
Co	282	89	69	69	79	96	80–100
Ni	266	85	66	66	75	92	70– 90
Cu	244	75	57	56	62	74	50– 70
Ge	225	66	49	45	48	57	40– 50
Zr	645	177	122	104	107	120	120–130
Cb	776	212	146	123	126	142	120–130
Mo	410	110	76	63	64	72	80–100
Rh	384	102	69	56	56	62	70– 80
Pd	324	85	57	46	46	50	50– 80
Ag	275	72	48	39	38	43	40– 50
Sb	157	40	26	20	20	23	30– 40
Hf	1897	450	272	187	167	163	150–180
Ta	1620	385	233	159	142	138	120–140
W	1037	245	147	100	89	87	80–100
Re	825	194	117	80	71	69	70– 80
Pt	850	198	118	79	69	67	70– 90
Au	590	138	82	56	51	46	40– 50
Pb	336	78	46	31	26	25	20– 40
Th	1980	452	262	170	143	133	120–140
U	1195	274	158	100	85	78	70– 80

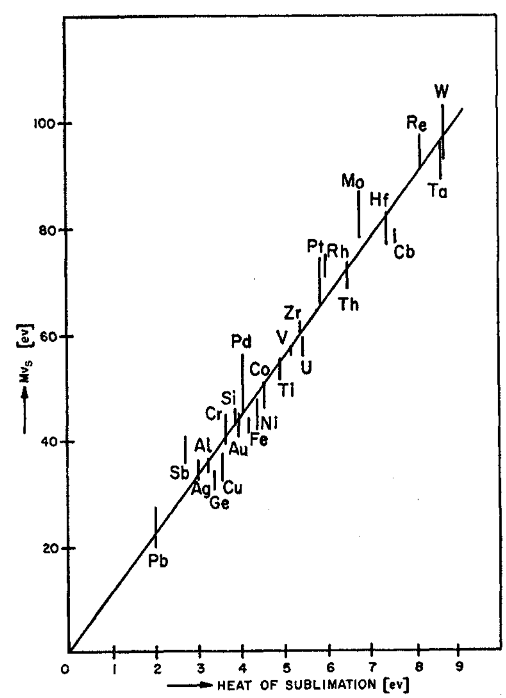


FIG. 10. Product of momentum and sound velocity of the target material *vs* heat of sublimation.

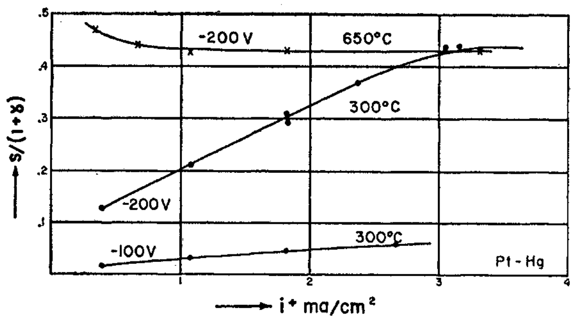


FIG. 11. Yield *vs* ion current density for Pt bombarded with Hg ions.

settle down on the target and are then cold-welded to the surface by deposits of sputtered material.

With the many parameters involved, it is not surprising that yield data reported by different authors show considerable discrepancies. In many cases insufficient information on target conditions and surface preparation is provided. Furthermore, yield measurements should always include a check as to whether the yield is independent of the ion current density, and within certain limits of the target temperature.

The knowledge of yield data for polycrystalline materials is not only of considerable practical interest, but in addition much useful information on the basic process of sputtering will certainly be derived therefrom as soon as a sufficiently large number of reliable and well-defined data will be available. This, however, has not been accomplished yet, and has been postponed in favor of single-crystal investigations which at present promised more immediate results of basic interest.

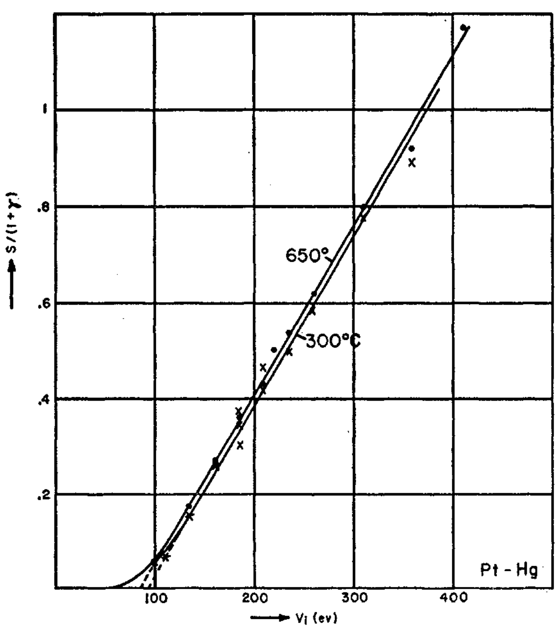


FIG. 12. Yield *vs* ion energy for Pt-Hg.

Thus far, only the yield of polycrystalline Pt under normal incident Hg-ion bombardment has been carefully measured. The extension of these measurements to other materials under controlled variation of the said parameters is planned in the near future.

Figure 11 shows the yield $S/(1+\gamma)$ of Pt *vs* the ion current density at 100-ev and 200-ev ion energy, the latter curve measured at 300°C and at 650°C. The curves show that the yield becomes independent of ion current density only above 3 ma/cm^2 and then reaches the same value obtained at 650°C, here being practically constant over the whole current density range. This result suggests strongly that either a protecting Hg film (adsorption of Hg from the vapor) or impurity layers are formed on the surface unless the target temperature or the ion current density are above certain critical values. Recent measurements of Fetz and Schiefer[23]

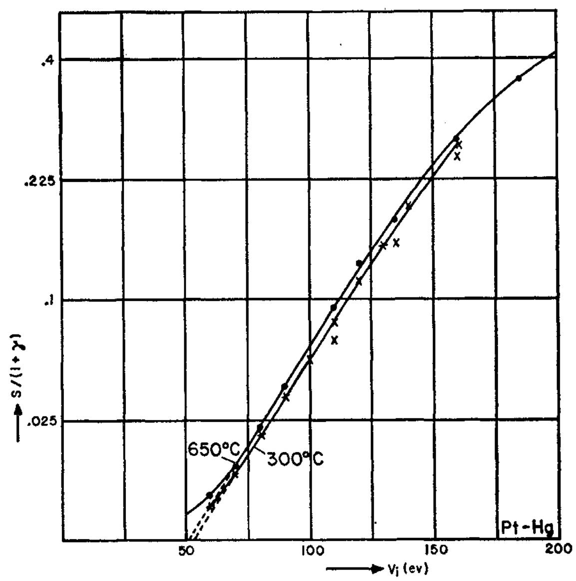


FIG. 13. Yield *vs* ion energy for Pt-Hg near threshold.

seem to give support to the first explanation, because their studies indicate that the strong temperature dependence observed in Hg at low ion current density (0.5 ma/cm^2) and most pronounced in the case of Pt-sputtering seems to disappear in the case of A^+ bombardment.

The yield $S/(1+\gamma)$ *vs* ion energy for target temperatures of 300°C and 650°C is plotted in Fig. 12. The difference between the two target temperatures is small and within the range of possible errors. This proves that Hg contamination of the target surface cannot have played a major role. $S/(1+\gamma)$ turns out to be roughly proportional to (V_i-V_0) with $V_0\approx 90$ ev. The yield of unity is reached at 380 ev as compared to a value of 500 ev measured for the same combination by Guentherschulze and Mayer.[5] The region near threshold

[23] H. Fetz and Schiefer (private communication).

where the yield tapers off towards the abscissa was measured in more detail and the result is plotted in Fig. 13. Here the relationship is better described as $[S/(1+\gamma)]^{\frac{1}{2}}$ proportional to $(V_i - V_0')$, where V_0' is about 50 ev. The same relationship with $V_0' = 40$ ev was found to hold near threshold by Wehner and Medicus[8] for the case $Pt-Xe^+$. The threshold which was determined with the simplified procedure and used in the threshold law as described above was 70 to 90 ev, that is, between the values V_0 and V_0' and closer to V_0.

At present, with the limited number of reliable yield data collected so far, and with the many solid state parameters which are involved in the case of polycrystalline targets, it is not yet possible to draw many useful conclusions on the basic process. It looked more promising to simplify conditions further by sputtering from metal single crystals.

(d) Ejection of Atoms from Single Crystals

It is surprising that systematic studies of sputtering of monocrystals apparently never have been made. The etch effects observed on sputtered polycrystalline targets, the momentum transfer results, as well as the fact that the elastic constants are involved in the threshold law, led to the belief that interesting results should be expected in the case of well-controlled low-ion-energy sputtering of monocrystals.

The first indication of an interesting new phenomenon was obtained when a tungsten single-crystal wire (so called Pintsch wire), mounted along the axis of a cylindrical glass collector, was sputtered. The sputtered deposit was not uniform, but made up of patches which were arranged in a pattern which is closely related to the crystal orientation. In another experiment, material sputtered from tungsten single-crystal balls (1-mm diam, 150-ev Hg ions) was deposited on a glass collector plate 1 cm away. In this case, patterns were obtained which resemble electron field emission patterns (Fig. 14). The difference from evaporation can simply be demonstrated by changing the polarity of the ball so that it is heated up under electron bombardment to a high temperature. Then the evaporated deposit shows not the slightest indication of a pattern, but follows more or less the expected cosine law.

Better adapted experimental conditions were obtained when a ring zone of a single crystal rod instead of a thin wire or little ball is sputtered. With the crystal orientation determined by x-ray methods, it turned out that in the case of fcc Ag and Cu the deposited patches corresponded to the [110] axes of the crystal. One might be inclined to believe that every patch contains material from a certain zone of the monocrystal surface. This however is not the case, as was shown by protecting different zones of the crystal surface from sputtering by painting with aquadag. A certain patch disappeared completely only when the whole area of the target visible from the patch was covered. This indicated that every patch contained material from all over the crystal side facing the patch, and the sputtered atoms must have been ejected at angles to the surface which were different at different regions of the circumference of the target rod. Another important result was that the patterns do not change with the developemnt of etch patterns on the surface; in fact, the deposit patterns were independent of the surface configuration, provided, of course, that distorted surface layers were already removed.

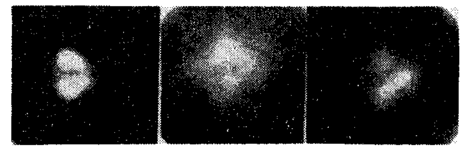


FIG. 14. Deposits obtained when W single-crystal balls were sputtered.

The direction in which atoms are ejected can most conveniently be studied when plane surfaces of low index (carefully machined and then electrolytically polished) are sputtered. The material sputtered from a small area (3-mm diam) of such planes was collected on a glass plate 1 cm distant and the simple characteristic patterns obtained in this case show clearly the directions of ejection. Figure 15, for instance, shows the patterns obtained from a {111} surface of a Ag (fcc) single crystal. The model of the atom arrangement is shown in the lower half of Fig. 15. The sticks mark the [110] directions, which are the directions of closest packed atoms. The patches in the threefold symmetrical pattern correspond to the three [110] directions pointing out of the surface. An indication of the six [110] directions which are in the surface plane is obtained when the

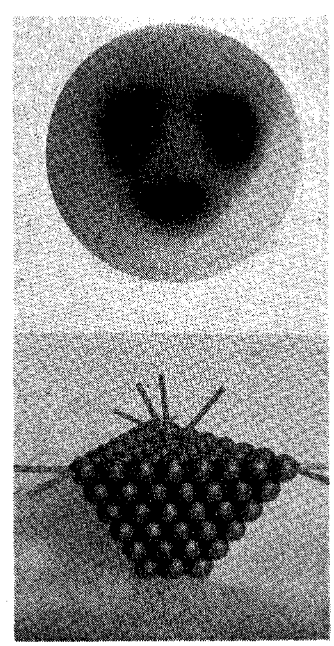


FIG. 15. Deposits obtained when a {111} silver plane is sputtered with 100-ev Hg ions.

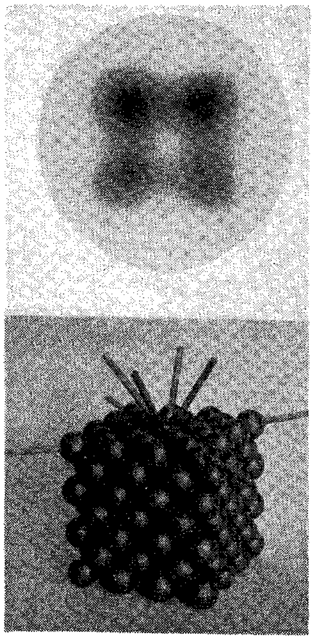


FIG. 16. Deposits obtained when a {100} silver plane is sputtered with 100-ev Hg ions.

collector is a glass cylinder surrounding the target with the cylinder axis normal to the {111} plane. The indication of these directions is rather weak because most of the sputtered atoms are trapped and not able to clear the surface. Figure 16 shows the fourfold symmetrical pattern obtained from a {100} Ag surface. Again the patches correspond to the four close-packed directions. Figure 17 shows the case of a {110} Ag surface. The central spot of the twofold symmetrical pattern corresponds to the close-packed direction normal to the surface. Identical results are found in the case of Cu.

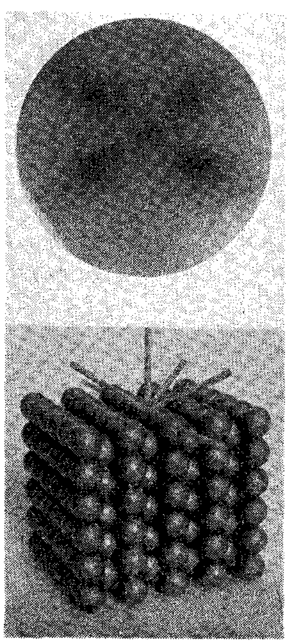


FIG. 17. Deposits obtained when a {110} silver plane is sputtered with 50-ev Hg ions.

In bcc crystals—thus far W, Mo, and α-Fe have been investigated—the direction of preferred ejection is again the direction of closest packing, which is in this case [111]. Figure 18, for instance, shows the pattern obtained from a {110} surface of α-Fe with two spots corresponding to the two [111] directions which project out of the surface and enclose an angle of 70°32′. The rather astonishing fact is that the contribution of directions of second-nearest neighbors, that is [100], although their distance is only 15% more than that of closest neighbors, is at 150 ev still negligibly small.

With Ge the diamond lattice was studied and it was again found that atoms are sputtered in the close-packed directions, that is, [111]. In this case, however, it should be noted that a single inside atom finds closest-packed neighbors only in four of the eight [111] directions (coordination number 4, against 8 in bcc crystals).

Of much interest are the changes these patterns undergo at different ion energies. On silver the three low-index planes {111}, {100}, and {110} were studied at ion energies of 50, 100, and 150 ev. It should be emphasized that it is much easier to visualize the following considerations on ball models of the corresponding surfaces than to describe them.

The largest changes were observed in the pattern of the {110} plane. At very low ion energy (40 ev), the center spot tends to disappear. Obviously, sputtering in the [110] direction normal to the surface requires a full 180° change of the direction of the original momentum, while the four other spots require less and hence become predominant near threshold. These latter spots are so well defined and their angle of ejection agrees so well with the corresponding [110] directions, that one must conclude that these atoms were not obstructed by neighbor atoms and cannot have been ejected from a filled plane nor from positions in a half lattice step (a position which is peculiar to a {110} plane) but only from more open positions such as from corners or kinks in a full lattice step as well as from filled full lattice steps which are parallel to a [100] direction. Atoms in these positions have only four nearest neighbors. This conclusion is further supported by the observation that the long axes of the oval spots in Fig. 17 do not point to the center of the pattern, but are inclined more toward the two [210] directions on both sides of the center [110] axis. The model surface shows that atoms can deviate from the four [110] axes in direction to these two [210] axes because no neighbors interfere here; deviation in direction to the two [221] axes on the other sides of the center [110], however, is not possible because such atoms would run into repulsive forces of interfering neighbors. Figure 19, a pattern obtained from a {111} plane at 100 ev shows these deviations still more pronouncedly, with a tendency toward two bands being formed which

indicate strong deflection in direction to the two [210] axes. Atoms which would preferably be deflected in this way are those ejected from half-steps (six nearest neighbors) which are parallel to a [100] axis in the surface. This pattern shows further that the center spot now becomes very predominant and is remarkably well defined. It can be concluded that atoms responsible for this spot come either from the more numerous positions in a half-step (six nearest neighbors) or the still more numerous positions in a filled plane (seven nearest neighbors).

Conditions are much simpler when a {100} fcc plane is sputtered. The pattern shows, in this case, hardly any change with ion energy. The pattern is very sensitive to small deviations in angle (only a few degrees) from the exact plane. Those [110] directions which make a somewhat smaller angle with the normal to the surface always come out much stronger. This cannot be caused by the difference in directional change of the original momentum because then the opposite spots should be more pronounced. This is another strong indication that atoms are not ejected from a filled plane (eight nearest neighbors) but from step positions. Such steps on surfaces which are slightly inclined against a low-index plane are always open in the direction in which the target surface is inclined against the low-index surface; hence the deposits from those [110] directions which are closer to the surface-normal become predominant. Atoms which are most readily sputtered beside those on top of filled planes (four nearest neighbors) are those from step corners or kinks in steps (five nearest neighbors) and from such filled steps which run in a [100] direction (six nearest neighbors). Sputtering from filled steps which run in a [110] direction (seven nearest neighbors) may account for the weak deposits (Fig. 16) that connect the four [110] spots, because atoms coming from such positions must have been deflected in such directions by obstructing neighbors.

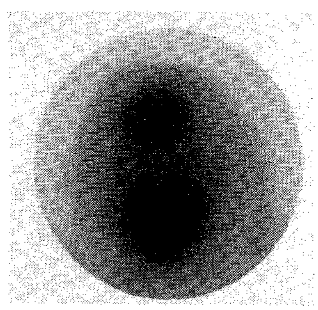


FIG. 18. Deposits obtained when a {110} α-iron plane is sputtered with 150-ev Hg ions.

Accordingly one has to conclude that in sputtering from the {111} Ag plane no atoms are ejected from a filled plane (nine nearest neighbors) at ion energies below 150 ev because no deflection of atoms in a direction to the center of the pattern which should take place in this case, is observed. Corner or kink atoms on steps (five and six nearest neighbors respectively) can be ejected unobstructedly and can be "accidentally" deflected in directions which account for the observed broadening of the three [110] spots in a circular direction (Fig. 15). Atoms can as well be ejected from filled steps which are parallel to [110] directions (seven nearest neighbors) but open in direction to the [110] axes nearest to the center [111] (in the model of Fig. 15, for instance, open to the rear side). Atoms from filled steps parallel to [110] but open in direction to the [100] axes nearest to the center [111] (open to the front side of the model) run into obstructing neighbors and should, as the model shows, be deflected in such directions as to fill the circle in between the three [110] spots. Figure 20 shows that this is actually the case when the ion energy is raised to 150 ev.

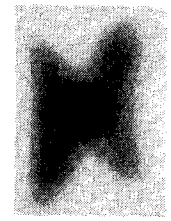


FIG. 19. Deposits obtained when a {110} silver plane is sputtered with 100-ev Hg ions

The conclusions which can be drawn from these ejection studies may be summarized as follows: (1) Atoms are preferably ejected in the directions of closest packing. Ejection in directions of second nearest neighbors, even in the bcc lattice, is negligibly small at ion energies below 150 ev. (2) At very low ion energy (near threshold) those close-packed directions which require less directional change of the original momentum are more pronounced. This result checks with the observation that atoms sputtered from polycrystalline material under oblique bombardment are ejected in a direction away from the direction of incidence. (3) At very low ion energy, only such atoms are sputtered which have a close-packed direction for ejection available which is not obstructed by neighbor atoms such as from positions on top of a filled plane, in corners, kinks in steps, or certain filled steps. (4) At higher ion energy, additional atoms are freed from the more numerous positions where neighbor atoms interfere with the close-packed directions. The obstructing atoms cause deflections and characteristic changes in these patterns. (5) Atoms sputtered in close-packed directions which are parallel to the target surface are mostly trapped and not able to clear the surface. (6) The bombardment of a surface with Hg ions of energies below 150 ev seems not to cause serious distortions in a surface layer; otherwise the patterns could not come

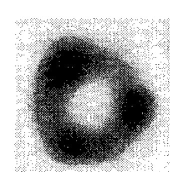


FIG. 20. Deposits obtained when a {111} silver plane is sputtered with 150 ev.

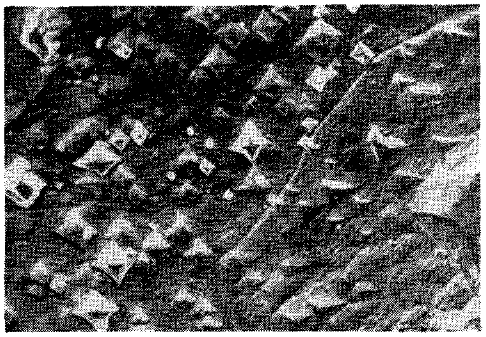


FIG. 21. Micrograph of polycrystalline Pt surface after sputtering with 150-ev Hg ions shows etch hillocks.

out as clearly as they actually do. (7) At least for the case of Ag, which was studied in more detail, one has to assume that the atoms in the ejection process behave remarkably similar to closely packed rather hard spheres. (8) The number of directions in which an unobstructed atom can be sputtered is proportional to the coordination number, that is, twelve in fcc and hcp, eight in bcc, and four in the diamond lattice. This must be of immediate consequence for the sputtering yield (not, however, for the threshold) and it provides an explanation for the observation that sputtering seems to decrease in the order fcc, bcc, and diamond lattice.[5]

The fact that the patterns to a first approximation are independent of the surface contours, especially of the etch patterns which developed on the surface after prolonged sputtering, provides a simple and reliable method for studying surface distortions and later, after such layers have been sputtered off, for roughly determining crystal structure and orientation of single crystals. For this purpose the crystal, whatever shape it may have, is immersed in the plasma and bombarded from all sides with low-energy ions. The sputtered material is collected on a surrounding glass cylinder. By replacing this cylinder after suitable time intervals, one can study the changes taking place when surface layers are removed and study the depth to which the deformation of the surface extends. Finally, when sputtering has proceeded to the undistorted bulk material, the patterns remain unchanged and the patches indicate the closely packed directions.

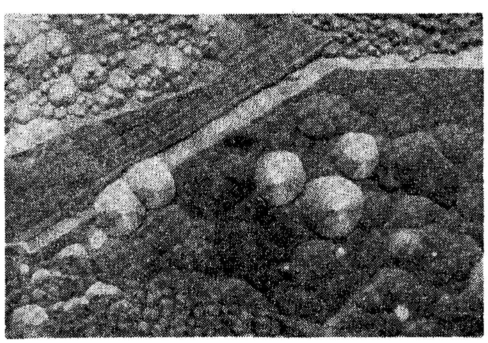


FIG. 22. Micrograph of polycrystalline Si surface after sputtering with 150-ev Hg ions shows etch pits.

(e) Etch Effects

Etch effects caused by sputtering have been observed long ago and were the subject of several investigations. All these studies, however, were made in the glow discharge, that is, under undetermined ion energy and angle of incidence, with part of the sputtered material returning back to the target. Under these conditions naturally the results were rather complex and seldom reproducible. Feitknecht,[24] as early as 1924, was well aware of this and pointed out the need for better controlled low-pressure studies. But this never seems to have been done, although the field of surface physics in the meantime has attracted enormous attention.

The microscopic inspection of polycrystalline surfaces after bombardment under normal incidence with Hg ions of 100 to 300-ev energy (≈ 10 ma/cm^2, target temperatures 100 to 200°C) shows several pronounced effects: Crystallites with different orientation are attacked at different rates. Grain boundaries are generally sputtered at a higher rate and appear as furrows. The opposite effect (grain boundaries elevated) was observed on a silver specimen which before had been oxidized heavily in air at higher temperature. This was obviously due to the lower rate of attack of silver oxide which had been formed preferably at the grain boundaries. Twin boundaries are attacked at the same rate as the crystallites. Grains often show oriented pits or hillocks. Their form and orientation is characteristic for the grain orientation. Figure 21, for instance, shows a Pt surface with threefold symmetrical hillocks at the right side of the picture, indicating a crystallite with a {111} plane parallel to the surface, and fourfold symmetrical hillocks at the left side indicating a grain with a {100} plane parallel to the surface. In many cases a layer structure appears on the surface. Figure 22 shows a polycrystalline Si surface with characteristic conical

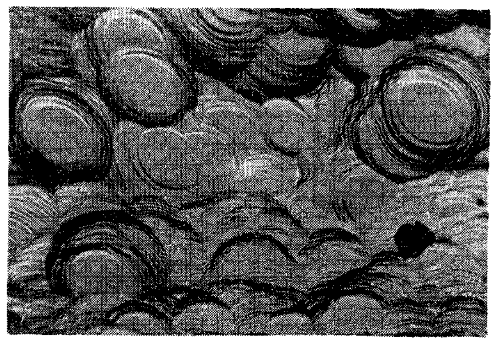


FIG. 23. Micrograph of {110} plane of silver single crystal rod after sputtering with 150-ev Hg ions shows etch pits.

[24] W. Feitknecht, Helv. Chim. Acta 7, 825 (1924).

pits, often arranged in clusters, which developed after sputtering. The appearance of sputtered surfaces closely resembles in many cases those obtained with certain chemical etchants.

Studies which go beyond these more general observations are better accomplished by sputtering single crystals with known orientation. A silver single-crystal rod, which had an orientation such that the rod axis almost coincided with a [211] axis, so that the rod surface contained two low-index planes, the {110} and the {111}, was sputtered from all sides. The inspection of the rod showed that the surface everywhere tends to develop {110} facets. Figure 23, obtained after sputtering with 150-ev Hg ions, shows the region of a {110} plane with pits in a layer structure which have the twofold symmetry to be expected. The long axis of the oval pits points in the surface direction [110]. This result is in agreement with the conclusion which was drawn from the ejection studies from a {110} plane: atoms from filled half-steps which are parallel to a [100] direction are easier to sputter than from filled half-steps which run in a [110] direction. At higher ion energy the difference between these two directions becomes less pronounced and the ovals assume a more circular shape. Figure 24 (125 ev) shows the {111} surface of the same rod with pronounced threefold symmetrical hillocks which have {110} facet planes. It is suspected that these hillocks are the result of crystal growth rather than etching. The {111} plane has six close-packed directions parallel to its surface; consequently, much material will be sputtered and trapped again, thereby being shifted back and forth in the surface. This process proceeds with a higher probability for those atoms which are in positions with higher surface free energy and those atoms which are in positions of perfect order have less probability of being resputtered. It is not quite clear yet why certain places are preferred for developing either pits on the {110} plane or hillocks on the {111} plane. It is possible that dislocations may play an important role here. Hillocks may as well develop underneath protecting insulating particles. It was observed, for instance, that electropolished targets show less tendency for hillock development than untreated surfaces.

Also of interest was the different rate of removal of material from different planes of this silver single-crystal rod. For this purpose the decrease of the rod diameter was measured as function of the cross-section angle after the rod had been sputtered from all sides for a long time. It turned out that the least amount of material is removed from the region where a {110} plane is parallel to the target surface (at 150 ev about 0.5 atom per ion). The rate of removal increases as the surface-normal becomes divergent from the [110] axes, and is highest in the vicinity of the {111} plane (at 150 ev about 0.8 atom per ion). The difference in sputtering yield of different planes tends to decrease

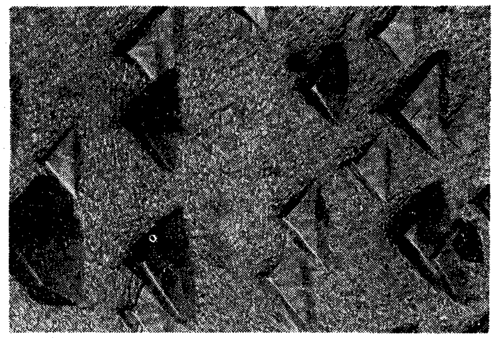


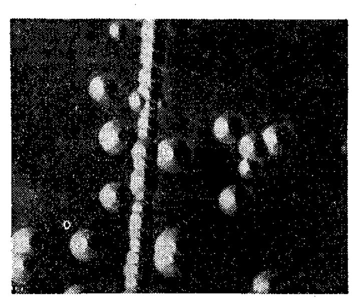
FIG. 24. Micrograph of {111} plane of silver single crystal rod after sputtering with 125-ev Hg ions shows etch hillocks.

with increasing amount of material removed. It seems to be higher at lower ion energies.

Essentially similar results are obtained in the case of a Cu single crystal. In bcc α-Fe, the inspection of the surface after sputtering shows that here the {100} facets tend to develop. It seems that those planes which have the most open structure or the least number of nearest neighbors (fcc: {110}, bcc: {100}), especially when they become inclined against the target surface, are preferentially attacked and therefore developed.

The influence which dislocations may play in sputtering was demonstrated in Ge targets. Figure 25 shows the surface of a Ge target after sputtering at 150 ev. Of special interest in this sample was a line of pits which developed after the sputtering treatment. The picture, even in details, resembles so closely a micrograph published by Vogel *et al.*[25] obtained on a Ge surface after treatment with CP-4 etchant, that no doubt can exist that the features brought out here are the same. Vogel[26] could prove that the row of pits indicates a lineage boundary, separating two crystals which are slightly tilted against each other but have a common crystal axis normal to the surface. The conical pits develop on those places on the surface where edge dislocations emerge. These places are regions of higher surface free energy; consequently they are more easily attacked in sputtering as well as with certain chemical etchants. It is interesting to see that under oblique bombardment (target edge in Fig. 26) the deepest point in these pits is displaced in the direction away

FIG. 25. Micrograph of germanium single-crystal surface after sputtering with 150-ev Hg ions shows etch pits and a lineage boundary.



[25] Vogel, Pfann, Corey, and Thomas, Phys. Rev. **90**, 489 (1953).
[26] F. L. Vogel, Acta Metallurgica **3**, 245 (1955).

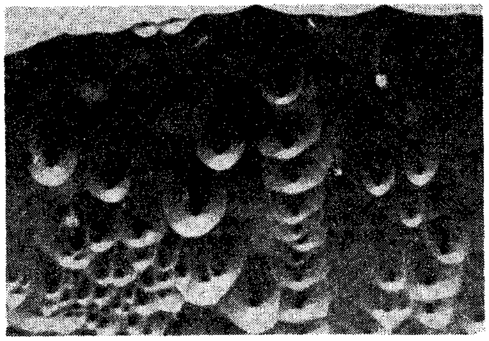


FIG. 26. Micrograph of the edge of a Ge single crystal target after sputtering with 150-ev Hg ions shows etch pits.

from the direction of incidence. This probably is due to the difference in angle of incidence of the ions on the sides near and away from the direction of incidence as well as to the effect of material being sputtered from the near side and ejected in such a direction that it is trapped and deposited on the opposite side.

An experiment was performed in order to prove that crystal growth by sputtering, suspected to be responsible for the development of hillocks in a fcc {111} plane (Fig. 24), is actually possible. For this purpose a W single-crystal wire was arranged on the axis of a polycrystalline W cylinder and both were sputtered at the same time. With the wire at -70 ev and the cylinder at -400 ev relative to plasma, the rate at which W atoms were deposited on the wire surface was slightly higher than the rate at which atoms are sputtered from the wire. Under these conditions the single crystal grew as a single crystal, and in about 40 hours time the diameter of the wire was increased from 0.3 mm to 0.7 mm. When, however, the wire is not under ion bombardment, the W atoms are deposited without relationship to the underlying single crystal and no single crystal growth is observed. The ion bombardment obviously is important because it helps to keep the surface free of impurities and such atoms which are in positions of perfect order are less likely to be resputtered than others. The possibility that bombardment-enhanced surface migration plays an important part cannot be excluded.

Etching by sputtering seems to have some definite advantages over chemical, electrolytical, or thermal etching. The method is equally well adopted for different metals and with the two parameters, ion energy and target temperature, the process and in particular the energy transferred to the surface can be well controlled. The results collected so far are still rather sketchy and preliminary, but they at least indicate that much useful information not only in relation to the basic process but more generally in such fields as surface physics, metallography, and crystallography, can be obtained. In particular, controlled sputtering promises to become a new tool in crystal growth and dislocation studies.

IV. CONCLUSIONS

From the experimental results, although they were limited to Hg-ion bombardment, it can be concluded that the basic process in sputtering at low ion energy (less than 300 ev) is most likely as follows: In the first step the ion, already neutralized a few angstrom units away from the surface, collides with one or several surface atoms and transfers momentum and kinetic energy. The important parameters which thus come into play are: the kinetic energy of the ion, the angle of incidence, and the atomic weights of ion and target atom. The second part of the process takes place inside the target and is concerned with the transport of energy and momentum. The momentum vector pointing to the inside of the target has to be reversed in direction in order to account for sputtering. A shock wave is initiated from the place of impact, the energy most efficiently travels along closely packed atom rows, and a small part of the original energy with momentum now pointing to the outside finally arrives at the surface. The important parameter in this stage is the sound velocity or the related elastic constants of the target material. The third stage is concerned with the separation of atoms from the surface and their escape. A surface atom—not necessarily the one which got the original impact—received an energy pulse from one of its close neighbors underneath. When this energy is sufficient to overcome the binding energy of the atom, and furthrmore when the atom is not obstructed by neighbor atoms in the direction in which it received the impact and is not trapped again on surface protrusions, it is sputtered. The important parameters which come into play in this stage are the heat of sublimation, the number of atoms in positions of weaker bond (grain boundaries, dislocations), the crystal structure and orientation—because they determine the number of possible directions for ejection—and the surface roughness.

At higher ion energy the process is probably different. With the formation of interstitial atoms and (neutralized) ions forced into the lattice, the process is probably better described in terms of evaporation from a localized region near the place of impact (von Hippel)[27] or radiation damage (Keywell).[28]

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[27] A. v. Hippel, Ann. Physik **81**, 1043 (1926).
[28] F. Keywell, Phys. Rev. **87**, 160 (1952), and Phys. Rev. **97**, 1611 (1955).

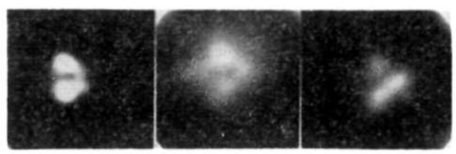

FIG. 14. Deposits obtained when W single-crystal balls were sputtered.

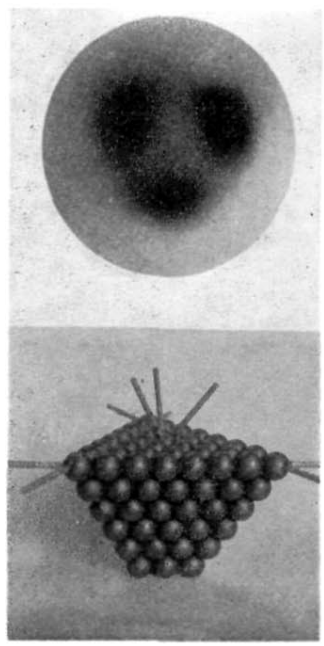

FIG. 15. Deposits obtained when a {111} silver plane is sputtered with 100-ev Hg ions.

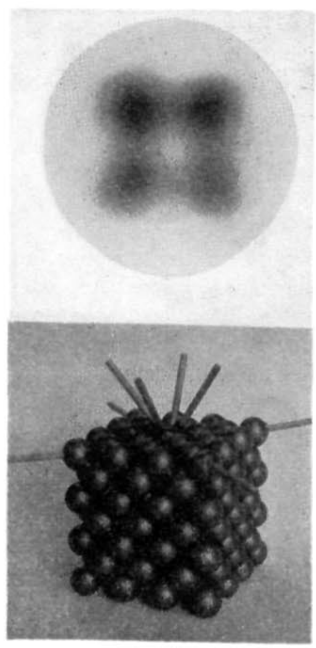

FIG. 16. Deposits obtained when a {100} silver plane is sputtered with 100-ev Hg ions.

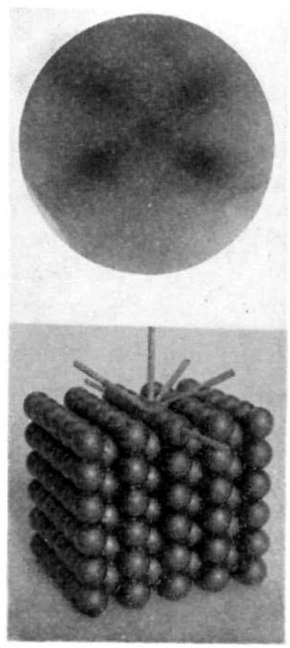

FIG. 17. Deposits obtained when a {110} silver plane is sputtered with 50-ev Hg ions.

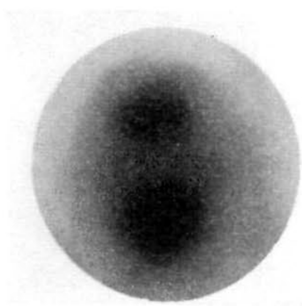

FIG. 18. Deposits obtained when a {110} α-iron plane is sputtered with 150-ev Hg ions.

FIG. 19. Deposits obtained when a {110} silver plane is sputtered with 100-ev Hg ions

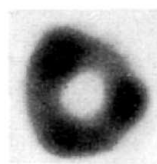

FIG. 20. Deposits obtained when a {111} silver plane is sputtered with 150 ev.

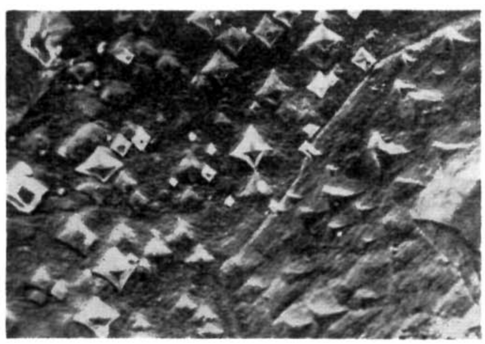

FIG. 21. Micrograph of polycrystalline Pt surface after sputtering with 150-ev Hg ions shows etch hillocks.

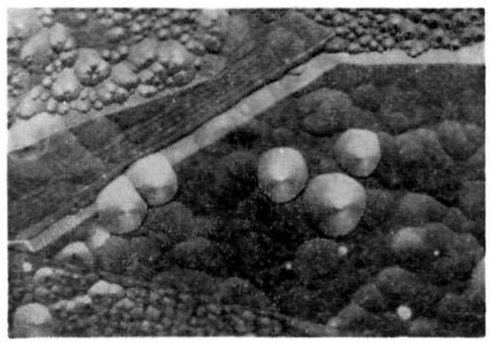

FIG. 22. Micrograph of polycrystalline Si surface after sputtering with 150-ev Hg ions shows etch pits.

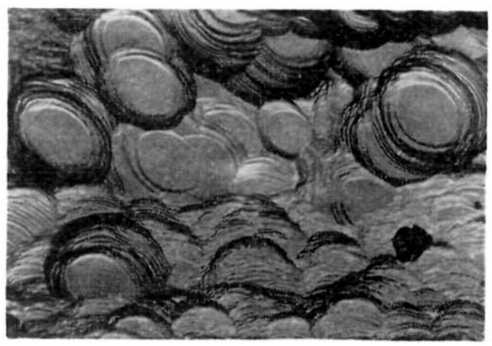

Fig. 23. Micrograph of {110} plane of silver single crystal rod after sputtering with 150-ev Hg ions shows etch pits.

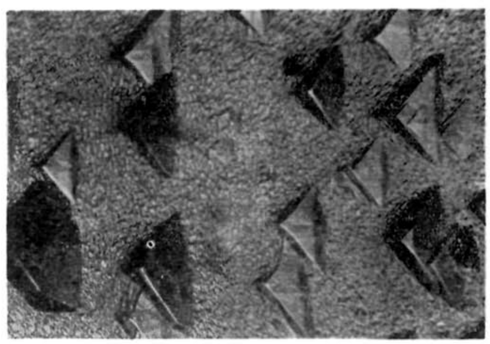

FIG. 24. Micrograph of {111} plane of silver single crystal rod after sputtering with 125-ev Hg ions shows etch hillocks.

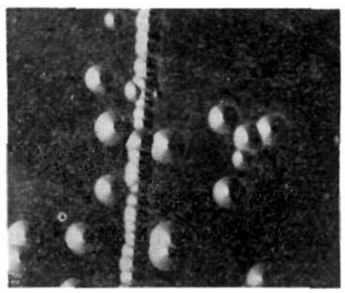

FIG. 25. Micrograph of germanium single-crystal surface after sputtering with 150-ev Hg ions shows etch pits and a lineage boundary.

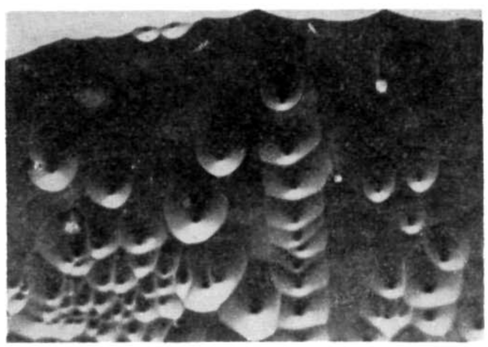

FIG. 26. Micrograph of the edge of a Ge single crystal target after sputtering with 150-ev Hg ions shows etch pits.

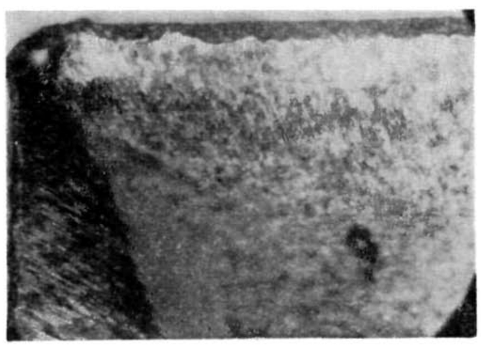

FIG. 3. Corner of metal sheet after sputtering treatment.

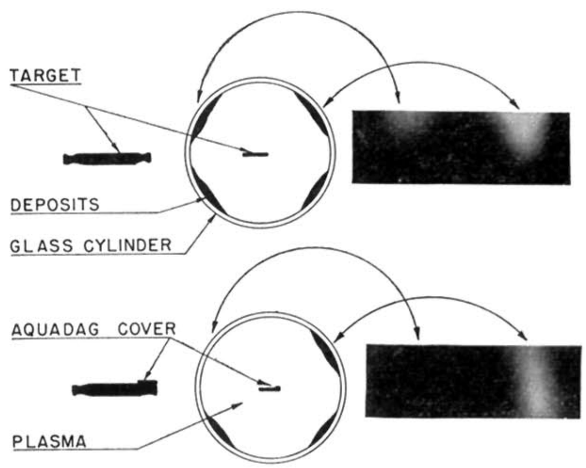

FIG. 5. Sputtering from metal strip indicating momentum transfer.