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Sputtering by Ion Bombardment

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I. INTRODUCTION AND SURVEY

Among the many phenomena which arise when ions strike a solid surface, the disintegration of the material, known as sputtering, is probably one of the least understood. The main reason for this is the lack of reliable quantitative yield data. Experiments and their interpretation are complicated because many gas discharge and solid state parameters are involved, and because sputtering is a very inefficient process. Aside from this, the sputtered atoms leave the surface uncharged, eliminating the

possibility for their electrical detection directly. Most of the earlier work was done in the glow discharge, which operates only at relatively high gas pressures. Here complications arise due to the large energy spread, the undetermined angle of incidence of the bombarding ions, and the problems connected with the diffusion of the sputtered material back to the target.

Reliable basic information on sputtering by positive ions is now being collected by either using ion beams or by immersing the target as a separate electrode into a rare gas plasma with low gas pressure. The phenomenon of surface ionization and the measurement of the change of the electronic work function of a collector for sputtered material, have been used as sensitive methods for measuring sputtered amounts. Reliable measurements, especially at low ion energies, require that sputtering must compete with the formation of surface layers (oxides, etc.). This requires either extremely pure discharge conditions or a high density of the bombarding ion current. The advantage of the latter is that large amounts of material are sputtered in a reasonable time, even at low ion energies.

Most experimental results have to be reviewed in the light of the discovery that the angle of incidence is an important and heretofore neglected parameter in sputtering. With a definite angle of incidence, it was found that a definite threshold energy is necessary for sputtering to set in, and is characteristic for every ion-metal combination. These thresholds are linked to the elastic constants of the target material (sound velocity) and to the heat of sublimation. Other interesting information comes from the study of etch-effects caused by sputtering and the investigation of sputtering from metal monocrystals.

Evidence is now definitely in favor of a momentum exchange process, and—at least at low ion energies—the “hot spot” evaporation theory must be abandoned. In recognition of the complexity of such a process, interesting studies have been made with a steel ball model.

The motivation for a better understanding of sputtering stems not only from physical interest; its practical aspects are also of considerable importance. In many gas discharge applications, sputtering is an undesired effect, as it accounts for the formation of deposits which cause poisoning of an oxide cathode or difficulties with insulation, field deformation, changes in light absorption, or secondary electron emission. The disintegration of the active layer of a thermionic cathode or of other electrodes may limit the useful life of such tubes. Etch-effects, gettering, removal of surface layers, preparation of thin layers of materials which are otherwise difficult to evaporate or to deposit, and certain crystal growth possibilities provide a wide field of useful applications.

Earlier results will be summarized and reviewed in the light of new knowledge as is necessary. This should be of benefit to those not closely engaged in our field, which promises to become of increasing interest in solid state and surface studies. The author hopes, thereby, to close a gap which lately developed in the literature. Reference may be made to articles of Mierdel (1) and Compton and Langmuir (2). Fruth (3) lists 113 references for the years 1852 to 1930. The most recent, but rather sketchy and sometimes not accurate survey of the subject is to be found in "Electronic and Ionic Impact Phenomena" by Massey and Burhop (4). Glockler and Lind (5) emphasize the electrochemical aspects of the problem.

The "Chemical Abstracts" and "Vacuum" list Cathode Sputtering in their subject index. Although much progress has been made in that the gas discharge part of the problem, by becoming fairly well understood, allows emphasis to be shifted more to the solid state problems, the main conclusion here does not differ from that of previous surveys: much more work—especially experimental—will be necessary before it can be said that the phenomenon is fully understood.

II. MEASURING METHODS

1. General

Information about sputtering depends above all on a reliable measurement of the yield S (number of released atoms per impinging ion) as a function of the parameters involved. Of special interest here is the region of low ion energies (threshold). Early recognized basic parameters are the ion energy, material to be sputtered, its surface condition and temperature, and the nature of the bombarding ions. Fairly new is the discovery that the angle of incidence of the bombarding ions and the orientation of the exposed crystal face are of importance. In the earlier glow-discharge work, these basic parameters were partly obscured by additional ones, such as gas pressure and tube geometry. A correct measurement of the bombarding ion current necessary for absolute yield data requires that allowance be made for the contribution of secondary electrons released by ion bombardment.

The number of sputtered atoms is usually determined by measuring either loss in weight of the target or increase in weight of a collector. The disadvantage of the first method is that initial surface layers, which in some cases are much more resistant to sputtering (most pronounced for oxidized Al, Th, Ta, etc.) and thereby protect the underlying bulk material, cannot be separated. This difficulty can be avoided in the second method by inserting a shutter which is opened under vacuum not before

such layers are sputtered off. In particular, the second method is based on the assumption that nearly every sputtered atom which reaches the collector or other surface sticks to it. From high vacuum evaporation, one knows that this is only the case above a minimum striking density, which is a function of the temperature and the chemical and physical properties of the collecting surface. The temperature below which singly arriving metal atoms, which have no chance of cluster formation, stick to a surface is much lower than the evaporation temperature (e.g., Cu: 350–575°C; Mg, Cd, Zn: –183 to –78°C) (6). Normally in sputtering experiments the density of atoms arriving at a collector is low, especially at low ion energies, and unless the collector is cooled, it may assume in the discharge a temperature which well exceeds these critical values. Fortunately, however, conditions are quite different as soon as a gas discharge is present. Ditchburn (7) could show that a slow ion bombardment, which automatically takes place on insulated surfaces which are exposed to a plasma (a current density $j = j^+ + j^- = 0$ can only be achieved by an insulating surface when it acquires a net negative charge), eliminates such difficulties, provided of course that no normal evaporation and no resputtering takes place. So it is advisable not to use an electrode with positive fall, such as a small anode, as collector and detector. The ion bombardment lacking in this case may well lead to errors.

Difficulties may at times arise from the influence of neutralized or positive or negative ions which are reflected from the target (4, 8). Such particles may have a considerable kinetic energy and, aside from complications in the interpretation of sputtering results, cause sputtering from other parts of the tube and resputtering of material from the collector. Although certain anomalies of the distribution of sputtered deposits behind apertures have been attributed to this effect (9–11), investigations under low gas pressure show that deposits must have come essentially from the target and no other place (shadows!), indicating that this effect is probably negligible in most cases (12). It is advisable, however, always to pay attention to the distribution of deposits, especially in the case of $M_m > M_o$ (atomic weight of the target material and of the ion, respectively) and to make sure that at higher ion energies this effect does not play a major role.

In order to assure any degree of reliability, the following questions have to be answered: (1) How well is the ion energy determined (this includes suppressing of discharge oscillations and doubly charged ions)? (2) How well have the initial surface layers been removed, and is the formation of new impurity layers during sputtering suppressed? (3) What is the angle of incidence? In the following pages we try to give a critical review of the more important measuring methods.

2. The Glow Discharge

The earliest and simplest way of observing sputtering (from the cathode) was in the glow discharge (abnormal glow), which operates well if the pressure region is of the order of from 0.1 mm to a pressure of several cm Hg. Although this discharge has furnished a wealth of qualitative data and is still widely used for practical applications, it is not suited for collecting basic reliable quantitative data. There are several reasons for this.

The first is that, with the mean free path of sputtered atoms $\lambda_m < d$ (λ_m = mean free path of sputtered atoms, p = gas pressure, and d = distance between cathode and collector), the transport of the sputtered material is a diffusion problem (13-16), and part of the sputtered material is reflected back to the cathode (17-19). How serious this influence can be was shown by von Hippel (15), who calculated that in a plane arrangement with the collector at a distance $d = d_c$ (d_c = thickness of the cathode fall region) at 0.1 mm gas pressure, the amount of material diffusing back to the cathode is of the order of 90%. The rate of loss of material from the cathode is then the difference between sputtering and rediffusion rate. The returned material may be deposited in a peculiar form (dust (10), cones (20)) and change the surface configuration and the yield in an unpredictable manner. The sputtered atoms may become charged in the discharge and their transport may be different from normal diffusion (11), or they may have such high velocities that their mean free path is considerably different from the mean free path of gas atoms (19).

A second reason is that with the mean free path of the ions $\lambda_i < d_c$ (λ_i = mean free path of ions), hence with collisions and the formation of new ions within the fall region, the ion energy, V_i , and the angle of incidence are rather uncertain. The possibility of formation of multiply charged ions, charge exchange, and the formation of molecular ions cannot be excluded. Of course V_i is much smaller than the cathode fall V_c (14). For instance, van Hippel (15) measured the ion current distribution, to a probe which was arranged a short distance behind a hole in the cathode, with a retarding field method, and at 0.1 mm Argon, 15 ma discharge current, and 1000 volts, he found that the average ion energy was of the order of 250 ev, with the energies spread over the whole cathode fall; most of the ions arrived at the cathode with zero kinetic energy.

On account of all this one has to deal with so many additional secondary parameters, such as gas pressure, form, size, and distances of electrodes and walls, that the interpretation of results becomes rather difficult, and their basic value rather doubtful.

Additional disadvantages of the glow discharge are that the three variables j^+ , V_c , and p cannot be changed independently of each other. The region of ion energies which can be covered is limited because the lowest cathode drops (normal glow) are fixed values, characteristic for the ion-metal combination and sensitive to the purity of the gas and the surface condition of the cathode. The current densities in the normal glow of rare gases are so small ($j^+/p^2 < 2 \times 10^{-4}$, j^+ in amp/cm²) that sputtering may not be able to compete with the formation of surface layers and it requires a long time to sputter measurable amounts. The ion current to the cathode cannot be divorced from the electron current leaving the cathode. Yield data are therefore usually given in $S/(1 + \gamma)$, leaving the actual value of γ (number of electrons liberated by one impinging ion) open for discussion (although at ion energies up to several hundred electron volts, γ of clean metal surfaces fortunately rarely exceeds 0.2 (4, 13, 21, 22)).

The reason for glow discharge popularity in sputtering experiments lies in its simplicity. With only two cold cathodes and pressures in the range of millimeters, comparatively clean conditions can be maintained and no major difficulties with gas cleanup are encountered.

An interesting alternative arrangement for measuring sputtering rates in a glow discharge without complications by diffusion effects was thought to be a method described by Guenterschulze (19). A hollow cathode completely encloses a small wire anode, which serves also as the collector. The material lost to the small anode is negligibly small, and every surface element of the cathode should receive as much material as is sputtered away. This should set up an equilibrium pressure of sputtered material, and the sputtering rate could be directly determined by measuring the weight increase of the anode. Seeliger (23) pointed out, however, that this would be only correct if the dimensions of the collector were small compared to the mean free path of the sputtered atoms. This, however, was not the case in Guenterschulze's experiments, and the data collected with this method can hardly be considered reliable. Another difficulty in such a hollow cathode arrangement is that the current density, and consequently sputtering, is generally different at different parts of the cathode, and material may be preferentially transported from one region to another (24).

Concluding this section on sputtering in the glow discharge, it must be stated that aside from uncertainties resulting from the undetermined angle of incidence, the determination of the two basically important values V_c and S is based on such strong extrapolations that quantitative results have to be judged with great caution.

3. Low Pressure Glow Discharge with Magnetic Field

A glow discharge with sufficiently high current density cannot be maintained at pressures lower than about 0.1 mm. The reason for this is that the electrons released from the cathode have such a long free path that many of them reach the anode without having a chance to ionize. Penning and Moubis (13) overcame this difficulty by applying a properly designed magnetic field, which increases the amount of ionization by lengthening the total electron path. The method can be considered as bridging the gap between $\lambda_m < d$ and $\lambda_m > d$. It offers two important

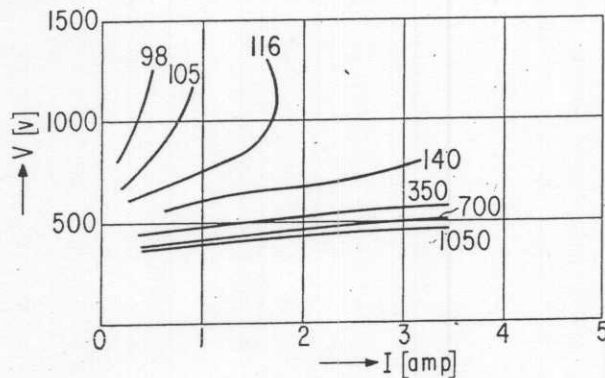


FIG. 1. Characteristics of glow discharge with magnetic field. Cu cathode, 0.014 mm argon. Parameter: magnetic field in oersteds (Penning and Moubis (13)).

advantages: the three variables V_c , j^+ , and p may be changed independently of each other (within certain limits) by varying the strength of the magnetic field, and the role of secondary electrons released from the cathode is minimized because many of them are bent back to the cathode.

The arrangement used by Penning and Moubis consisted of a tube 10 cm in diameter with a cylindrical water-cooled cathode (2 cm diam., 25 cm long) surrounded at the ends by two anode rings. The magnetic field was parallel to the cathode cylinder. The amount of sputtered material was determined by measuring the weight increase of small mica discs. Several of these could be successively exposed without opening the tube. The characteristic of the discharge and the range which could be covered (14 micron A, Cu-cathode) are shown in Fig. 1. The pressure region was found to be low enough to make the sputtering rate independent of pressure. The high ion current densities (20 ma/cm²) increase the reliability in several respects: (1) The sputtering times are rather short. It was, for instance, reported that at a voltage drop of 500 volts

