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SPUTTERING IN A GLOW DISCHARGE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

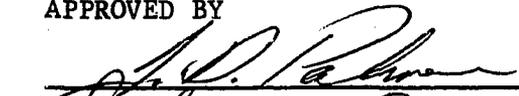
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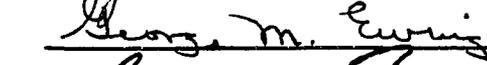
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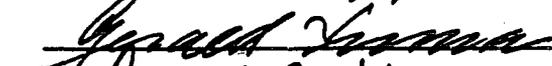
SPUTTERING IN A GLOW DISCHARGE

APPROVED BY











DISSERTATION COMMITTEE

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SPUTTERING IN A GLOW DISCHARGE

CHAPTER I

INTRODUCTION

Sputtering is the name given to the process whereby surfaces are eroded under bombardment by gas particles. The most prevalent form of sputtering is the removal of material from cathodes of electronic devices. Some of the material removed may be returned to the cathode, especially at high gas density, while other particles are deposited on nearby surfaces. The deposited material may be either the original metal or a compound of the cathode atoms combined with gases present. There are several important uses for sputtering. It is frequently used for the deposition of thin metal films (50, p. 401). It is also used for cleaning semiconductor surfaces, cleaning work prior to the evaporation of metal films, and as a getter in the evacuation of systems. The undesirable features of the process, however, are probably of greater importance. The worst feature of sputtering is the erosion, and eventual destruction, of cathodes of electronic devices. In controlled thermonuclear work, atoms sputtered from interior surfaces contaminate the plasma and have a pronounced cooling effect.

Sputtering was first observed by Grove in 1852. In the intervening years a tremendous amount of work has been devoted to study and

experimentation on this phenomenon. Most early investigators employed the medium of the glow discharge for production of sputter. The glow discharge possesses several inherent features which make it unsuitable for this purpose. The total glow phenomenon is composed of such a multiplicity of closely interrelated processes that it is extremely difficult to determine quantitatively the cause and effect of each. Also, the glow is generally operated at relatively high gas pressures. The concomitant gas density causes an appreciable portion of sputtered atoms to return to the cathode but it is difficult to determine this proportion. The combination of these circumstances made quantitative analyses of the sputtering mechanism quite difficult and the results unreliable.

Early work included formulation of theories of sputtering and study of the general characteristics of the process but a large amount of the effort went into experimental determination of net quantities of sputter produced by various gas-metal combinations. Several excellent theories of sputtering were developed. The rate of net sputtering was accurately determined for many gas-metal combinations for fixed parameters of the glow discharge, and from this data empirical formulas for the determination of amount of sputtered material were developed. A considerable portion of this research was carried out in Germany. Güntherschultze, who achieved many of his results in the decade of the nineteen twenties, is probably the outstanding name in this effort.

Much of the earlier work had been accomplished before the state-of-the-art permitted dependable, precise results being obtained. Some of the factors which plagued earlier workers were: poor vacuum pumps and systems; lack of appreciation of the importance of materials purity and

inadequate techniques for obtaining the requisite purity; and inadequate potential sources. In many cases these factors made the results of experiments totally undependable. Often a mere trace of a residual gas in the operating gas, or a gas layer on the surface of an electrode can cause results which are quite different from those obtained when pure gases and atomically clean electrodes are used. The erroneous results obtained for individual processes, when applied to the cumulative actions taking place in a discharge, frequently led to misinterpretations. For example, Townsend originally postulated that the supply of electrons in a self-sustaining discharge was replenished by ionizing collisions of the positive ions traveling towards the cathode. Later investigation showed that the discharge fields were totally inadequate to provide the energy required by positive ions before they could ionize a neutral atom.

Modern sputter research is conducted in low pressure environments. Under this condition no sputtered atoms are returned to the cathode because of striking gas atoms. Also, isolated sources, such as discharge plasmas or Kunsman filaments, of sputtering ions are utilized. This method permits the density and energy of the ion beam to be carefully controlled. In addition to the two above factors, modern techniques for vacuum and high potential creation and control and for insuring materials purity, have enabled operators to secure extremely reliable data. The result is that dependable data is now available on the gross yield of sputtered atoms as a function of ion energy for many combinations of gases and metals. The outstanding investigations of sputter in recent years have been conducted by Wehner. His data are now considered the standard in the field.

Modern laboratory techniques have also been employed in study of all the processes which combine to create a glow discharge, with the result that improved data is now available on these processes.

Since the advent of improved techniques for conducting sputter studies, very little interest has been evident in the old problem of sputtering in the glow discharge. It is believed that modern advances in knowledge of sputtering, coupled with modern data on the individual processes occurring in the glow, could be employed to obtain a reasonably accurate analysis of the mechanism of sputtering in the glow discharge. This is the purpose of the present program: to obtain a quantitative expression for sputter by utilizing modern data in the analysis of sputtering in the glow discharge.

The plan of the paper is as follows. First, the glow discharge will be discussed in general terms, with emphasis being placed on the interrelation between the processes which combine to produce this phenomenon. Second, the various theories of sputtering will be described. Third, the glow discharge and related processes will be analyzed in great detail to determine which processes contribute to eventual sputtering and the degree to which each is effective. The outcome of this analysis will be an expression, or formula, for determining the quantity of sputter expected for given parameters of the discharge. Fourth, laboratory experiments will be conducted in which the loss of weight of the cathode, by sputtering in the glow discharge, will be determined. Finally, comparison of the amounts of sputter determined theoretically and experimentally will be made and evaluated.

It was originally hoped that one universal formula could be developed which would be applicable under all conditions. It was quickly

discovered, however, that different gas-metal combinations react to each different process in a manner which can be determined only by experimental data for the given process. The derivation thus had to be limited to one gas-metal combination. Copper electrodes in argon gas were selected. It was found further that the characteristics of the discharge undergo rather abrupt changes at certain points. For example, the product of pressure and length of Crookes dark space was reasonably constant except at low voltages. Also, cathode emission of electrons was constant at all except very high voltages. Such abrupt changes meant that different formulas must be evolved for each region, or else some mathematical device, such as a voltage step function, must be employed. Either procedure would have resulted in a cumbersome and complicated expression. In the interests of simplicity, attention was concentrated on the region of medium voltages.

The program of work produced a formula which agrees with experimental results with about thirty per cent accuracy. This is believed to be a very satisfactory result in view of the many complications and indeterminates involved in the phenomena examined, as well as the fact that it represents a decided improvement over previously presented formulations.

CHAPTER II

DISCUSSION OF GLOW DISCHARGE AND SPUTTERING

Introduction

Glow discharges and sputtering are frequently considered as almost inseparable processes. Holland (50) explains in detail how glow discharges are used today to produce commercial sputtered films. Prior to World War II use of the glow discharge was the normal method for producing and studying sputtering. Cobine (15, p. 115), writing in 1941, states that the glow discharge was used as the method for producing sputter. The two processes are not, however, inseparable. Sputtering can be produced by using a completely different source of bombarding ions, such as a Kunsman filament. Also, sputtering occurs to a small degree in such devices as vacuum tubes where some of the atoms of residual gases are ionized and produce sputter from the cathode upon impact. Normal glows can be operated with low-sputtering electrodes in such a manner that essentially no sputter is produced. The point to be emphasized is that the glow discharge and sputtering are two separate mechanisms. The next chapter will search for the interrelationship between the glow and sputtering but the purpose of this chapter is to examine the two separate mechanisms.

Glow Discharges

In this section glow discharges are discussed in general; the mechanisms of the major processes are examined; problems involved in working with glows are pointed out; and the main discrepancies between the results and theories of different workers are noted.

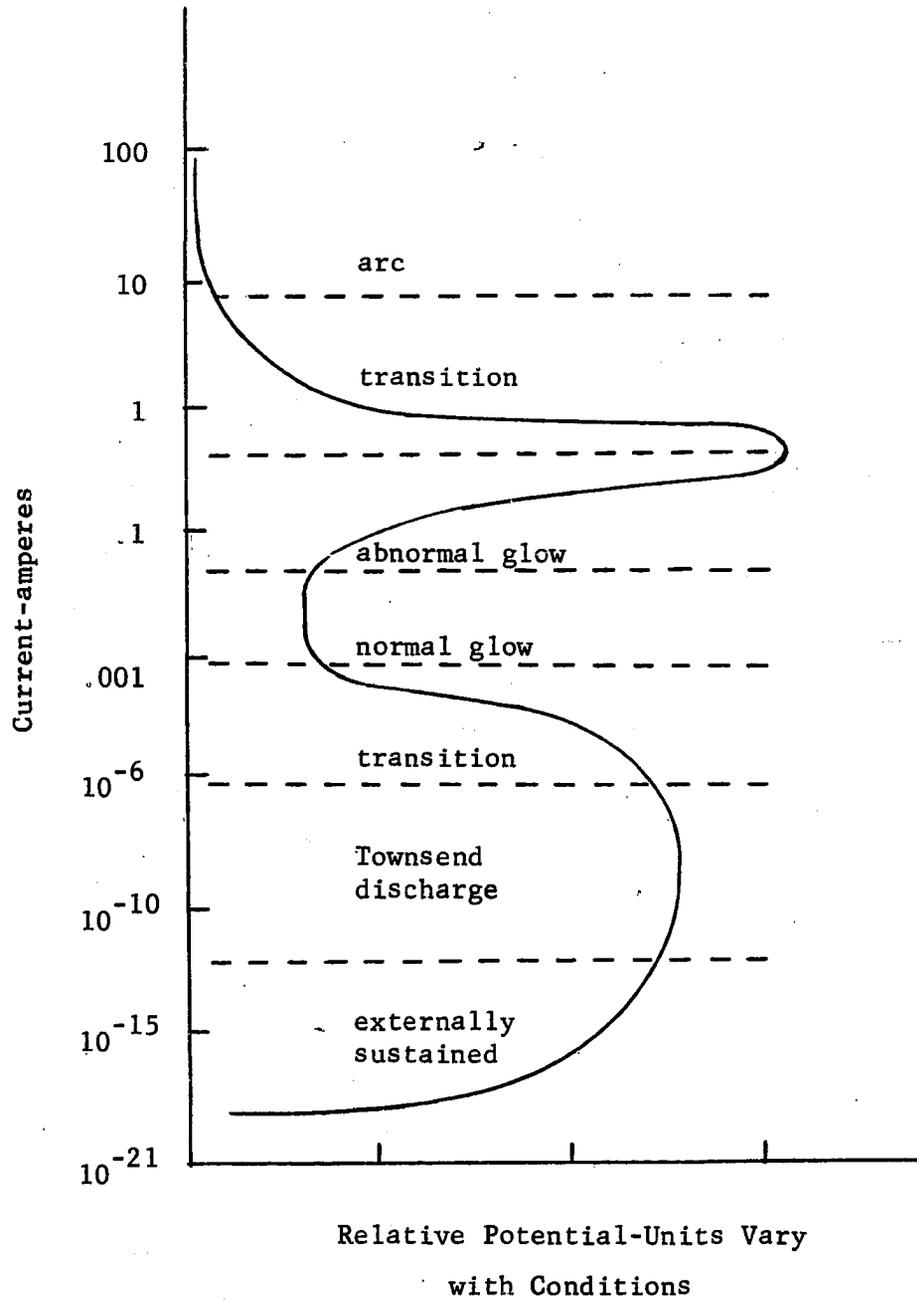
Glow discharges had undoubtedly been created before but the earliest definitive work on them probably starts from the efforts of Crookes and Hittorf about 1880 (108, p. 238). Townsend's experiments and theories, dated at about the turn of the century, did much to advance an understanding of this phenomenon. Langevin, J. J. Thomson and Aston contributed further to an explanation of many of the characteristics of the discharge in the next twenty years. During the period from 1920 to 1940 there were so many workers in this field that it is difficult to single out any for particular mention; however, Güntherschultz, Compton, Loeb, Oliphant and von Engel produced results which have never been improved. The above chronology makes no attempt to list all of those who have contributed to a knowledge and understanding of glow discharges; it, at best, gives credit to a few of those who have produced outstanding results, and some of whose names have become a part of the mechanism itself. After the war many physicists turned their attention away from gas discharges and towards the newer and more glamorous fields of nucleonics and space technology. H. B. Dorgelo (99, p. XI), in opening the International Symposium on Electrical Discharges in Gases in 1955, did say, however, that a renewed interest in gas discharges was beginning to be felt.

The mechanics of the glow discharge are so well-known and have been covered so often (15, p. 205; 22, p. 129; 27, p. 60) that no attempt

will be made to cover all the ramifications here. Instead, only an outline of the sequence of events will be given.

A glow discharge ensues when a volume of gas, at a pressure in the approximate range of from ten microns to ten millimeters of mercury, is enclosed between two electrodes and a potential of from about one hundred to several thousand volts is applied. Current densities may vary from several hundredths to many tens of milliamperes per square centimeter. The glow constitutes a portion of the broader phenomenon of gas discharge. The gas discharge includes the dark, or Townsend, discharge at currents smaller than those of the glow and the spark at currents greater than those of the glow. Each phenomenon is separated from the glow by a transition region. The glow may be either normal or abnormal, as will be discussed later. The complete spectrum is shown in figure 1.

It was stated earlier that the development of the glow is explained in many references. One feature for which no satisfactory, quantitative explanation could be found was the source and quantity of electron-ion pairs present in the gas and which are required to trigger the subsequent chain of events. For the combined reasons that no satisfactory explanation could be found and the question seemed of such importance to a complete understanding of subsequent events, detailed research was conducted into the problem of initial electron-ion production. The resulting analysis was quite long and involved and, since it is not essential for continuity, it has been placed in Appendix A. The conclusions of this analysis are that, at atmospheric pressure and unless special provisions are made for pair production, cosmic rays and natural radiation will produce about ten electron-ion pairs per cubic centimeter per second. An



Gas Discharge Characteristic

Figure 1

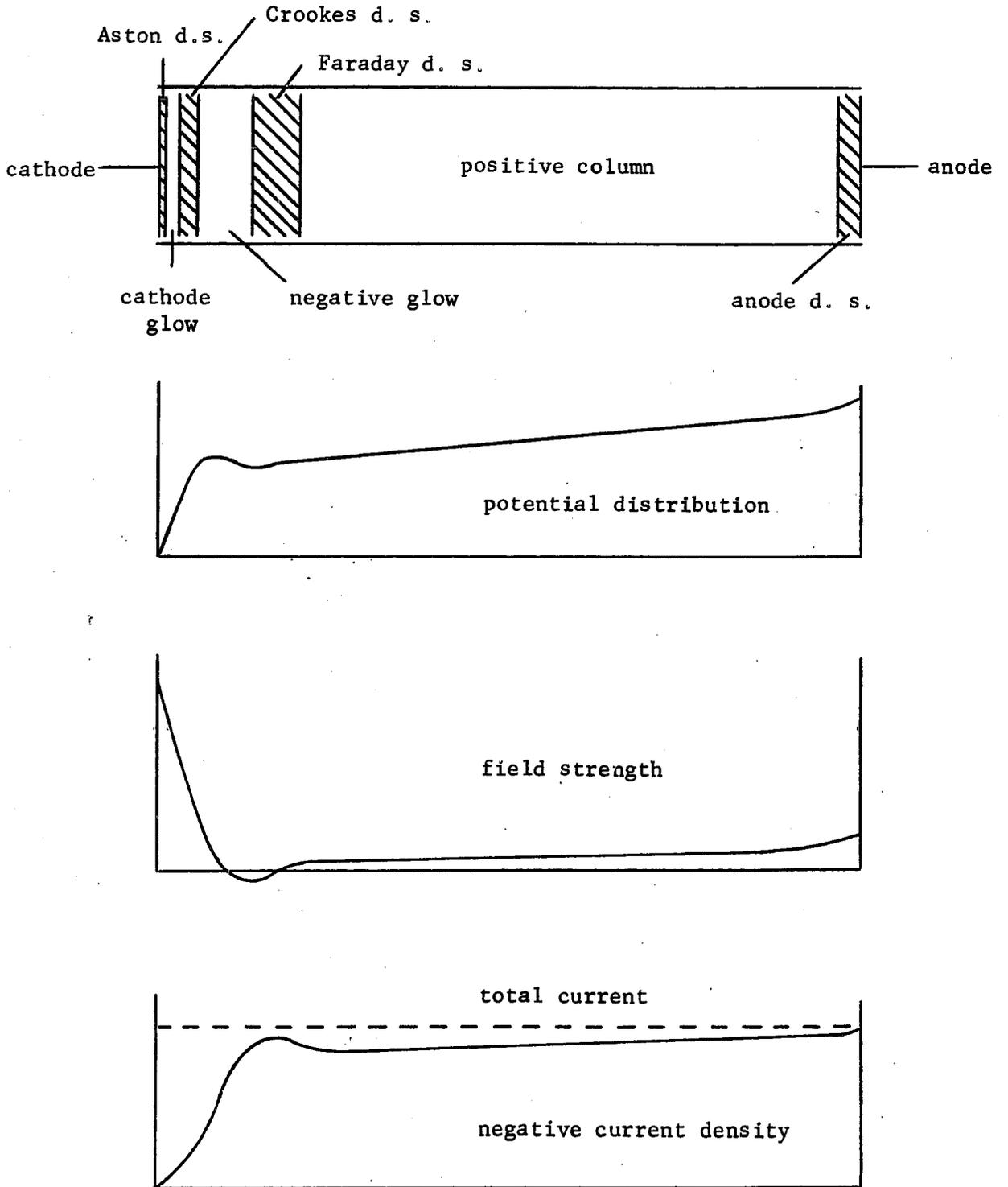
equilibrium condition of about seven hundred and fifty pairs per cubic centimeter will be reached, at which recombination removes pairs as rapidly as they are produced. These numbers vary directly with the gas pressure.

If a volume of gas is enclosed between two electrodes and an increasing potential is applied, some of the electrons and ions will be attracted to the anode and cathode, respectively. At low potentials only those charged particles produced in the vicinity of the electrodes will be captured and the current will be extremely small. The current increases, as the voltage is advanced to several tens of volts. At about this point, depending on pressure and length of gas volume, the field is strong enough to remove all charged particles, prior to their recombination, and a saturation current is reached. The magnitude of the current in this Townsend discharge region will vary up and down from about $(10)^{-18}$ amperes. The current is so small at low pressures and small volumes that it consists of pulses created by individual charges. The charge density is too small to effect the electrical field, thus the latter remains constant. The constant field is too small to produce ionization of atoms by electron impact.

Further increase of the voltage gives the electrons sufficient energy to begin ionization of gas atoms, with resultant increase of current. The current continues to rise with increasing voltage. Eventually the electrons created by electron ionization, themselves become ionizing projectiles and the current rises exponentially. In the meantime, energetic electrons have been exciting atoms. These excited atoms decay to lower energy levels in about $(10)^{-8}$ seconds, with the emission of radiation. Some of this radiation will be of sufficient energy to release

secondary electrons from the cathode. Also, the energetic ions striking the cathode will release secondary electrons. At some point the combined secondary emission by ions, radiation and a contribution from metastables becomes large enough, coupled with the ionization produced by these secondary electrons when accelerated by the field, to produce a current which increases without limit. At this stage, the transition, or breakdown, region between Townsend and glow discharges is reached. The current is now controlled by the external line resistance. If this resistance is of suitable value the discharge will operate in the normal glow region.

Conditions in the normal glow differ considerably from those in the dark discharge. The very large increase of current in the transition into the glow results in a heavy charge concentration in the gas. The electrons, being many orders of magnitude lighter than the ions, are quickly swept towards the anode, leaving a predominantly positive space charge. Compton (16, p. 205) explains the distribution of this charge by the principle of minimum energy dissipation. According to this principle, the potential distribution in the cathode fall space must be that one most favorable to ionization, subject to limitations imposed by Poisson's equation. The normal glow is also characterized by a fixed value of: cathode potential drop, current density, and pressure times length of fall space product; for a given combination of gas and electrode material. Only a sufficient portion of the cathode is active to produce this fixed current density. If the glow current is increased, by increasing the supply voltage or decreasing the line resistance, the conducting area of the cathode increases to maintain constant current. The glow is illustrated in figure 2. It consists of the Aston dark space, the cathode glow,



Glow Discharge Quantities

Figure 2

Crookes dark space, negative glow, Faraday dark space and positive column.

Operation of the glow proceeds as follows. Electrons are emitted from the cathode under the combined effects of positive ions, radiation and metastable atoms. These electrons are accelerated by the field across the Aston dark space until they gain excitation energy. This dark space is so short that it is visible only in helium at low pressures. The decay of excited atoms produces radiation which contributes to the cathode glow. Ions approaching the cathode are neutralized a short distance away by electrons from the cathode. This decay also contributes to the visible light of the cathode glow. Beyond the cathode glow the electron energy has passed the peak of the excitation function and has entered the ionization region. The decreased excitation explains the Crookes dark space. The electrons create electron-ion pairs, in the Crookes dark space, by inelastic collisions with gas atoms. Since the field decreases to zero at the negative glow, the electrons gain no further energy from the field beyond this point; instead, they dissipate their remaining energy in ionization and excitation collisions in the nearly field-free glow. Electrons enter the positive column with very little energy. The positive column is a plasma, composed of nearly equal concentrations of electrons and ions and having a small constant field. Here the electrons are alternately accelerated to excitation and ionization energies and decelerated by exciting and ionizing atoms. Both ions and electrons drift towards their respective electrodes and, by ambipolar diffusion, towards the chamber walls. There is some recombination in the plasma but most recombinations occur at the walls. Those electrons which reach the anode are collected there.

The parameters of the normal glow do not change with increasing current until the entire cathode surface becomes active. After the full surface of the cathode is covered by glow, further increase of current requires an increase in cathode fall voltage and the abnormal glow regime is entered. The increased cathode fall voltage is accompanied by a decreased length of Crookes dark space. The combination of actions increases the field considerably, with the result that both electrons and ions receive greater energy from the field. The ion energy increase enables the ions to produce a slightly larger number of electrons from the cathode. The electron energy increase causes the electrons to enter the negative glow with greater energy; this, in turn, results in more excitations in the negative glow. At this point there is some disagreement on the chain of events. Druyvesteyn (22, p. 135) thinks that, of the increased number of ions produced in the negative glow, an appreciable number diffuse across into the Crookes dark space where they are picked up by the electric field and accelerated to the cathode, there to produce more electrons. Von Engel (75, p. 217) thinks that a negligible number of ions can cross the glow-Crookes dark space boundary. He attributes the increased, abnormal glow current to the increase of photoelectric electrons emitted from the cathode by the increased negative glow radiation. In any event, either action would cause the current to increase slowly with voltage.

The current increase with voltage continues until a point of instability is reached, as the glow transforms into the arc. The exact cause of this transition is not known but it is generally thought that points of high temperature develop on the electrodes. The resultant high thermal emission currents produce the arc. The arc will not be discussed further as it is not germane to the subject.

Theories of Sputtering

Two radically different types of sputtering mechanisms are known to exist; namely, chemical and physical.

Some of the early workers tried to explain all sputtering by a chemical theory. They postulated that the gas formed volatile compounds with the cathode material. These compounds diffused through the gas until they struck the cool walls of the tube or container where the loss of heat caused decomposition, the metal remaining as a deposit on the wall and the gas reentering the parent gas. Sputtering in the rare gases did not invalidate this theory as it was thought that these gases in their ionized state might exhibit more active chemical characteristics than in their inert, neutral state. Some cases of sputtering could not be explained by the chemical theory, as the fact that non-volatile and stable refractory compounds covering the surface of the cathode may be removed by sputtering.

Güntherschultze (32), in his extensive investigation of sputter, found that when he employed H_2 as the gas and certain elements, particularly C, Se, Te, As, Sb and Bi, as the cathode an unusual form of sputtering occurred. The H_2 formed a volatile hydride with the cathode material. This hydride diffused through the gas to cooler parts of the tube where it decomposed and left a metal deposit. He called this mechanism chemical sputtering. He found that chemical sputtering could be contrasted with the more common physical sputtering by several distinctive characteristics. He listed the following:

1. Location of deposit.

Physical: The deposit collects on the tube in the vicinity of the cathode.

Chemical: The tube is clear of deposit in the vicinity of the cathode. The sputter is deposited on the tube beyond the length of the Crookes dark space from the cathode.

2. Electrode spacing.

Physical: The amount of sputter increases as the electrodes are brought closer together.

Chemical: Spacing of electrodes has no effect on the amount of sputter.

3. Normal glow.

Physical: There is negligible sputtering in the normal glow.

Chemical: Appreciable sputtering takes place in the normal glow.

4. Sputtered element.

Physical: Only the cathode is subject to sputtering.

Chemical: Elements sputter either when employed as cathode or if only placed in the path of the discharge.

It is now generally accepted that most sputtering processes are caused by the physical impact of the positive ions against the cathode. The kinetic energy, in manners to be discussed, causes the removal of the cathode material, generally in a free, neutral, atomic state. The chemical process applies generally only to limited elements in hydrogen, although some secondary chemical effects may take place when an active gas is present either as the primary or residual gas. For this paper, the preceding discussion of chemical sputtering will dispose of that subject. All further reference to sputtering will pertain to physical sputtering.

Over the years some six main theories of physical sputtering, some with several variant forms, have been developed. These are the theories of:

- a. Gas explosion.
- b. Cathode local, high temperature.
- c. Ionic rebound momentum.
- d. Double evaporation.
- e. Ion cooling.
- f. Ionic momentum transfer.

a. Gas explosion. One of the early theories of sputtering was that the kinetic energy of the bombarding positive ions heated small pockets of gas, occluded near the surface of the cathode, to a temperature which caused an explosion, blowing off particles of the cathode face. This theory is credited to Berliner as originator and Bush and Smith (13) as major contributors. A weakness of this theory is that metals at high temperature and also liquids may be sputtered. In both cases there is very little adsorbed gas. Also, Baum (7) showed, in 1925, by spectroscopic studies of the metal deposit, that the surface was formed by single atoms rather than by aggregates.

b. Cathode local, high temperature. Von Hippel is generally credited with developing, in the mid-twenties, the theory of sputter being produced by local, high temperature; however, Güntherschultze (32) gives credit to Hittorf. The impact of an energetic positive ion upon the cathode causes a sudden transfer of energy to the cathode. The time required for the adjacent metal atoms to transfer this heat away from the point of impact is of such length that temperatures high enough to vaporize and expel

some of the metal will be reached. An objection to this theory is that such temperatures would also cause thermionic electron emission and this has not been observed.

c. Ionic rebound momentum. In 1923 Kingdon and Langmuir published results of extensive and carefully conducted research on sputtering of a thoriated tungsten filament (65, p. 148). Their conclusions were that one ion expended its energy in depressing the filament surface. A second ion struck in this depression and rebounded with enough remaining energy to remove one or more of the thorium atoms which surrounded the initial depression. This theory is accepted for the special conditions under which it was developed; however, it is not applicable to the general case.

d. Double evaporation. Chauncey Starr (106), in 1939, advanced the theory of double evaporation. Ion bombardment causes emission of the metal atoms by direct energy transfer, at a rate inversely proportional to the heat of evaporation. This metal vapor condenses into a fine aggregate of metal powder after leaving the cathode surface. Subsequent exposure to the heat of recombination of the ions and electrons near the cathode surface would again cause evaporation, the metal vapor thus produced depositing on nearby surfaces. The formula developed by Starr is

$$W = C/H^2,$$

where W = mass of sputter per ampere-hour

C = constant of the conditions

H = total heat of evaporation, including the following:

heat capacity from room temperature to melting point plus

heat of fusion plus heat capacity from melting point to

boiling point plus heat of evaporation.

e. Ion cooling. A more recent theory of sputtering was proposed by Keywell (64) in 1952. He invoked the theory of neutron cooling in a moderator to explain the process. Just as a neutron is cooled in a moderator, so the energetic positive ion is cooled by the lattice of the cathode material. The ion loses energy exponentially as it collides with the lattice atoms and each collision sputters one atom. According to this theory the threshold energy E_n of the ion, below which it will not produce sputter, is obtained from

$$E_n = E_o e^{-nF},$$

where E_o = initial energy of ion

n = number of collisions, hence sputtered atoms

$$F = 1 - \frac{(M - m)^2 \ln \frac{M + m}{M - m}}{2Mm}$$

M = atomic weight of cathode atom

m = atomic weight of ion.

The threshold energy must be known from other sources. The number of sputtered atoms is then given by

$$n = \frac{\ln E_o / E_n}{F}$$

Keywell verified this theory by experiment, using a silver cathode in Argon with a threshold energy of 39 electron volts. F was computed to be 0.59. The number of atoms sputtered by each ion of 4520 electron volts was 8--exactly the number calculated by the formula.

f. Ionic momentum transfer. Through all the history of sputter studies the theory that the momentum of the impacting ion was mechanically transferred to the sputtered atom has been prominent. Langmuir's theory of ionic rebound as described above is a special case. Lamar and Compton (69)

also advanced a theory of momentum transfer. They assumed that the atoms behaved like elastic spheres. The most recent and best accepted version of the momentum transfer theory, as formulated by G. K. Wehner (121 through 125), is presented in subsequent paragraphs.

The basic sputtering process at ion energies below about three hundred electron volts--the area of interest in this paper--is most likely as follows. In the first step the ion, already neutralized a few anstrom units away from the surface, collides with one or several surface atoms and transfers its momentum and kinetic energy to these atoms. The impact 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 atoms.

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 travels most efficiently 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 constant, of the target material.

The third stage is concerned with the separation of atoms from the surface and their escape. A surface atom--not the one that received the original impact--receives an energy pulse from one of its close neighbors underneath. When this energy is sufficient to overcome the binding energy of the atom, and furthermore, when the atom is not obstructed by neighboring atoms in the direction of the impact vector 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 (at grain boundaries and dislocations), the crystal structure and orientation--because they determine the number of possible directions for ejection--and the surface roughness.

At ion energies greater than those treated in this work, the process is probably different. With the formation of interstitial atoms and neutralized ions forced into the lattice, the action is probably better described in terms of von Hippel's theory of evaporation from a localized region near the point of impact, or by Keywell's theory of radiation damage.

CHAPTER III

THEORETICAL ANALYSIS

In this chapter the glow discharge will be analyzed to determine quantitatively those processes which contribute to sputtering and about which a knowledge is required in order to develop an expression for the amount of sputter to be expected. A glow discharge may be produced with a large variety of electrode materials and gases. The detailed analysis of each combination requires that cognizance be taken of the characteristics and peculiarities of the specific metal and gas employed. In order to keep the discussion within bounds and add to its objectivity, the specific materials, copper electrodes and argon gas, will be used throughout. A similar analysis would apply to other combinations, provided the properties of the selected materials were properly evaluated.

The plan of attack is to use the sputtering data of G. K. Wehner as the starting point. These data show the net number of atoms sputtered per impacting positive ion of designated kinetic energy. The data are shown in figure 9, page 62. This leads to the first problem of determining the proportion of sputter produced by positive ions and then to the main problem of determining the number and kinetic energy of these ions.

Sputtering Processes

There are three possible processes which might remove atoms from the cathode; namely, bulk heating to the point of vaporization, ionic impact and impact by fast neutral atoms. There is no evidence at all that any of the other processes which occur in the glow discharge could produce this result; therefore, such phenomena as photon action, electron impact and metastable atom effects will be disposed of with no further comment.

Evaporation. Atoms will definitely be removed from the cathode if the latter reaches a sufficiently high temperature. The vaporization temperature of copper is 1270 degrees Centigrade (50, p. 111), a temperature well above that reached in any of the experiments conducted. It is known that the cathode never reached the temperature of 1080 degrees Centigrade, the melting point of copper, since it showed no evidence of melting. This criteria (melting point lying below the vaporization point), does not apply to all metals, as one third of them do have vaporization points below the melting point. In order to determine the cathode operating temperature with greater precision, lead cathodes were used for temperature estimation. It was found that there was no melting at 14 watts input to the discharge but some melting was observed at 16 watts. The power input is a good measure of the energy dissipated at the cathode, since it has been estimated that more than eighty per cent of the power input goes to cathode heating. The above results for lead show that the cathode temperature is approximately 328 degrees Centigrade, the melting point of lead, when the power input to the discharge is approximately 15 watts.

The estimates of cathode temperature obtained by the use of a lead electrode were verified by heat theory calculations. The cathode was

mounted on a seven centimeter steel rod of one square centimeter cross section and the rod was mounted on a relatively massive metal end cap. This was the same physical arrangement that was used in all data collection runs. The power input was set at 15 watts and the temperature of the end cap measured as 40 degrees Centigrade after heat equilibrium was reached. The standard formula for temperature differential between the ends of the rod was used (57, p. 182):

$$\Delta T = \frac{Wxd}{4.2KA} \text{ degrees Centigrade,}$$

where ΔT = temperature differential between ends of rod in degrees Centigrade

d = length of rod in centimeters

W = input power in watts

K = thermal conductivity in gram-calories per centimeter cube per degree Centigrade

A = area in square centimeters,

and K for steel is 0.086 (57, p. 294).

Inserting the given values in the formula gives

$$\Delta T = \frac{7 \times 15}{4.2 \times 0.086 \times 1} = 290 \text{ degrees Centigrade,}$$

and $290 + 40 = 330$ temperature of cathode in degrees Centigrade. The close agreement in cathode temperature obtained by using a lead cathode and by the formula shows both: that at 15 watts input the cathode does not exceed about 330 degrees; that the formula used is accurate for the arrangement to which it was applied. Most data runs were made with less than 15 watts input; however, some high pressure, high current runs were made at up to 45 watts, with end cap temperatures running up to 70 degrees Centigrade. Application of the heat flow formula gives:

$$20 \times 45 + 70 = 970 \text{ degrees Centigrade}$$

as the maximum temperature reached by the cathode. Thus it is shown that normally the cathode was operated far below the vaporization temperature of copper and even at extreme maximums it was still over 300 degrees Centigrade below. It follows that vaporization of atoms due to bulk heating of the cathode may be eliminated. Local heating due to ionic bombardment is another problem, to be discussed under impact theory.

Fast neutral particles. The sputter of cathode atoms by fast neutral particles will be considered next. Most discussions of sputter assume, or imply, that all sputter is caused by positive ions. This practice is so prevalent in the literature that even the definition of sputtering is sometimes given (15, p. 228) as "disintegration of the cathode by bombardment by positive ions." Francis (28, p. 40) points out that fast neutral atoms, as well as positive ions, may cause disintegration of the cathode. According to the discussion of charge transfer on page 34, fast neutrals and positive ions will exist in equal numbers at the last charge exchange collision in front of the cathode. The most generally accepted, modern view of ionic sputtering is that it is caused by the transfer of the kinetic energy of the ions to the lattice of the metal, thereby removing atoms from the metal. It would appear logical that a neutral atom, with the same kinetic energy as the ion, should be just as effective in removing metal atoms. Also, the theory of sputtering due to high local temperatures is derived on the basis of these temperatures being caused by the kinetic energy of the positive ions. Here, again, fast neutrals should produce the same results. For the above reasons it is necessary that the effectiveness of fast neutrals in producing sputter be investigated.

Diligent search of pertinent published material has unearthed no definitive data on sputtering by fast neutrals. The only positive reference to this process is made by Oliphant (95, p. 241), one of the outstanding workers in the field. Oliphant found that the fast neutral atoms produced far less sputter than ions with equivalent kinetic energy. This result came as a by-product of his investigations of the production of metastables by ions striking a metal surface at glancing incidence, hence he did not publish detailed data in support of his findings. Since his conclusions are the only ones found which were based on actual experiment, they are accepted as the best evidence available. His comment on the process was: "If the sputtering produced by positive ions were due entirely to local heating and vaporization at the point of impact of each ion, as suggested by Hipple in the most comprehensive theory of cathode sputtering yet produced, then the impact of neutral atoms with similar kinetic energy should produce identically the same effects. Actually it is found that while some disintegration is produced, it is far less intense than that produced by positive ions. The charged condition of the ion must therefore play a part in the process of cathode disintegration."

Oliphant suggests that the charged condition of the ion must play some part in the sputter process. Modern sputter studies have been conducted in high vacuum with controlled ion beams, both conditions serving to eliminate the complicated chain of processes which are involved in glow discharge sputtering. The charge of the ion plays no part in any of the theories of the sputter mechanism which are based on these modern experiments. In the glow discharge, on the other hand, the charge of the ion does play an indirect part according to the following reasoning. At the

last charge exchange collision before reaching the cathode there will be one slow ion and one fast neutral. The free path of the ion is then, from equation (5), page 37,

$$L_* = 0.011/p \text{ centimeters.}$$

Equation (3), page 31, shows that the free path of the neutral atom is

$$L_n = 0.005/p \text{ centimeters,}$$

less than half that of the ion. Little and von Engel (75, p. 220) estimate that the path of the atom is only a fourth of that of the ion. Since the path of the atom is appreciably less than that of the ion, the atom will have a high probability of losing half of its energy by one or more collisions prior to striking the cathode. Examination of figure 9, page 62, shows that a particle with less than 120 volts energy would produce no sputter after losing half of its energy while, similarly, one with greater than 120 volts would produce only about one third as much.

On the basis of the foregoing discussion, fast neutral gas atoms will be assumed to produce one third of the amount of sputter that is produced by ions.

Positive ions. Positive ions are generally conceded to be the primary agents which cause sputtering; however, there are still differences of opinion on the mechanics of the process. The various theories were discussed in Chapter II under Theories of Sputtering. The actual sputter yield from ionic bombardment will be discussed later in this chapter after other related processes have been examined.

Cathode Field

The electric field in the cathode dark space, like most other phenomena occurring in the glow discharge, has been a subject of much investigation, speculation and controversy for many years. Most observers agree generally that the field is a linearly decreasing function of the distance from the cathode to the far end of the cathode dark space, falling to zero at the termination of the dark space. In fact, the point of zero field provides a more reliable indication of the extent of the dark space than do visual methods; hence, is frequently used in measurement of the length of the dark space. Field measurements of this region have proven quite difficult due to the high concentration of space charge. The common method of field measurement, by use of Langmuir probes, has proven entirely unsatisfactory because of the heavy space charge. Aston (3), in 1910, measured the field by observing the deflection of a beam of electrons projected perpendicularly to the field. A very weak beam was used so that it would produce no significant change in the field. Little and von Engel (75), using the same technique but employing more modern equipment and procedures, conducted similar measurements in 1954. Both Aston and von Engel found a linear field of the form:

$$E = C(d - x),$$

with E = field

C = constant

d = length of dark space

x = distance from cathode.

The potential distribution is

$$V = \int_0^x E \, dx = C \int_0^x (d - x) \, dx = C(dx - x^2/2).$$

The normal definition of cathode drop, V_c , is the potential drop across the dark space; hence,

$$\begin{aligned} \text{at } x &= d, & V &= V_c . \\ \text{then } V_c &= C(d^2 - d^2/2) = Cd^2/2; & C &= 2V_c/d^2 \\ \text{and } V &= (2V_c/d)(x - x^2/2d), \\ E &= dV/dx = (2V_c/d)(1 - x/d) . \end{aligned} \quad (1)$$

This is the field that will be used in future calculations.

Ion Energy

There is not a great deal of experimental data available on the subject of ion energies in a glow discharge. General observations on the subject are sometimes made in summary type books and articles on glow discharges but these observations can usually be traced back to three basic sources; the works of J. J. Thomson (109), von Hippel (115) and the joint efforts of Chaudri and Oliphant (14). Each of these workers permitted some of the positive ions to penetrate a small hole in the cathode of a glow discharge and they then measured the energy of the ions passing through.

Thomson applied electric and magnetic fields to the space through which the ions passed and then permitted them to strike a fluorescent screen. He obtained a general idea of the energy distribution of the ions by observing the intensity and deviation of the parabolic figure which they traced on the screen; however, his results were of a qualitative nature only.

Von Hippel and Chaudri both used the same method of providing two electrodes in the space through which the ions passed. One electrode collected the ions to determine the ion current, while the other provided a

retarding potential. By observing the change in current as the potential changed they were able to determine the energy distribution of the ions. Von Hippel found ions with energies distributed from zero to one-half the anode to cathode potential of the discharge. A rough calculation of his data shows the mean value of the kinetic energy to be about one-fifth of the cathode fall voltage.

Chaudri and Oliphant, on the contrary, found some ions with energies up to the full cathode fall voltage. They contrast this with von Hippel's finding of maximum energy as one-half the cathode fall by saying that they believe von Hippel failed to account for those ions which were stopped by the retarding potential before they reached the collecting electrode. They further state that they do not believe that positive ions lose energy by collision in the dark space. This is not a new theory as it had been advanced earlier by Ryde and Güntherschultze. Compton (16, p. 306) comments that such action would be incompatible with other investigations of collision and charge exchange cross sections. Computations from Chaudri's data show the mean ion energy to be about one-third of the full cathode fall.

Townes (112) attacks the problem of ion energy from a theoretical standpoint. He employs the hard sphere model for both atom and ion, ignores polarization effects and Coulomb attraction and makes use of kinetic theory in determining the gain of energy from the field by the ion between collisions with atoms and the loss of energy upon collision.

The mean thermal velocity of an argon atom, or ion, at room temperature, is (88, p. 35)

390 meters per second.

The velocity of the ion may be obtained from

$$\text{K.E.} = mv^2/2 = eV \text{ joules,}$$

or

$$v = \left(\frac{2eV}{m} \right)^{\frac{1}{2}} = \left(\frac{2 \times 1.6(10)^{-19} V}{6.64(10)^{-26}} \right)^{\frac{1}{2}} = 2200V^{\frac{1}{2}}, \quad (2)$$

where K.E. = kinetic energy

$$m = 40 \times 1.66(10)^{-27} = 6.64(10)^{-26} = \text{ion mass in kilograms}$$

v = velocity of ion in meters per second

$$e = 1.6(10)^{-19} = \text{electronic charge in coulombs.}$$

The above calculations show that when the ion receives kinetic energy greater than four volts from the field, its field velocity is much greater than its thermal velocity; therefore, its velocity may be considered entirely in the field direction and the atom considered stationary compared to the ion. The ion thus receives an energy in each free path

$$\text{K.E.} = EL \text{ volts,}$$

where E = electric field

L = ion mean free path, assumed in this discussion to be the same as the atom mean free path.

The atomic mean free path is (88, p. 35)

$$6.66(10)^{-6} \text{ centimeters}$$

at normal temperature and pressure. This gives

$$L = 6.66(10)^{-6} 760/p = 0.005/p \text{ centimeters} \quad (3)$$

with p = pressure in millimeters of mercury.

The minimum cathode fall voltage and maximum length of Crookes dark space occur in the normal glow. They are given (15, p. 217, 218) as

$$V_c = 130 \text{ volts}$$

$$d = 0.23/p \text{ centimeters.}$$

The minimum field strength for the glow discharge in the immediate vicinity of the cathode may be found by substituting the above values of V_c and d in equation (1) and equating x to zero, to give

$$E = 2V_c/d = 260p/0.23 = 1130p \text{ volts per centimeter}$$

$$EL = 1130p \cdot 0.005/p = 5.65 \text{ volts.}$$

This minimum value of ion energy is greater than the four volts required by equation (2).

The ion loses energy on collision according to the formula from kinetic theory,

$$\Delta K.E. = 2mM/(m + M)^2,$$

where $\Delta K.E.$ = fractional loss of energy by positive ion upon impact with an atom

m = mass of ion

M = mass of atom.

Since the masses of the ion and atom are essentially equal,

$$\Delta K.E. = 1/2.$$

If the field is constant the ion will gain energy EL between collisions and lose one-half its energy at each collision, with the following results:

Collision	Energy Before	Energy After
1	EL	$EL - EL/2 = EL/2$
2	$EL + EL/2 = 3EL/2$	$3EL/2 - 3EL/4 = 3EL/4$
3	$EL + 3EL/4 = 7EL/4$	$7EL/4 - 7EL/8 = 7EL/8$
4	$EL + 7EL/8 = 15EL/8$	$15EL/8 - 15EL/16 = 15EL/16$

It can be seen from the above that the ion approaches an energy of $2EL$ in three or four free paths. The dark space of the normal glow is approximately fifty free paths long so it is reasonable, in view of equation (1),

to assume the field constant a few path lengths away from the cathode. Actual integration of equation (1) over several paths shows that the assumption of constant field gives an error of less than two per cent in three path lengths.

Townes' maximum value for the mean energy of impacting ions, $2EL$, may be expressed in terms of the cathode fall voltage by use of equations (1) and (3); namely,

$$E = 2V_c/d$$

$$L = 0.005/p$$

giving $K.E. = 2EL = 2(2)V_c \cdot 0.005/dp = 0.02V_c/dp$.

Figure 4, page 38 (118, p. 105), shows that at higher voltages pd is of the order of 0.07 centimeters times millimeters of mercury. This value in the last equation gives

$$K.E. = 2EL = 0.02V_c/0.07 = 0.3V_c$$

This represents a maximum value for the mean ion kinetic energy as calculated by Townes and it includes the energy gained over the last full path. A more reasonable calculation would assume the ion might strike the cathode at any point in the last path with equal probability, making the final energy increment $0.5EL$ rather than EL and the total energy $1.5EL$ rather than $2EL$ giving, in terms of V_c ,

$$K.E. = 3 \times 0.3V_c/4 = 0.225V_c$$

The value thus derived falls between von Hippel's value of $0.2V_c$ and Chaudri's $0.33V_c$.

The above discussions of ionic kinetic energy would determine the mean value to lie somewhere between $0.2V_c$ and $0.33V_c$. Each of these determinations, however, possesses shortcomings. Chaudri's data was taken

at pressures below 135 millimeters of mercury and showed a definite pressure dependence. Von Hippel's work has been questioned on experimental accuracy. Townes' derivation ignores too many factors which are known to be effective in a calculation of this type.

The method for determining the mean value of positive ion kinetic energy which was finally adopted is based on charge exchange phenomena and was suggested by von Engel (75, p. 220). Von Engel argues that the high field in the abnormal discharge will produce high energy ions. Both experimental evidence and wave mechanical analysis show that such ions exhibit pronounced forward scattering with relatively little loss of forward momentum. This agrees with the observation of Chaudri (14, p. 675) mentioned earlier. Thomson (109, p. 302) also supports this view. Von Engel goes further, however, to explain that ions will, in effect, lose energy through charge exchange and this becomes the controlling factor in determination of ionic energy.

Charge exchange is a very common phenomenon and is quite effective for ions travelling in their own gas. This process involves the transference of an electron from a neutral gas atom to an ion passing nearby. The former ion then becomes a neutral atom but retains its kinetic energy while the former atom becomes an ion but gains no additional kinetic energy. The net result is the same as though the ion had lost all its energy to the atom; i.e., after the exchange a zero kinetic energy ion and a fast neutral atom exist. In view of the way in which this process operates, the maximum energy which an ion can gain is that produced over one free path for charge exchange. The path of interest will be the last one prior to impact with the cathode and this one will occur in the high field

region of the cathode. Since the new ion will be produced by charge exchange with equal probability at any point up to one path length in front of the cathode, and the energy varies directly with distance traveled, the mean kinetic energy of impacting ions will be that gained in one-half of a path.

The data used for charge exchange cross section determination is that of Cramer (19) shown in figure 3. This data was obtained in 1959 and agrees within ten per cent with values found by Hasted (43), as well as the results of several other workers recently. This data shows that the cross section for charge exchange exhibits the usual energy, or velocity, dependence common to most types of cross sections, however, in this case the dependence is not as critical as usual. Utilization of figure 3 requires a rough knowledge of the ionic kinetic energy. The mean energy,

$$\text{K.E.} = 0.5EL_* = 0.5E/pQ,$$

where L_* = mean free path for charge exchange

Q = macroscopic cross section for charge transfer at 1 mm. pressure

p = pressure in millimeters of mercury

may be expressed in terms of cathode fall voltage by using equation (1), with x equal zero,

$$\text{K.E.} = 0.5E/pQ = 0.5 \times 2V_c/pdQ = V_c/pdQ. \quad (4)$$

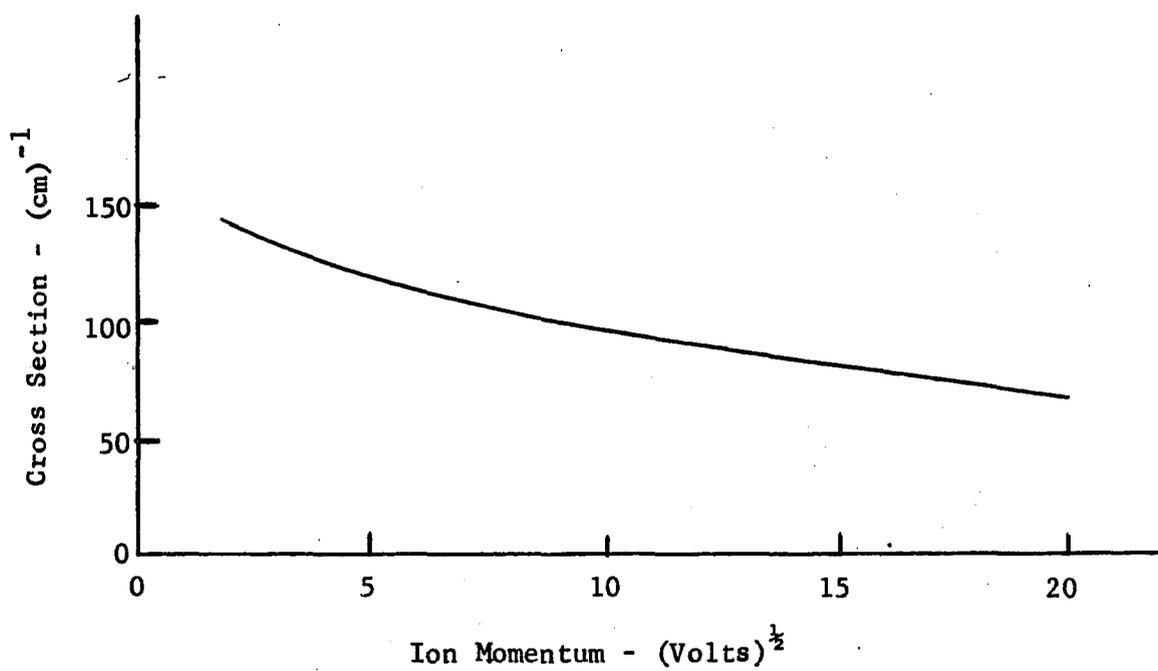
Since pd is approximately 0.07 from figure 4,

$$\text{K.E.} = V_c/0.07Q \text{ electron volts.}$$

The cathode fall voltages used ran from about 400 to 2500 volts, giving

$$\text{K.E.} = 5700/Q \text{ to } 36(10)^3/Q.$$

When figure 3 is entered with these values, trial and error methods give values of Q ranging from 80 to 100. The value of 90 was selected as a



Charge Exchange Cross Section

Figure 3

reasonable mean which differs by less than ten per cent from the maximum and minimum values. The value of

$$Q = 90$$

gives
$$L_* = 1/pQ = 0.011/p \text{ centimeters} \quad (5)$$

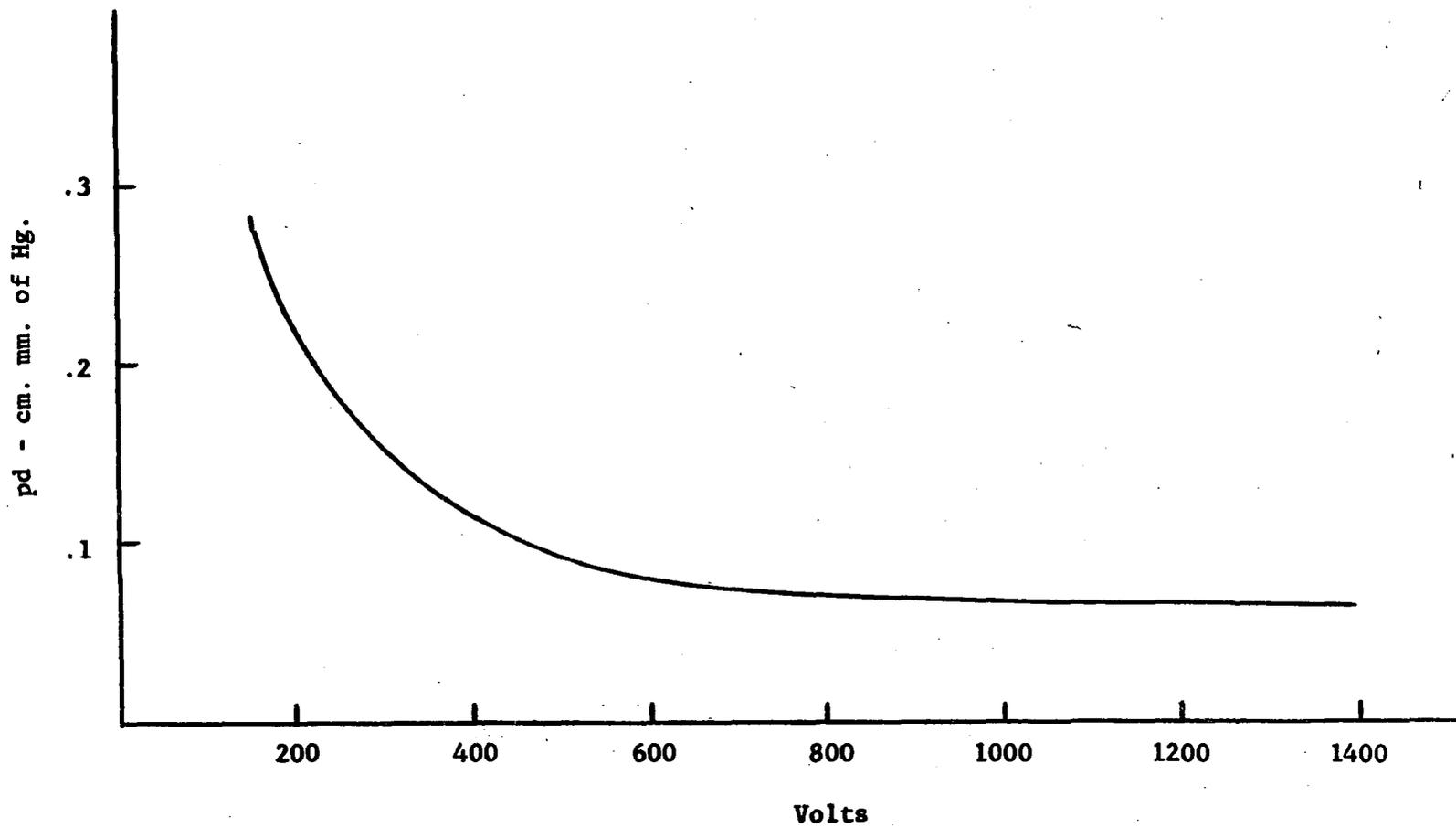
as the mean free path of the ion for charge exchange.

Figure 4 relates the product of pressure and length of dark space, to cathode fall voltage. The figure actually applies to an iron cathode; however, the discharge characteristics of iron and copper are so similar that the two can normally be interchanged in computations with very little error. The value of the product, pd , plays such an important role in the discharge that further investigation of its derivation was made. The figure appears in Cobine (15, p. 229), von Engel and Steenbeck (118, p. 105) and in most other summary texts on gas discharges. The origin of this figure is not clear but it seems to be a composite of data from the work of Aston (4, 5, 6) and Güntherschultze (35), possibly supplemented by other sources. Aston did the most extensive work on the cathode dark space, so his results will be examined in detail. It is interesting to note that it was in this series of experiments that he discovered the dark space next to the cathode that bears his name.

In the years from 1907 to 1912 Aston conducted extensive investigations on the relationship between the following parameters of a glow discharge; cathode voltage, pressure, current and length of dark space. He developed the following two equations

$$d = A/p + B/(j)^{\frac{1}{2}} \quad (6)$$

$$V_c = C + F(j)^{\frac{1}{2}}/p, \quad (7)$$



Cathode Drop vs. Product of Pressure and Length of Crookes Dark Space

Figure 4

where d = Crookes dark space in centimeters

p = pressure in millimeters of mercury

j = current density in milliamperes per square centimeter

V_c = cathode fall voltage

A, B, C, F = gas constants. For argon on copper: $A = 0.058,$

$B = 0.1, C = 190, F = 93.$

Actually, Aston worked primarily with an aluminum cathode, for which he obtained the value of

$$A = 0.04$$

and the other constants essentially as given. He then ran a series, using oxygen on various metals, which showed that a correction factor of

$$8.9/6.1 = 1.45$$

must be applied to A when copper rather than aluminum electrodes were used. The correction factor gives

$$1.45 \times 0.04 = 0.058.$$

The parameter j can be eliminated from equations (6) and (7) to give

$$pd = A + BC/(V - E). \quad (8)$$

Equation (8) does give pd as a function of the cathode voltage alone and is possibly the basis for figure 4. Aston explains, however, that although both equations (6) and (7) hold for common gases such as oxygen, nitrogen and hydrogen, only equation (6) holds for the rare gases. Equation (8), which incorporates equation (7), is thus not valid for argon.

Equation (6) for argon on copper is

$$d = 0.058/p + 0.1/(j)^{\frac{1}{2}}.$$

Multiplying this value of d by p gives

$$pd = 0.058 + 0.1p/(j)^{\frac{1}{2}} = 0.058(1 + 1.7p/(j)^{\frac{1}{2}}). \quad (9)$$

Experimental values for p and j were substituted into equation (9) and in all cases the result was within the range

$$pd = 0.070 \pm 0.005 .$$

Very little error will be involved if the pressure dependence of equation (9) is removed through use of the average value

$$pd = 0.07 .$$

Examination of figure 4 shows that the product pd varies only slightly for values of V_c greater than about 400 volts. Also, the mean value in this range is 0.07, exactly the same value obtained from Aston's more detailed analysis. The preceding discussion justifies the use of

$$pd = 0.07$$

as a reasonable mean value for cathode fall voltages above

$$V_c = 400 \text{ volts.}$$

This value will be used in all future calculations. It is to be noted that figure 4 shows that pd rises rapidly below the above value of V_c , so that this assumption is valid only for cathode fall voltages greater than 400 volts.

The values of Q and pd may now be entered in the expression for the mean kinetic energy of ions striking the cathode, equation (4),

$$\text{K.E.} = V_c / (0.07 \times 90) = 0.158V_c . \quad (10)$$

This value will be used in future calculations.

Cathode Current

Through all the many years during which the glow discharge has been studied so intensively there has been more controversy on the composition and production of the cathode current than on any other phase of the subject. This is partly understandable when it is considered that

the cathode current may vary from almost purely ionic; in the case of weak electric fields and ionization of the gas by external sources; to almost purely electronic for low pressures and external heating of the cathode. The range of the glow covers a wide segment between these two extremes. The very definition of the glow as a self-sustaining discharge removes it from the first extreme. It is true that Townsend did initially propose a mechanism of ionization of the gas by positive ions which would have eliminated any requirement for an electron component of the cathode current; however, this theory has been disproven and now the accepted belief is that there must be at least some electron emission from the cathode to sustain the discharge. Glow discharges never reach the second limit of purely electron current from the cathode as this stage of the discharge ceases to be a glow and becomes an arc. This point will be discussed more fully later in connection with the Richardson-Dushman equation for thermionic emission. The true composition of the glow cathode current probably varies considerably between these two extremes. Thomson (109, p. 427) and Little and von Engel (75, p. 217) believe that the cathode current is largely electronic in the abnormal discharge. Druyvesteyn and Penning (22, p. 135) agree that the proportion of electrons increases from the normal glow to the abnormal but they derive an ion component three times larger than the electron component even when the glow is highly abnormal.

A second point of disagreement concerns the agents which produce electron emission from the cathode. The possible processes which might cause electron emission are: photons, heat, high electric fields; and impacting electrons, ions, metastables and neutral atoms. Frequently this

question can be avoided by combining all producing agents into one emission factor, commonly called Townsend's second coefficient (15, p. 154). This procedure is satisfactory for many theoretical and experimental studies of some features of glow discharges. Another common method is to assume that all electron emission is caused by positive ion bombardment and ignore all other agents.

The solutions to the above problems can be determined only by an examination of all the possible agents which may cause electron emission from the cathode. The contribution of each of these to the total cathode current of the glow discharge must be determined in order that the proportion attributable to the positive ions may be evaluated. The number of positive ions striking the cathode may then be found from the total cathode current.

The thermionic emission of electrons from a metal is governed by the Richardson-Dushman equation (105, p. 442),

$$j = AT^2 \exp(-ew/kT) ,$$

where j = current density in milliamperes per square centimeter

A = material constant = $65(10)^3$ milliamperes per square centimeter for copper

e = charge of electron = $1.6(10)^{-19}$ coulombs

w = work function = 4.38 volts for copper

k = Boltzmann constant = $1.4(10)^{-23}$ joules per degree Kelvin

T = temperature in degrees Kelvin.

The copper electrodes never showed any evidence of melting in the most strongly abnormal glows encountered so the melting point, 1356 degrees Kelvin, may be taken as an extreme temperature. This temperature substituted in the above formula gives

$$j = 65(10)^3 (1356)^2 \exp \left(\frac{1.6(10)^{-19} \cdot 4.38}{1.4(10)^{-23} \cdot 1356} \right) = 0.135(10)^{-4}$$

milliamperes per square centimeter, which is a trivial figure compared to the smallest current encountered, of about 0.1 milliamperes. Thus thermionic emission may be eliminated as contributing to the cathode current.

The above calculation shows that thermionic emission is a trivial factor at a temperature as high as the melting point of copper. Although it has no bearing on sputter in the glow, the importance of thermionic emission in the next stage of the discharge, the arc, will be calculated for the purpose of contrast. When the voltage is raised to the extreme limit of the abnormal glow, the cathode reaches temperatures at which thermal emission becomes slightly effective. Each thermal electron creates new electron-ion pairs by cumulative ionization and each ion adds to the cathode current, further increasing the cathode temperature. The cumulative process continues at an almost explosive rate until the glow passes suddenly into the arc. The temperature of the electrodes of the arc is at least the boiling point of the metal (15, p. 290), 2573 degrees Kelvin for copper. At this temperature the Richardson-Dushman equation gives

$$j = 65(10)^3 (2573)^2 \exp \left(\frac{-5(10)^4}{2573} \right) = 1390 \text{ milliamperes}$$

per square centimeter, or more than one ampere per square centimeter.

This heavy thermal current, plus the ionic current created by ionizations, causes the very high currents found in the arc discharge.

Electron emission by high electric fields is found by a method very similar to that used for thermal emission. The Fowler-Nordheim equation (105, p. 453), derived by wave mechanics theory, applies

$$j = \frac{1.6E^2 (10)^{-3}}{w} \exp\left(\frac{-7(10)^7 uw^{3/2}}{E}\right) \text{ milliamperes per square centimeter}$$

$$\text{where } u = 1 - 14(10)^{-8} E/w^2$$

E = electric field in volts per centimeter.

The field in the abnormal glow is unlikely to run higher than about 20,000 volts per centimeter. This value gives

$$u = 1 - 14(10)^{-8} 2(10)^4 / (4.38)^2 = 1 \text{ approximately,}$$

$$j = \frac{1.6(10)^{-3} 4(10)^8}{4.38} \exp\left(\frac{-7(10)^7 (4.38)^{3/2}}{2(10)^4}\right)$$

$$= 1.4(10)^5 \exp\left(-32(10)^3\right) \text{ milliamperes per square centimeter, a ridiculously small value.}$$

Calculations show that fields do not cause effective emission until they reach values of about 10^7 volts per centimeter. This is more than a thousand times greater than the fields found in glow discharges. Here, again, this source may be ignored in calculating the total cathode current.

The emission of secondary electrons from a metal surface which is bombarded by energetic primary electrons is a well-known phenomenon. Brown (12, p. 202) presents the standard graph, which applies roughly to all metals, showing a maximum yield of approximately one secondary per primary, at energies of from 300 to 800 volts. The yield falls rapidly from this maximum to essentially zero at about twenty volts. Theoretical analysis shows that the minimum energy necessary to cause any secondary emission is approximately four volts, the work function of the metal.

The volume of the discharge just in front of the cathode, and extending for about the distance of the Aston dark space, will contain a

fairly high concentration of electrons. They are emitted from the cathode by agents, and with energies, yet to be determined. The simplest mechanism through which these electrons could return to the cathode would be for them to strike an atom and thereby rebound towards the cathode. This would require that the particle travel two path lengths. The minimum mean free path for slow electrons at one millimeter pressure is (15, p. 31)

$$L_e = 0.0125 \text{ centimeters.}$$

While traveling this distance the electron will be subjected to a high retarding electric field. The minimum value of this field may be determined by the parameters of the normal glow for copper in argon at one millimeter pressure. From equation (1)

$$E = 2V_n/d_n = 260/0.2 = 1300 \text{ volts per centimeter,}$$

where $d_n = 0.2/p = 0.2 \text{ centimeters (12, p. 280)}$

$$V_n = \text{normal cathode fall voltage} = 130 \text{ volts (12, p. 281)}$$

$$d_n = \text{normal cathode fall length.}$$

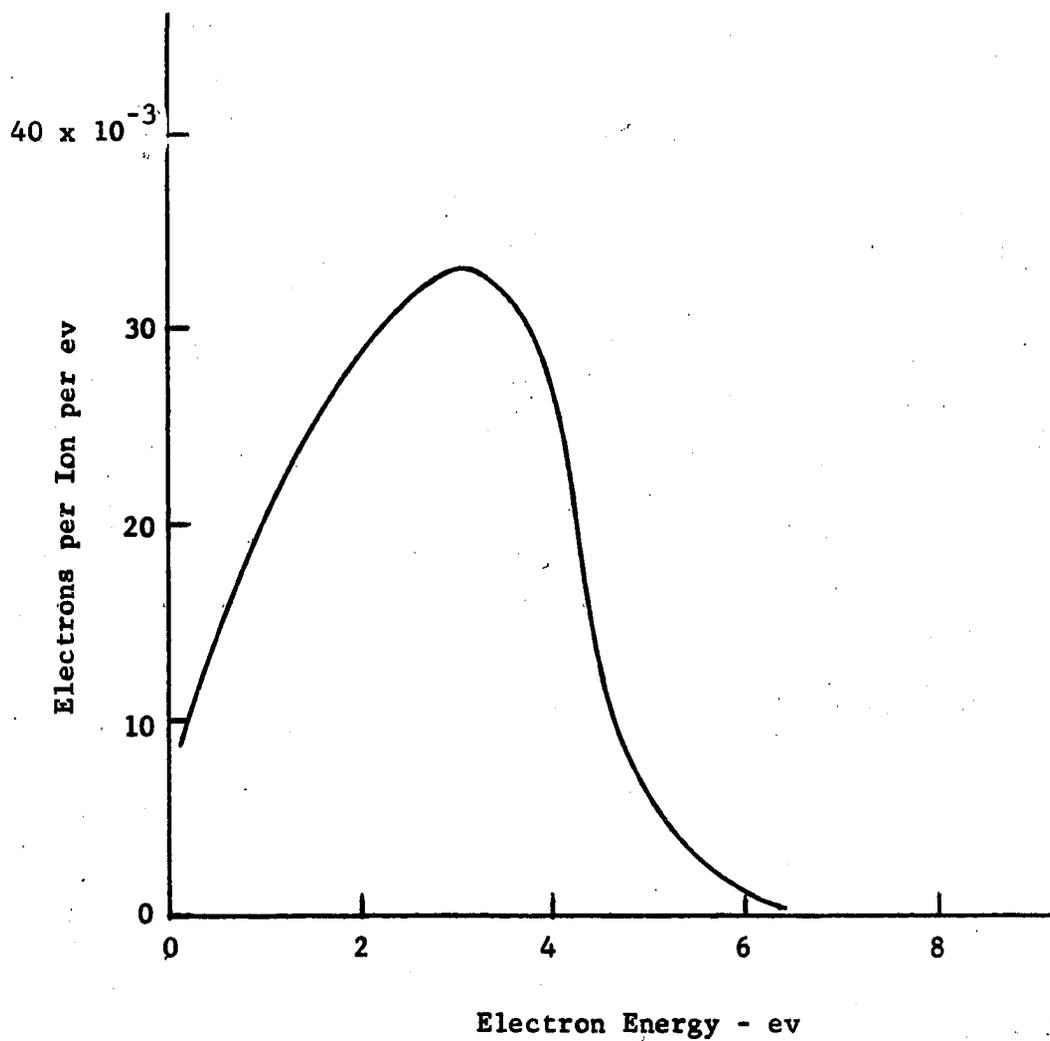
An electron traveling two path lengths in this field would lose energy

$$2EL_e = 2 \times 1300 \times 0.0125 = 38 \text{ volts.}$$

The theoretical minimum energy the electron can have to produce a secondary electron upon impact with the cathode is 4.38 volts. This energy, added to the energy lost in two paths, gives approximately 43 volts of energy that the primary electron must have when originally emitted from the cathode if it is to be able to cause the emission of a secondary electron. No exact data could be found which gave the energy distribution of the electrons near the cathode for copper in argon. The summary of this section, on page 59, shows that ions and radiation produce the bulk of the

electrons that are emitted from the cathode; therefore, the energy of such emitted electrons will next be examined. Figure 5 (88, p. 646) shows the energy distribution for electrons produced by 40 volt argon ions on molybdenum. Copper should give approximately the same result (figure 7 shows an example) since the work functions of the two metals are very nearly the same. Figure 6 shows that the energy of emitted electrons does not vary significantly with the energy of the ions. It may be deduced from these figures that no ion-produced electrons will have energies greater than about 8 volts--far below the required 43 volts. The most energetic radiation which will be produced in the argon gas is the 16 electron-volt radiation caused by direct recombination of an electron-ion pair. Four volts of this energy are required to liberate an electron from the cathode. The remaining 12 volts are, again, much less than the 43 volts required by the primary electron to liberate a secondary electron. The conclusion to be drawn from this paragraph is that there will be no secondary electron emission caused by electrons striking the cathode.

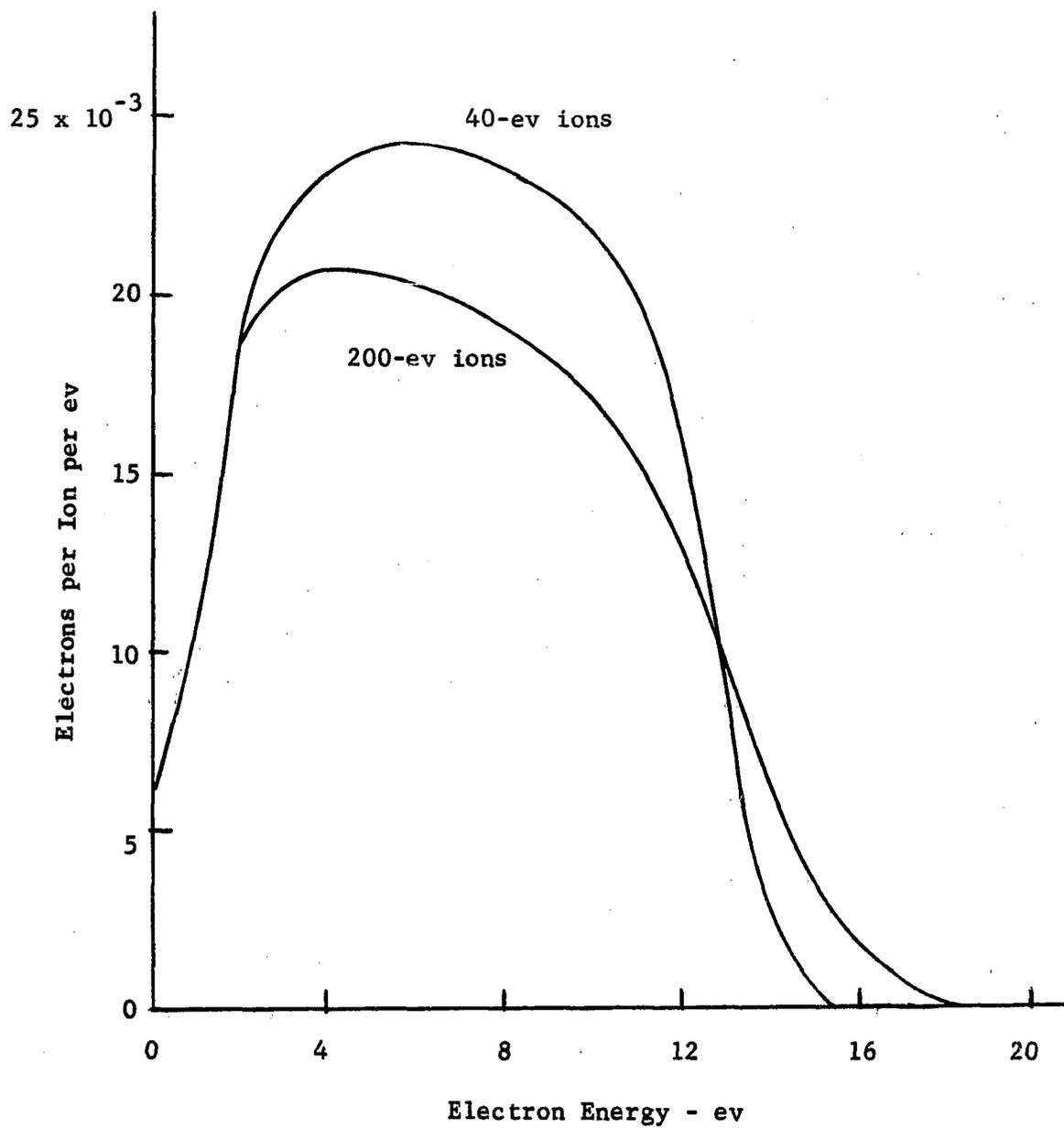
Positive ions are one of the most common and prolific agents which produce electron emission from a metal surface. The number of electrons produced per impacting ion, γ_1 , varies widely with the nature and energy of the ion and the nature and condition of the metal. The phenomena is caused by two distinct processes (88, p. 637); potential ejection at low ion energies, and kinetic ejection at higher energies. In potential ejection the ion approaches to within a few angstroms of the metal surface. At this point the field of the ion lowers the energy level of the metal sufficiently for an electron to tunnel through and neutralize



Energy Distribution of Secondary Electrons

Ejected from Mo. by 40-ev Argon Ions

Figure 5



Energy Distributions of Secondary Electrons
Ejected from Mo. by He⁺ Ions of 40 and 200 ev

Figure 6

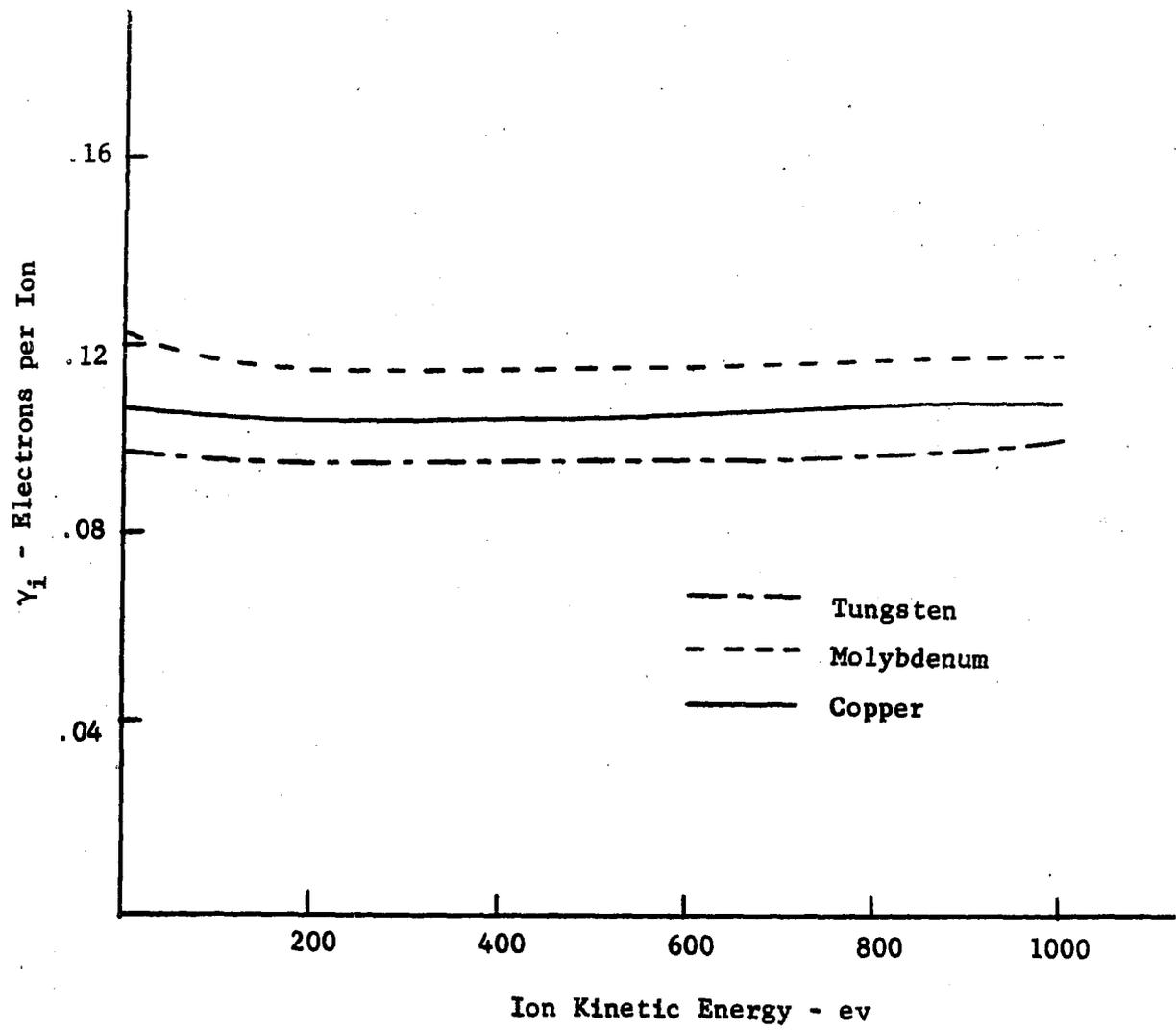
the ion. The energy released by the electron is absorbed by a second electron which may then escape from the conduction band of the metal. The second electron most frequently does not escape, for if its motion is in any direction other than towards the surface it will dissipate its energy in the lattice of the metal. This process requires that the ionization energy of the ion must be at least equal to twice the work function of the metal, any excess being carried away by the second electron. The neutralized ion then strikes the metal and is reflected as a neutral atom, less than 0.1 percent being reflected as ions (88, p. 656). The process effectively results in one electronic charge being carried to the metal by the ion and, if the second electron escapes, one charge being carried away as an electron.

Kinetic ejection normally occurs at energies greater than any attained by ions in a glow discharge. This process is not so well understood but is thought to be caused by excitation of bound surface states. Figure 7 (40, p. 672) shows the emission in argon. The original source showed the yield from tungsten and molybdenum. The curve for copper was interpolated, based on the work function of copper compared with that of the other two metals. It will be noted that argon on copper gives a nearly constant yield of

$$\gamma_i = 0.1 \quad (11)$$

This is the value that will be used in future calculations.

Fast neutral atoms, also, may cause the emission of electrons from metals, however they are effective only at energies generally above 1000 electron volts (28, p. 39). This may be explained by examination of the emission process. It can be seen from the previous discussion of



Electron Yield by Argon Ions

Figure 7

emission by ions that the ion removes an electron from the metal, by means of its potential energy, while still a short distance from the metal. It then strikes the metal as a neutral atom but this final impact is ineffectual in removing electrons unless the ion has a large kinetic energy. It is logical, then, that a neutral atom, carrying no potential energy, would behave in the same manner and cause electron emission only at high kinetic energies. This has been found to be true. There will be a supply of fast neutral atoms striking the cathode. These will be produced, as discussed earlier under Ion Energy, by those ions undergoing charge exchange near the cathode. Fast neutrals produced further from the cathode lose half their energy upon each impact with other gas atoms, hence cease to be fast atoms after several collisions. The fast neutrals which strike the cathode will have a maximum energy, from equation (10),

$$K. E. = 0.158V_c .$$

Before they may become efficient agents for electron emission they must have a kinetic energy of approximately 1000 electron volts, giving

$$V_c = 1000/0.158 = 6300 \text{ volts,}$$

a value far above any used for sputter determination. Electron emission by fast neutral atoms will, therefore, be eliminated from further consideration.

Photoemission is a process that is known to be quite effective in ejecting electrons from a metal. The analysis of this complicated process is based on that given by Little and von Engel (75, p. 220).

The total electron current from the cathode is

$$j^- = \gamma_i j^+ + Dj^- + Pj , \quad (12)$$

with j^- = total cathode electron current

j^+ = cathode ion current

γ_i = electrons emitted per ion striking the cathode

$D = n_d f_d \gamma_d$ = number of electrons emitted from the cathode by photons from the dark space, for each electron leaving the cathode. The components of D are:

n_d = photons created in the dark space for each electron leaving the cathode

f_d = fraction of photons reaching the cathode

γ_p = electrons leaving the cathode for each incident photon.

$P = n_g f_g \gamma_g$ = number of electrons emitted from the cathode by photons from the glow for each electron entering the glow. The components of P are:

n_g = photons created in the glow for each electron entering the glow

f_g = fraction of photons reaching the cathode

j = electron current entering the glow from the Crookes dark space.

This is also the total tube current for the following reason. Few, if any, ions can pass from the glow to the Crookes dark space as there is a slight decelerating field at this point; thus, the electrons entering the glow constitute the total current across this interface.

The total current at the cathode is the sum of the ion and electron currents

$$j = j^- + j^+ .$$

Substituting this value in equation (12)

$$j - j^+ = \gamma_i j^+ + Dj - Dj^+ + Pj$$

and
$$j^+ = j(1 - D - P)/(1 - D + \gamma_i) . \quad (13)$$

The value of P will be determined next. The coefficient for electrons produced per photon, of from ten to twenty electron volts energy, is nearly independent of the photon energy and is approximately

$$\gamma_p = 0.1 . \quad (14)$$

This energy range includes both the resonance and ionization potentials of argon. The number of photons emitted from the negative glow per electron entering, n_g , is given by the number of fast electrons entering times the number of photons produced by a fast electron. The number of photons produced by a fast electron is of the order of but larger than the number of ions produced by the electron. Fast electrons are taken to be those with energy greater than one hundred volts. They are assumed to have the energy of the potential between their point of creation and the glow, thus all electrons coming from a distance y will have energies greater than 100 electron volts. This distance may be found from equation (1),

$$V = \frac{2V_c}{d} \left(x - \frac{x^2}{2d} \right) ,$$

where V is the potential from the cathode and d is the length of the dark space. This may be converted to the potential V_g from the glow to point y from the glow by substituting

$$V_g = V_c - V$$

and
$$y = d - x ,$$

giving
$$V_c - V_g = \frac{2V_c}{d} \left(d - y - \frac{d^2 - 2dy + y^2}{2d} \right) ,$$

and
$$V_g = (y/d)^2 V_c .$$

The distance y from the glow to the point having a potential of 100 volts

is then

$$y = d(100/V_c)^{\frac{1}{2}}.$$

Electrons will multiply cumulatively from the cathode where

$$y = d$$

to y , giving

$$\exp s \left(d - d(100/V_c)^{\frac{1}{2}} \right)$$

fast electrons entering the glow for each electron emitted from the cathode, with s the average ionization coefficient in the dark space. Similarly, a total of

$$\exp(sd)$$

electrons will enter the glow for each electron leaving the cathode. Thus the ratio of fast to total electrons entering the glow is

$$\frac{\exp \left(sd - sd(100/V_c)^{\frac{1}{2}} \right)}{\exp(sd)} = \exp \left(-sd(100/V_c)^{\frac{1}{2}} \right).$$

The average energy of the fast electrons which enter the glow will be less than the glow potential V_c by some factor b . The number of photons produced by one fast electron which loses all its energy in the glow will be a factor c times the average energy of the fast electrons. Combining the above expressions gives

$$n_g = cbV_c \exp \left(-sd(100/V_c)^{\frac{1}{2}} \right)$$

photons emitted from the glow for each electron entering. The expression for P is, therefore

$$P = f_g \gamma_p n_g = f_g \gamma_p cbV_c \exp \left(-sd(100/V_c)^{\frac{1}{2}} \right). \quad (15)$$

Since $sd = (s/p)pd$,

equation (15) may be written

$$P = f_g V_c cb \gamma_p \exp \left(-(s/p)pd(100/V_c)^{\frac{1}{2}} \right). \quad (16)$$

The numerical value of P may be found by inserting known values from experimental data for nitrogen into equation (16). The various states, and most experimental curves, for nitrogen and argon are very nearly the same so it does not seem unreasonable to use the nitrogen data for argon in deriving this approximation. The values used are

$$\frac{f V}{g c} = 110 \text{ a constant.}$$

The explanation for this is that as the voltage increases the energy of the electrons entering the glow increases, which increases the range and hence the length of the glow. As the center of photon production moves away from the cathode the fraction of the photons reaching the cathode is decreased by a geometrical factor and increased absorption and scattering in the gas. The result is that approximately the same number of photons reach the cathode whether a few are produced nearby or many further away.

$$\gamma_p = 0.1 \text{ electrons per photon striking the cathode, from equation (14).}$$

$$cb = 1/50 \text{ meaning 50 volts of the average energy of fast electrons are required to produce one photon.}$$

$$s/p = 8 \text{ ions per centimeter produced in the dark space}$$

$$pd = 0.07 \text{ centimeters-millimeters of mercury, from figure 4.}$$

These values in equation (16) give

$$P = 110 \times 0.02 \times 0.1 \exp \left(-8 \times 0.07 (100/V_c)^{\frac{1}{2}} \right),$$

or

$$P = 0.22(0.57) (100/V_c)^{\frac{1}{2}}$$

electrons emitted from the cathode by photons from the glow, for each electron entering the glow. The value of P varies by only ten percent from a mean value of 0.18 as V_c varies from 400 to 2500 volts, therefore the mean value will be used for all calculations. Thus the final value of

P is

$$P = 0.18 \quad (17)$$

The quantity D in equation (13) remains to be determined. Since there is such a paucity of data on the creation of photons in the dark space, it will be assumed that each electron creates photons at about the same rate as it creates ions. Also, new electrons created by ionizing collisions between atoms and old electrons will, in turn, create photons. The exponential production of photons gives

$$n_d = \exp(sd) = \exp(sp/p)$$

From the legend below equation (12)

$$D = n_d f_d \gamma_p$$

The value of f_d will be taken as 0.5 and γ_p from equation (14) is 0.1.

Values of

$$s/p = 8$$

and

$$pd = 0.07$$

were previously determined. These values are inserted in the expression for D giving

$$D = 0.5 \times 0.1 \exp(8 \times 0.07) = 0.087 \quad (18)$$

Equation (13) shows that D is subtracted from both the numerator and denominator which, coupled with its small value in relation to P and γ_i , shows the ineffectiveness of photons from the dark space in emitting electrons from the cathode.

The value of the ion component of the tube current may now be obtained by substituting

$$\gamma_i = 0.1 \text{ from equation (11)}$$

$$P = 0.18 \text{ from equation (17)}$$

$$D = 0.087 \text{ from equation (18)}$$

into equation (13), giving

$$j^+ = j \frac{1 - D - P}{1 - D + \gamma_i} = j \frac{1 - 0.087 - 0.18}{1 - 0.087 + 0.1} = 0.7j, \quad (19)$$

which shows that ions constitute 0.7 of the cathode or total discharge current. This is the factor that will be used in final calculations of sputter.

Metastables, or long-lived excited atoms, are the final agents which might contribute to the emission of electrons from the cathode. Metastable atoms are known to be effective agents for producing electron emission from metals (28, p. 39). They are frequently mentioned as being active in gas discharges but there is very little published information on the definitive part played by these agents. There is also a dearth of experimental data on metastable production coefficients, what little there is being mainly on helium. The primary difference between normal excited states and metastables is that the lifetime of the latter is very much greater. Normal excited atoms exist for only about 10^{-8} seconds and then decay, according to selection rules, to a lower state, with the emission of a photon of radiation. During this short life, these atoms are very unlikely to drift from their point of creation to the cathode. Metastables exist in a state from which there is very small probability, according to selection rules, of their decay. This small probability is the cause of them having lifetimes of the order of one tenth of a second. During this period the particle may travel considerable distances, thus greatly increasing its chance of striking the cathode and causing the emission of an electron. Since the metastable is electrically neutral it, unlike the ion, receives no energy from the electric field; instead, its movement is governed by its thermal velocity, plus any concentration gradient which may exist.

In the absence of other information, it might be assumed that metastables are produced in the dark space at approximately the same rate as ions. The ion concentration is uniform in the dark space, as may be demonstrated by substitution from equation (1) in the Poisson equation. If the metastables conformed with the ion distribution, there would be no concentration gradient and hence no diffusion. The metastables, being uninfluenced by the electric field, are unlikely to conform to the ion distribution gradient. If a decreasing gradient towards the cathode exists, metastables will have a diffusion component of velocity towards the cathode. In view of the lack of contrary information, and also because most published treatments of the glow do not account for metastable contributions to the cathode current, it will be assumed that only those metastables created near the cathode live long enough to reach the cathode under the weak influence of thermal and diffusion forces and hence the effects of metastables may be ignored. This view may be further justified by examination of the mechanism of electron emission by metastables. If the metastable potential energy is greater than the work function of the cathode metal, which is true for copper in argon, it may produce the emission of an electron upon striking the metal. The potential energy of the metastable is transferred to an electron in the conduction band, permitting this electron to escape if its motion is towards the surface. The successful process thus contributes to the electron stream from the cathode but not to the positive current into the cathode. Also, the number of metastables has been assumed, above, as a function of the total number of electrons leaving the cathode. Examination of equations (12) and (13) shows that the metastable coefficient would enter this equation in the same manner as the coefficient

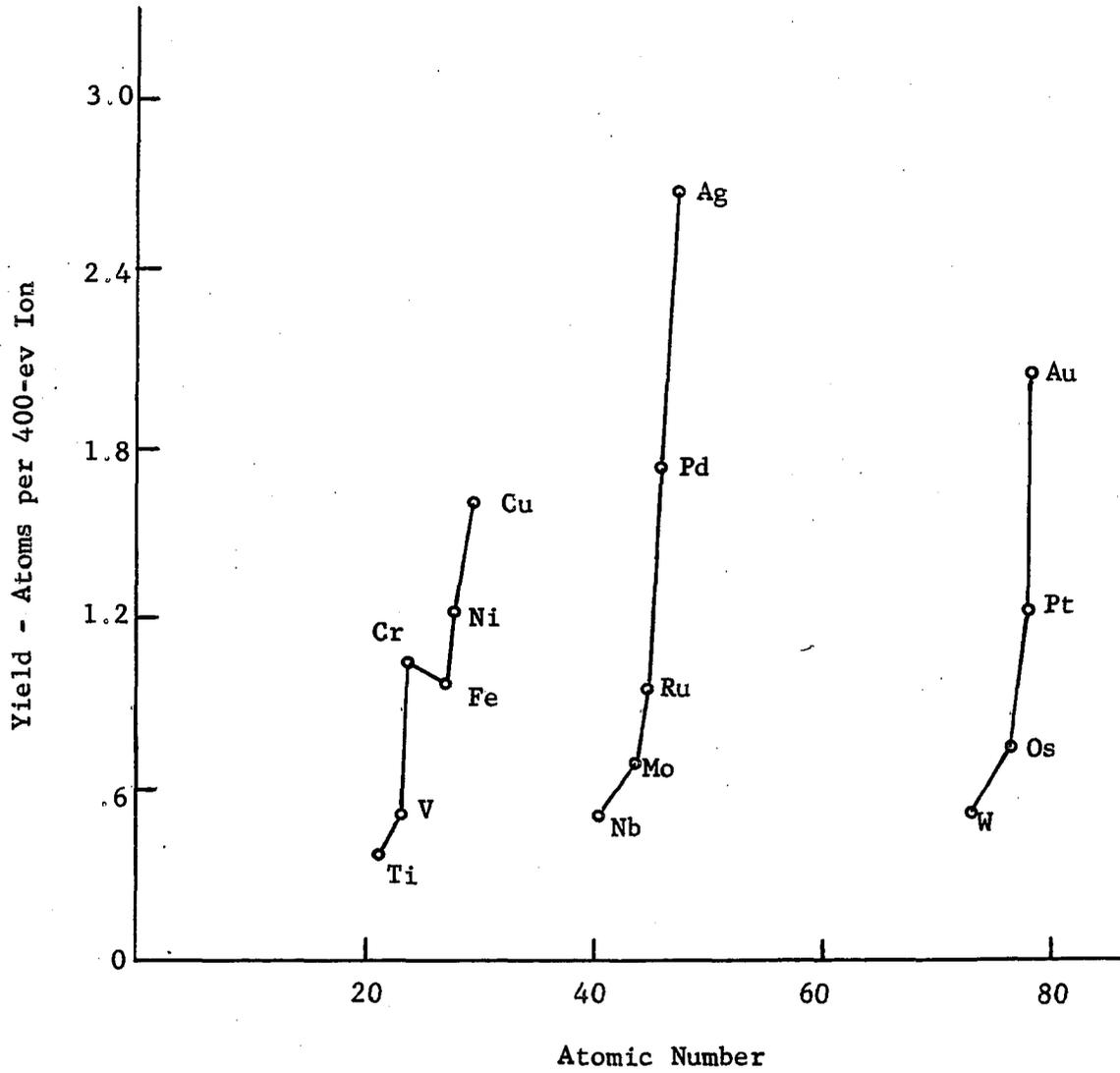
D. Since it would be subtracted from both the numerator and denominator, its effect on the ion current would be minimized.

The analysis of this section shows that the cathode current is composed of only a positive ion component and an electron component which is created by electrons emitted from the cathode by positive ions and photoelectric radiation. Furthermore, the ion component is related to the total current by equation (19).

Sputter Yield

The gross sputter yield, Y_g , is defined as the number of sputtered atoms per impacting ion. There are several factors which govern the relative yields of various gas-metal combinations. Some metals, especially aluminum and magnesium, sputter slowly because of oxide formation on their surface. The yield increases with the atomic weight of the gas atom. Wehner (66, p. 365) has found that the yield increases for metals as the d shell, in the periods of the table of elements, fills. This is shown in figure 8. The higher yield with increase in weight of the gas and the filling of the d shell is interpreted to mean that such conditions prevent the gas ion from penetrating deeply into the metal where its energy would be less effective in causing sputter. The gas atom is more effective in removing atoms from the metal when its energy is transferred to surface layers.

For a given gas-metal combination there are additional conditions which effect the yield. The yield increases with the angle of incidence of the gas projectile. This, also, is believed to be a result of the greater effectiveness of the ion when it operates on surface atoms. The yield increases with the smoothness of the metal surface. Irregularities



Sputtering Yields for 400-ev Argon Ions on

Various Elements

Figure 8

of the surface, which obstruct the path of a sputtered atom, prevent the escape of the atom. The primary determinant of the yield is the kinetic energy of the impacting ion. There is a threshold value of ion energy, for each gas-metal combination, below which no sputtering takes place. Wehner (122, p. 633) has determined a formula for this threshold which depends on; the atomic weights of the gas and metal, the heat of sublimation of the metal and the velocity of sound in the metal. Above the threshold the yield increases fairly rapidly with increasing ion energy to a broad maximum, dependent on the gas-metal combination, and then falls slowly. The point of maximum yield varies from ion energies of four thousand electron volts for helium to over fifty thousand for xenon.

Langreid and Wehner (66, 67) have determined the yields for many metals as a function of the kinetic energies of the ions of various gases. The result for copper in argon is shown in figure 9. The portion of this curve which is of primary interest for the purpose of this paper can be determined from equation (10),

$$\text{K.E.} = 0.158V_c \text{ ion energy in electron volts.}$$

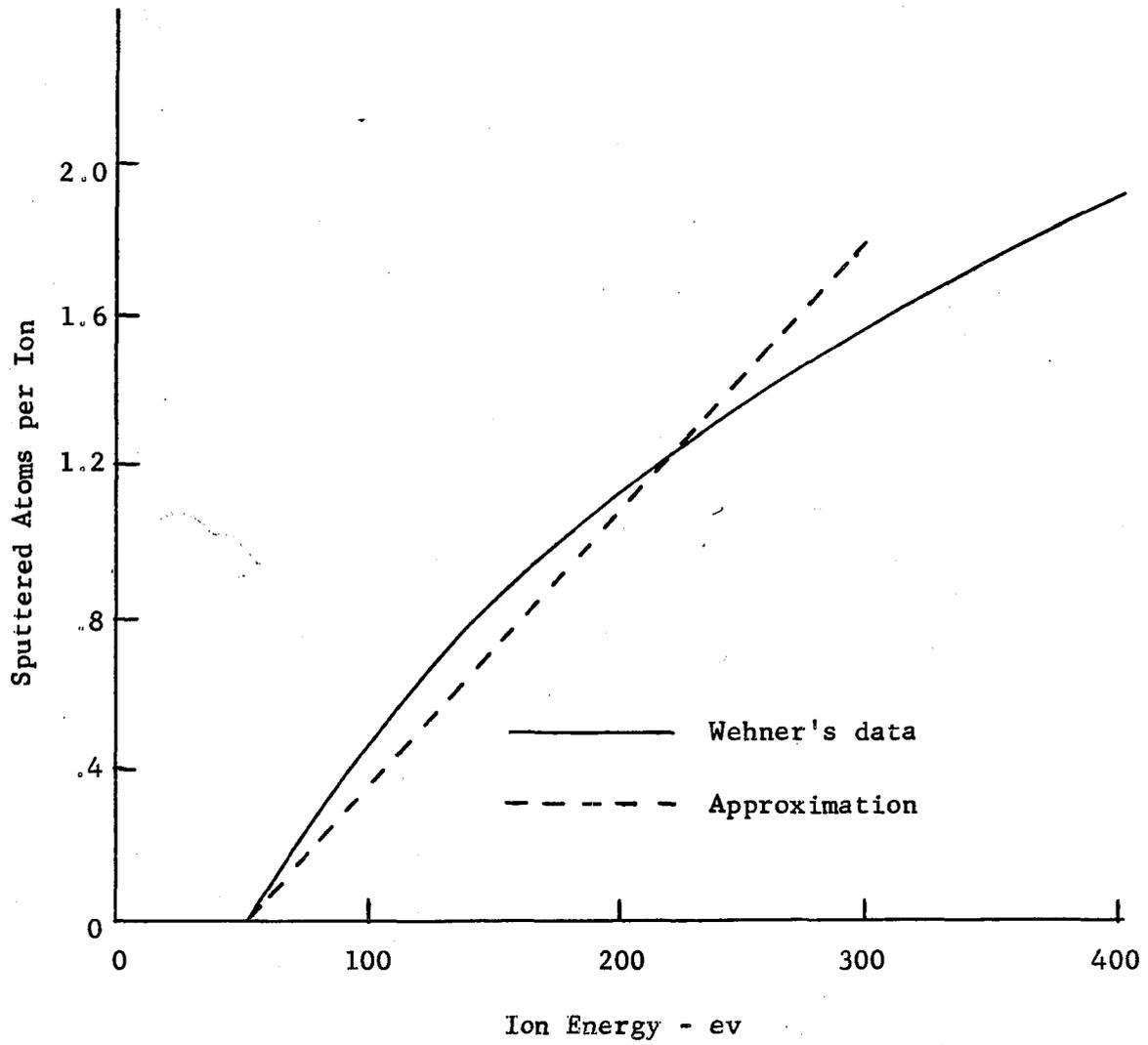
Most laboratory runs were made with cathode fall potentials of less than 2000 volts. Substitution in equation (10) gives

$$\text{K.E.} = 0.158 \times 2000 = 316 \text{ volts.}$$

The curve for copper in figure 9 can be closely approximated from the threshold at 60 volts to the maximum value of interest at 300 volts, by the line shown. The equation of this line is

$$Y_g = (1.8/240)(\text{K.E.} - 60) .$$

The value of the kinetic energy from equation (10) is next entered in this expression for yield to obtain



Sputtering Yield for Argon Ions

Figure 9

$$Y_g = (1.8/240)(.158V_c - 60) = 1.19(10)^{-3}(V_c - 380) \quad (20)$$

atoms per impacting ion as the expression to be used for gross ionic sputter yield. The yield from fast neutral atoms will be included in equation (27), page 68.

The gross yield of sputter just determined must be corrected to give the net yield, the difference lying in those sputtered atoms which are returned to the cathode. The difference between the gross and net amounts of sputter is recognized by all authorities on the subject and is often listed as one of the major obstacles in deriving dependable sputter data from the glow discharge. Townes (112, p. 320) is the only one who has made a positive contribution to the solution of this difficulty. His work is frequently quoted and is the only such effort which is referred to. Because of the uniqueness of his effort, Townes' solution will be derived.

The following definitions will be used:

dS_1 = vector element of cathode surface S_1

dS_2 = vector element of surface S_2 surrounding cathode on which sputtered material is deposited.

J_0 = rate at which atoms leave the cathode surface

J = rate of deposition on S_2

N = concentration of cathodic atoms between S_1 and S_2

D = diffusion coefficient of sputtered atoms in discharge gas

v = average velocity of sputtered atoms in discharge gas

L = mean free path of sputtered atoms in discharge gas

j = current density of sputtered atoms in discharge gas.

From diffusion theory (48, p. 162)

$$j = Nv = -D\nabla N,$$

therefore the rate of deposition is

$$J = -D \int_{S_2} \nabla N \cdot dS_2$$

Kinetic theory analysis shows that the current density of particles is

(15, p. 44)

$$j = vN/4, \quad (21)$$

therefore the rate at which atoms return to the cathode is

$$J_0 - J = (v/4) \int_{S_1} N \cdot dS_1$$

The preceding equation is derived on the assumption that the only losses from N are the atom currents going to the receiver and those being returned to the cathode. J_0 is assumed constant; therefore, in the steady state the atom concentration must satisfy the Laplace equation

$$\nabla^2 N = 0$$

with the boundary conditions

$$(v/4) \int_{S_2} N_2 \cdot dS_2 = -D \int_{S_2} \nabla N_2 \cdot dS_2 = J \text{ at } S_2$$

and
$$(v/4) \int_{S_1} N_1 \cdot dS_1 - D \int_{S_2} \nabla N_2 \cdot dS_2 = J_0 \text{ at } S_1$$

If $J_0 \gg J$ and if atoms are emitted uniformly over the cathode, the boundary conditions become

$$N_2 \approx 0$$

and
$$J_0 \approx (v/4) N_1 S_1,$$

where N_1 and N_2 are the values of N at S_1 and S_2 respectively.

N may be written as

$$N = f(x,y,z) N_1 = (4J_0/S_1 v) f(x,y,z)$$

and
$$J = (-4DJ_0/S_1 v) \int_{S_2} \nabla f \cdot dS_2,$$

where f is a solution of the Laplace equation which is zero on S_2 and unity on S_1 . From kinetic theory (78, p. 265)

$$D = \pi v L / 8 .$$

Therefore,

$$J = -(\pi J_0 L / 2 S_1) \int_{S_2} \nabla f \cdot dS_2 .$$

For the case where S_1 and S_2 are two equal parallel planes, separated by a distance d , the function f is

$$f(x) = 1 - x/d$$

and

$$\nabla f = -1/d$$

$$J = -\left(\frac{\pi J_0 L}{2 S_1}\right) (-1/d) S_2 = \pi J_0 L / 2d \text{ atoms deposited}$$

per second. From this result it is seen that the approximation

$$J_0 \gg J$$

is justified when

$$L \ll d .$$

The above derivation from Townes is certainly original and elegant but it possesses several weaknesses which cast doubt on the validity of the results. First, it ignores the velocity of emission of sputtered atoms. Ions will strike the cathode nearly normally, since this is the direction of the field and the field velocity of the ions is much greater than their random thermal velocity. It has been found (88, p. 655) that ions of several hundred volts energy, upon striking the cathode normally, cause the emission of atoms which have an initial energy of some tens of volts and whose initial directions of motion are distributed in proportion to the cosine of the angle their direction of motion makes with the normal to the cathode (Knudsen's cosine law). Normal diffusion, according to

Holland (50, pp. 406, 422), can take place only after the metal atoms have lost their initial energy through impact with gas atoms. Second, it uses the standard expression $vN/4$ from kinetic theory for the number of particles crossing unit surface in unit time. McDaniel (88, p. 580) points out that this expression applies only where there is no concentration gradient. It is very doubtful, in view of the initial energy of the metal atoms discussed above, that there will be zero concentration gradient toward the cathode at the cathode surface. Third, Townes' derivation is idealized in that he ignores all lateral losses from the atomic stream. This would be acceptable for electrode configurations such as concentric spheres or infinite parallel plates but certainly not for parallel plates whose separation is of the order of, or greater than, the electrode diameter. Finally, actual laboratory runs showed that observable sputter deposits existed as much as 150 free path lengths from the cathode. Townes assumes negligible sputter at the order of 10 path lengths away.

In addition to the above deficiencies of Townes' method, it was found that its application to the present work required that additional assumptions concerning the atom concentration be made to fit the configuration of the cylindrical collecting surface. For all of the above reasons Townes' formulation of the net quantity of sputter was not used even though it is the only quantitative analysis known.

The method adopted for obtaining the net sputter from the gross amount was to take one half of the latter. The basis for this calculation is as follows. If a sheet of one gas were created, and constantly replenished at some location in a cylinder containing a second gas, the first gas would diffuse in equal quantities in both directions. The conditions

in the discharge chamber under discussion conform with the above example. A cloud, or sheet, of metal atoms is created in front of the cathode where the energetically emitted atoms approach thermal energies through collision with gas atoms. This cloud diffuses equally in both linear directions; half returning to the cathode and half diffusing towards the anode. The latter group will also diffuse radially and condense on the enclosing sleeve. This radial movement and deposit will constantly remove atoms from the stream so that the deposit decreases constantly with distance from the cathode. This reduction factor of one half applied to equation (20) gives

$$Y = 0.595(10)^{-3} (V_c - 380) \quad (22)$$

as the net yield of sputtered atoms for each ion striking the cathode.

The weight of sputtered copper atoms is given simply by multiplying the atomic weight of copper by the atomic mass unit, where

$$\begin{aligned} 63.54 &= \text{atomic weight of copper} \\ 1.66(10)^{-21} &= \text{atomic mass unit in milligrams} \\ W_a &= 63.54 \times 1.66(10)^{-21} = 1.06(10)^{-19} \quad (23) \end{aligned}$$

milligrams per sputtered atom.

The final formulation for the amount of sputter produced in a glow discharge, employing argon gas and copper electrodes, may now be made.

Noting that the surfaces of the electrodes are one square centimeter, making the current and current density identical, equation (19) shows that the ion current in terms of tube current is

$$i^+ = 0.7i \quad (24)$$

The ion current may be converted to number of impacting ions per second by

$$N^* = (10)^{-3} i^+ / e = 0.7i \times 0.624(10)^{16} = 0.437(10)^{16} i, \quad (25)$$

where i is current in milliamperes.

The net number of atoms sputtered by ions per second, N_1 , is obtained by combining equation (25) above with equation (22):

$$N_1 = N^*Y = 0.437(10)^{16} \times 0.595(10)^{-3} (v_c - 380),$$

$$\text{or } N_1 = 2.6(10)^{12} (v_c - 380)i. \quad (26)$$

This value of atoms sputtered by ions must be increased by one-third to account for sputtering by fast neutral gas atoms, as discussed previously, on page 27, giving

$$N = 3.46(10)^{12} (v_c - 380)i \quad (27)$$

total number of atoms sputtered per second.

The weight, W_s , in milligrams of sputter per second is found by multiplying the value of W_a from equation (23) by N in (27):

$$W_s = W_a N = 1.06(10)^{-19} 3.46(10)^{12} (v_c - 380)i,$$

$$\text{or } W_s = 3.66(10)^{-7} (v_c - 380)i. \quad (28)$$

The total weight of sputter is provided by multiplying equation (28) by $60t$

$$W = 3.66(10)^{-7} (v_c - 380)i 60t$$

$$\text{or } W = 2.2(10)^{-5} (v_c - 380)ti \quad (29)$$

milligrams of sputter, with t in minutes and i in milliamperes. Equation (29) is the final equation for the total amount of sputter produced.

CHAPTER IV

EQUIPMENT AND PROCEDURE

Equipment

The fundamental quantity to be determined in a study of sputtering is the amount of sputtered material produced under various controlled conditions. Over the years a variety of methods have been used to determine this quantity. Güntherschultze (33, p. 79) suspended the cathode from a calibrated spring and computed the material lost by the upward displacement of the cathode. The General Electric Company of England employed a filamentary cathode and measured the loss of weight by the increased resistance of the wire. Other workers have used spectroscopic, light transmission, optical interference and resistance measurements to determine the thickness of a measured area of deposit. The simplest and most feasible procedure is to weigh the deposit and this, with optical verification, was the technique employed in the present work.

The decision to determine sputter by weight dictated that the cathode and collecting surfaces should be of minimum size and weight in order that the small amount of sputter expected would have the largest possible ratio to the weight of the weighed component. The only practical method of attaching the cathode to a support was by means of a threaded connection. No adhesive could be used because it would be subjected to considerable heat, would interfere with heat conduction from the cathode to the support

and would introduce extraneous material into the weighing process. Six millimeters was found to be about the minimum cathode thickness which permitted suitable threading. To satisfy the above two requirements a cylindrical cathode of one square centimeter cross section and six millimeter thickness was selected.

The vacuum chamber, figures 10 and 11, was constructed from two standard Pyrex, 702EJ, "O"-ring sections of twenty-five millimeters inside diameter and twenty centimeters length. These sections were provided with flared ends and a groove to accommodate a rubber "O"-ring vacuum seal. The demountable vacuum seal originally consisted of a machined collar and end plate, bolted together and compressing the rubber ring. This arrangement provided a good seal but there was a tendency for the collar to crack the flared end of the tube when the bolts were tightened. To remove this difficulty three eight millimeter diameter polystyrene insulating rods, slightly longer than the tube, were fitted at each end with one-eighth inch diameter threaded metal rods. When these assemblies were secured to the end caps with nuts the pressure was applied longitudinally and no glass damage was experienced. One-half centimeter diameter outlets were provided at each end of the chamber for pump, gauge and gas.

The electrodes were threaded and screwed onto one square centimeter cross section stand-off supports which, in turn, were screwed onto the sealing end caps. No provision was made for moving the electrodes during an experiment; instead, a set of supports of varying lengths was made so that any desired separation of the electrodes could be achieved.

It was foreseen that there would be a problem of conduction from the lateral surfaces of the electrodes and supports and from the inside face

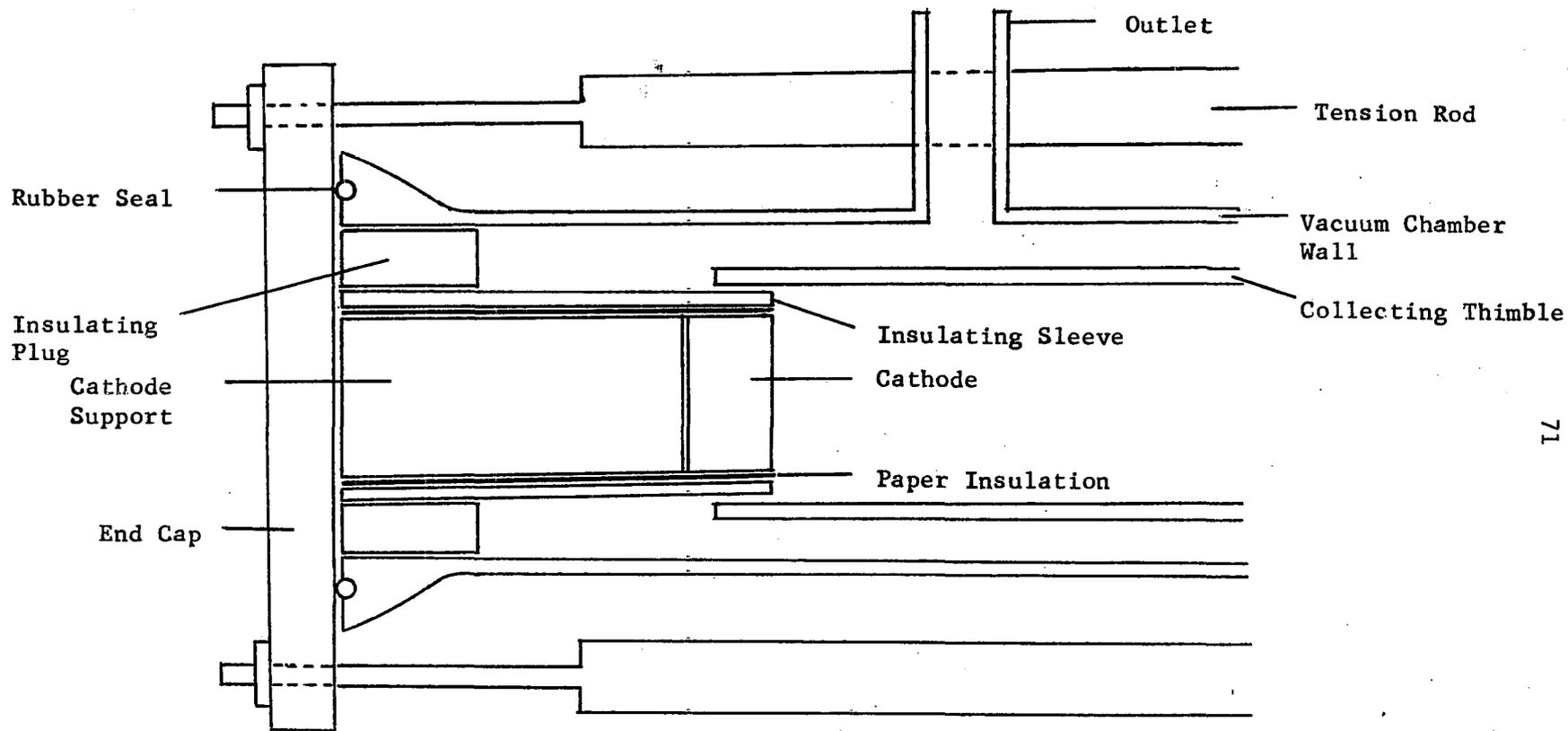


Diagram of Test Chamber

Figure 10



Photograph of Test Chamber

Figure 11

of the end plates. Such conduction could not be permitted since only the known area of the faces of the electrodes could be allowed to conduct if any meaningful quantitative results were to be obtained. Although the problem of conduction from undesired surfaces was foreseen, the difficulty of its elimination was not. It was anticipated that some common insulating coating would very simply eliminate it. A first crude attempt was made by coating such surfaces with a readily available liquid plastic, nail polish. This worked surprisingly well at lower voltages and temperatures but broke down at higher voltages, especially as the temperature of the cathode rose. Next, a coating of red glyptol insulating varnish, with a dielectric strength of 1400 volts per mil and an operating temperature of 300 degrees Fahrenheit, was used. This worked satisfactorily, except in areas near the cathode where the temperature was highest, and here it broke down and permitted conduction. A commercial preparation by the trade name of "No-Arc," with breakdown at 2500 volts per mil and no specified operating temperature was used, but with the same results that were experienced with the glyptol. The electrodes and their supports were then encased in close-fitting glass sleeves. The small annular gap between the sleeve and the electrode was filled with paper around the cathode. This method completely insulated the electrode and support and did not break down at high temperatures.

An attempt was made to insulate the end cap with a glass disk but this was not effective due to fabrication difficulties, disk breakage when the vacuum seal was applied and poor vacuum seal. Insulation of the end caps was finally achieved through the use of molded plastic plugs, one inch in length and provided with a hole in the center for the electrode support. The plugs were made from "Eccogel" potting epoxy resin, using one and one-half

parts of hardener to one part of basic material and curing at two hundred degrees Fahrenheit for three hours. The tube itself was used as a mould, after lubrication with vacuum grease to prevent adhesion of the resin to the tube. These plugs effectively insulated the end caps at all temperatures encountered. The use of the glass sleeves and end plugs enabled the tube to operate smoothly from zero to three thousand volts. This range of voltage covered all phases of gas discharge; from the Townsend discharge, through the normal and abnormal glows and into the arc. Naturally there were points of instability in passing from the dark discharge to the glow and from the abnormal glow to the arc.

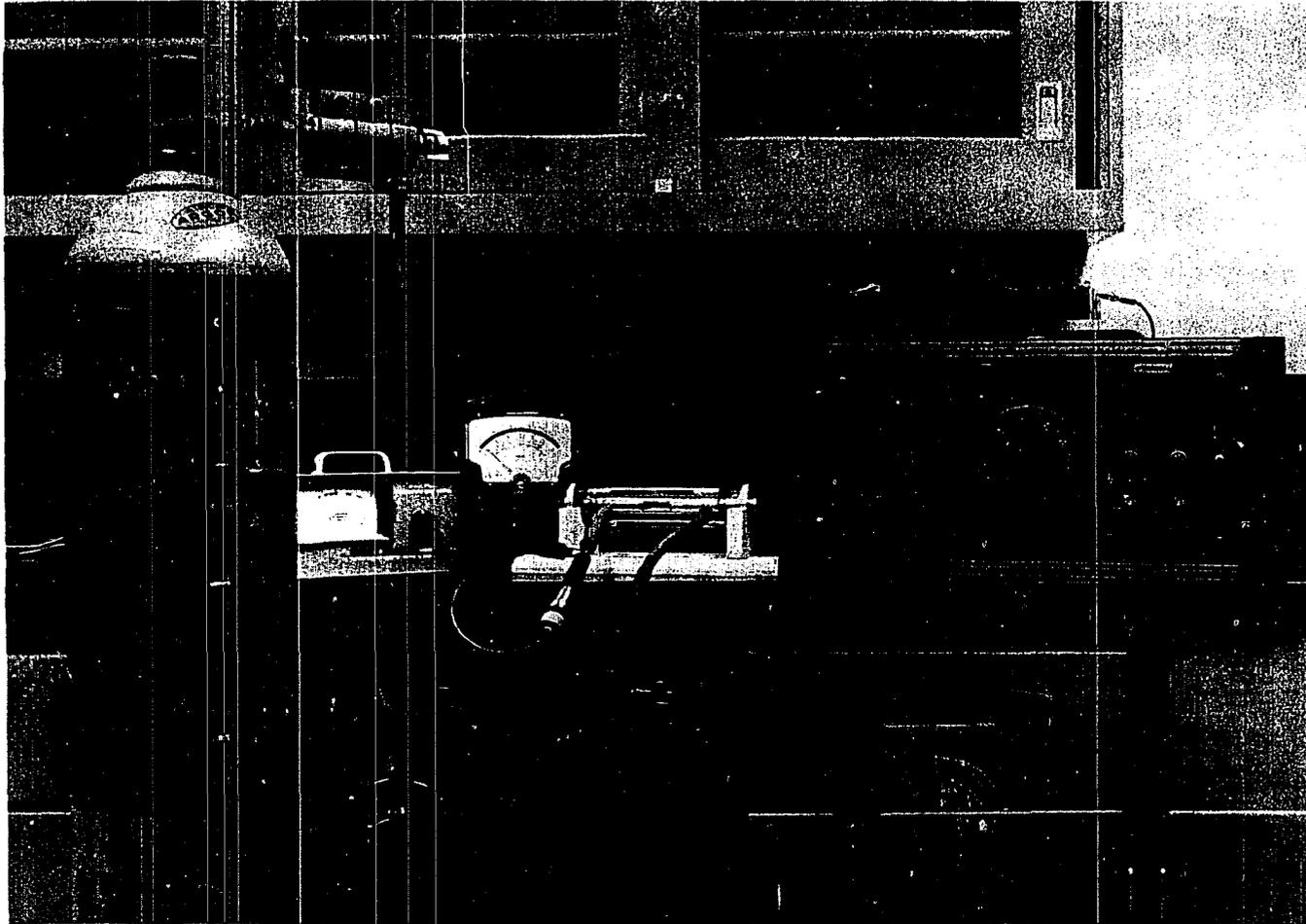
A fifteen millimeter-diameter glass thimble, which gave a sliding fit; i.e., close but not vacuum-tight, was fitted over the electrode sleeves to contain the discharge and to collect the metal sputtered from the cathode. Generally, discharge runs were made with an electrode gap of approximately three centimeters. This distance was sufficient to sustain the cathode fall, negative glow and a small section of the positive column. These phenomena were the ones of interest. Occasionally the gap was lengthened to as much as fifteen centimeters in order that the positive column and striations could be studied.

Accessory equipment. The power supply consisted of a rectifier and capacitive-input filter, constructed in the Electrical Engineering shop, and rated at 3000 volts, continuously variable, and 300 milliamperes. A Wegner mechanical pump, number 1410, was used for most runs. This pump is rated to produce ten microns (millitorrs) of mercury but, probably because of age and wear, about fifty microns in five hours of pumping was the lowest vacuum produced. An oil diffusion pump, of hybrid construction, was available

during one period and it would evacuate to less than one micron of mercury. The vacuum gauge was a Kinney thermocouple type, model KTG-1. This gauge registered from one to three thousand microns but was very unreliable in the range of one millimeter and higher. A simple mercury column manometer, consisting of a three millimeter inside diameter glass tube formed into a one meter-long "U," was used for measuring pressures greater than about one millimeter of mercury. A Triplett multimeter, with current ranges of from 120 microamperes to 12 amperes, was used for current measurements. A ballast resistor bank, made up of five 2000 ohm, 200 watt resistors, was connected in series with the power supply and discharge tube. This ballast limited the discharge current to the 300 milliampere rating of the power supply, thus permitting operation in the high voltage portion of the abnormal glow without danger of heavy arcing and equipment damage. The 10,000 ohm resistor bank was used for most sputter data-collection runs; however, larger resistors, up to 25 megohms, were used at times for special purposes.

Commercial bottled argon was employed as the active gas. Normally commercial gases are about 99.2 per cent pure (42, p. 1473). The argon was fed to the tube through an Oxweld flow meter. The balance used for weight measurements was manufactured by Henry Troemmer, Philadelphia. This balance measured from 5 milligrams to 10 grams with pan weights. The balance-arm, which was graduated into 100 parts, was equipped with a 10 milligram rider. One graduation thus equalled .1 milligrams or 100 micrograms. Half graduations could also be read, giving 50 micrograms as the minimum detectable weight differentiation.

The equipment is shown in figure 12.



Photograph of Sputtering Equipment

Figure 12

Procedure

Sputtering Runs

Electrodes were prepared by first removing all visible contamination with metal polish and a cloth. Next they were washed in clear water and polished on a soft, lintless cloth. Finally they were rinsed in alcohol and air dried. When thoroughly dry the cathode was weighed and then attached to the electrode support. The support and electrode were inserted into a thin paper cylinder, this combination placed in a close-fitting glass sleeve, the end cap was screwed into the support, the end plug was fitted onto the sleeve, a rubber seal was lubricated with vacuum grease and placed against the plug, a clean glass collecting thimble was telescoped onto the sleeve, and this assembly was inserted into the vacuum chamber. The anode was prepared in a similar manner, excluding the weighing, paper sleeve and collecting thimble. The tension rods were placed in both end caps and securely tightened.

The assembled tube was placed in a holder, the pump was attached to one inlet and the gas supply and gauge were connected, by means of a tee joint and short rubber tubing, to the other. The power supply was connected to the tube through the milliammeter and 10 thousand ohm, one kilowatt resistor bank. Voltage readings were taken on the power supply meter. The ballast resistor limited the current to a maximum of 300 milliamperes, thus preventing heavy arcing and damage to the equipment. The power supply was fused and a sixteen milliamperes-blow fuse protected the milliammeter for normal currents.

A Wegner mechanical pump was employed to pump the vacuum chamber down to one hundred microns in thirty minutes. The tube was filled with

argon and repumped three times to clear out as much oxygen and residual gas as possible. In many runs the original pumping lasted for over three hours, a pressure of fifty microns being obtained. It was hoped that this method would remove more adsorbed residual gases from the chamber and compensate for the lack of proper degassing; i.e., heating in vacuo. The experimental values obtained after thirty minutes or three hours of pumping showed no detectable difference. An oil diffusion pump was available for a short period. This pump would quickly take the chamber to below one micron of mercury, the minimum reading of the vacuum gauge. Unfortunately, this pump was not available by the time that laboratory technique had been sufficiently well established to permit record runs to be made. Data on sputter behavior from one to one hundred microns of mercury might have been most interesting. Also, there is considerably more data on the parameters of the glow discharge for this range of pressures than for any other range.

After the vacuum chamber had been thoroughly flushed, argon was bled in slowly while the pump was kept in operation. The desired pressure could be set reasonably accurately with the flow meter valve. A clamp was fitted on the rubber tubing between the chamber and pump. Adjustment of this clamp enabled fine adjustment of the chamber pressure. Approximately ten minutes were allowed for the pressure to stabilize. The power supply voltage was then set to the desired value, the current was recorded and the time noted. The run was continued until observation of the sputtered film showed that a sufficient quantity of material had been removed to obtain reasonable weight measurements.

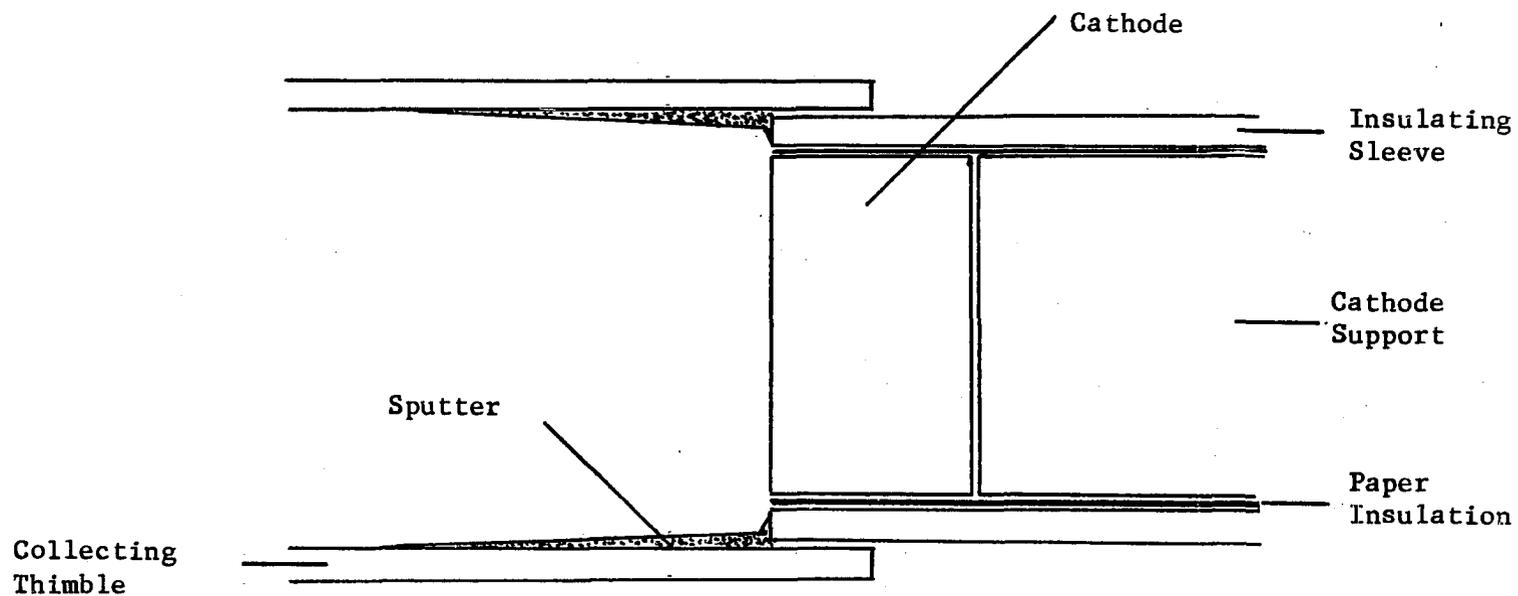
The discharge was then turned off and the cathode was removed and weighed. The difference between this weight and that taken before the run

gave the amount of material removed. Laboratory notes were made on the appearance of the cathode, the appearance and length of the film, and on any unusual observations made in the course of the experiment. The measured amount of sputtered metal was later compared with the amount predicted by the formula, equation (29).

Determination of Quantity of Sputter

Initially, attempts were made to obtain and weigh sputtered metal films. This was accomplished by covering the inside surface of the glow-enclosing thimble with cellophane or cellulose. The sputtered deposit was collected on the cellulose and the latter removed by dissolving in acetate. This method had the shortcoming that the heat developed, when heavy currents were drawn, warped and even charred the film nearest the cathode. Also, the process of dissolving the cellulose proved cumbersome and unsatisfactory.

A better method was found to be to collect the deposit directly on a glass thimble, slightly longer than the gap between electrodes. The thimble was carefully cleaned and weighed before receiving the deposit and then weighed with the deposit, the difference in weights being the amount of sputter. Most of the deposit would collect on the glass thimble, as shown in figure 13; however, some collected on the face of the circumference of the glass sleeve, which surrounded and insulated the cathode. No deposit was detectable on the anode, or its insulating sleeve, as long as these were kept more than two centimeters away from the cathode. The only other place for the sputter to go was for it to escape from the glow area defined by the electrodes and collecting thimble. In this event the material would condense on the walls of the main glass vacuum chamber; however, with many hours



Thimble - Showing Sputter Deposit
(Four times actual size)

Figure 13

of operation, there was never any evidence of a deposit on the chamber walls.

The plan for determining the amount of sputter was to: first, weigh the cathode loss and second, verify this loss by the weight of sputtered material collected. In early tests only the collecting thimble and anode were comparatively weighed to determine the collected sputter. During these tests it was found that the anode could be eliminated as a collector if it was placed more than two centimeters from the cathode. The amount of sputter collected on the thimble was appreciably less than the loss of weight of the cathode. Next, the insulating glass sleeve around the cathode was comparatively weighed, in addition to the thimble. The total material collected by the thimble and sleeve turned out to be appreciably greater than that lost by the cathode. This anomalous result led to lengthy tests and trials to eliminate the cause of the discrepancy.

Early tests had been conducted with air as the gaseous medium. At this time it was observed that the sputter, regardless of the metal used for cathode, was generally of a dull brown or nearly black color. Also, the resistance of most sputtered films was many megohms. It was assumed that the sputtered material oxidized, either in transit or on the walls of the thimble, with the plentiful supply of oxygen in the air. However, when inactive argon was used as the gas, the sputtered material still had the same general appearance as before. Since it was extremely difficult to construct a leak-proof, demountable, vacuum chamber, it was assumed that sufficient air was leaking in to provide the oxygen for oxidation.

Oxygen elimination. An attempt was made to eliminate the oxygen content of the sputtering tube, caused by air leaks through the tube end-seals. A four-inch diameter plastic tube, closed at one end and fitted with

a rubber-sealed cap at the other, was constructed. This large tube was fitted with four gas inlets and two electrical lead-ins. The small sputtering tube was inserted into the large tube. Two gas inlets inside the large tube were connected by flexible tubing to two inlets in the small tube and the two electrical connections were connected to the electrodes of the small tube, the other two gas inlets were connected to the argon supply and vacuum pump. The line to the vacuum pump was also connected, by a "tee," to a U-shaped glass tube containing mercury.

Both tubes were pumped down to 50 microns of mercury and then filled, to a pressure of two atmospheres, with argon. This was done three times and the third time valves were closed to seal the big tube at two atmospheres of argon pressure. The small tube was then pumped for an hour, to about one micron of mercury, to degas the vacuum chamber and its contents. Argon was then slowly bled into the working chamber until the desired working pressure, generally from 10 to 1000 microns of mercury, was obtained. A sputtering run was then taken.

Each pumping from 2 atmospheres, 1520 millimeters of mercury, to 100 microns, 0.1 millimeters of mercury, reduced the number of gas molecules by

$$1/15200, \text{ or less than } 10^{-4},$$

from the relationship

$$p = nkT$$

or

$$n = p/kT .$$

The subsequent addition of pure argon then diluted the air-argon ratio by

$$10^{-4} .$$

Since there are

$$3.54(10)^{15} \text{ gas molecules per cubic centimeter}$$

at 100 microns pressure, four pumping-flushing cycles should reduce the oxygen concentration to

$$3.54(10^{-4})^4 (10)^{15},$$

which is less than one oxygen molecule per cubic centimeter. Five cycles should reduce the oxygen content of the 4000 cubic centimeter pressure tube to less than one molecule. This calculation takes no cognizance of the small but indeterminate air leakage into the large pressure tube during the dilution process. Such unpreventable leaks would increase the final oxygen content to a small degree. There should be essentially no air leakage into the large pressure tube or associated tubing and connections after dilution is accomplished because the system is maintained at an argon pressure twice that of the surrounding atmosphere.

The system just described served only to prevent air leakage through the rubber-sealed end caps of the working tube. Some air will enter the latter through hoses and connections to the pump, gauge and argon supply.

Sputter runs were made with the equipment configuration just described. The sputtered films obtained by this method showed the same evidence of contamination that had been present in films produced by normal procedure. Also, the amount of sputter collected still exceeded the weight loss of the cathode. It was concluded that this contamination was not being caused by oxygen leaking into the sputter chamber but rather by residual adsorbed gases from the materials in the sputter tube. Dushman (23, p. 71) has found that these residual gases consist primarily of carbon dioxide and water vapor, along with smaller amounts of carbon monoxide and other gases. He further recommends that the vacuum chamber be heated in an oven to a temperature of five hundred degrees Centigrade for one hour and that it be evacuated to the

lowest possible pressure during the heating.

No facilities were available for degassing the system in this manner. Also, the rubber seals, paper insulating shells and plastic insulating plugs would never withstand such temperatures. The seals could have been replaced by silastic (a silicone which will withstand temperatures of 200 degrees Centigrade) or, possibly, soft metal and the paper by thin asbestos sheets; however, the plastic plugs would have posed a problem. Brenner (10) points out that, although much is being done to develop a high temperature plastic, the deterioration of plastics under high temperatures is their greatest failing.

It was finally determined that the sputtered metal was combining with residual gases to produce collected material of greater weight than that lost by the cathode and that there was no method of removing these gases with the equipment at hand.

Film thickness and composition. The sputtered film having been determined to be composed of copper compounds, the next step was to identify these compounds. Inquiries to the Chemical Department at the University of Oklahoma indicated that it was not feasible to analyze the film chemically. Equipment was then set up to examine the film optically.

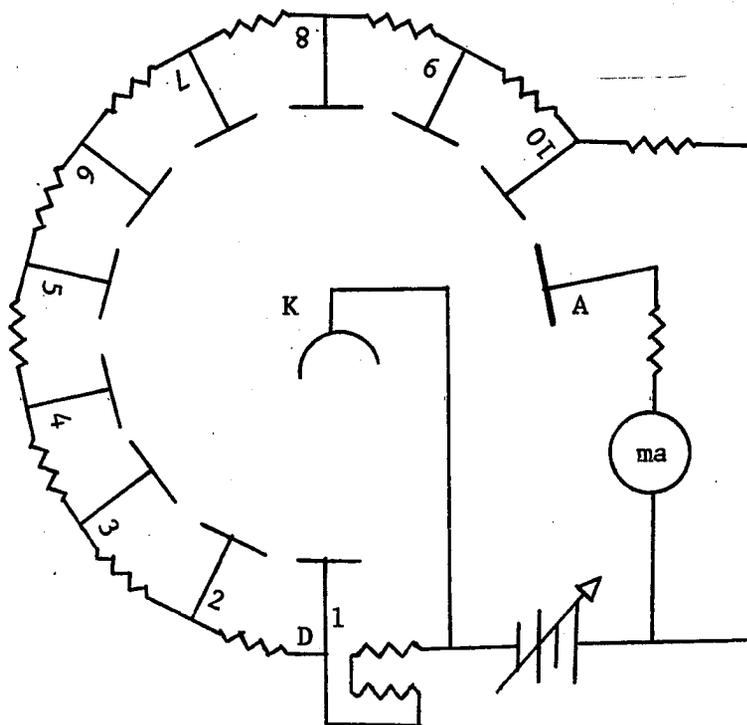
An RCA 5819 multiplier phototube was connected in the circuit shown in figure 14 and mounted in a black box. Power was supplied by a modified Furst Electric Company, Model 810-S, regulated, continuously variable, 0 to 2000 volt unit. Supply potentials were read on a Triplet Model 630 NA multimeter. Anode currents were taken from a Boonton, Model 95A, precision meter, with continuous ranges down to $(10)^{-12}$ amperes. A one inch diameter hole was cut in the five millimeter thick end-plate of the box. Thin brass

A anode

K cathode

D dynodes

all resistors 82 kilohms



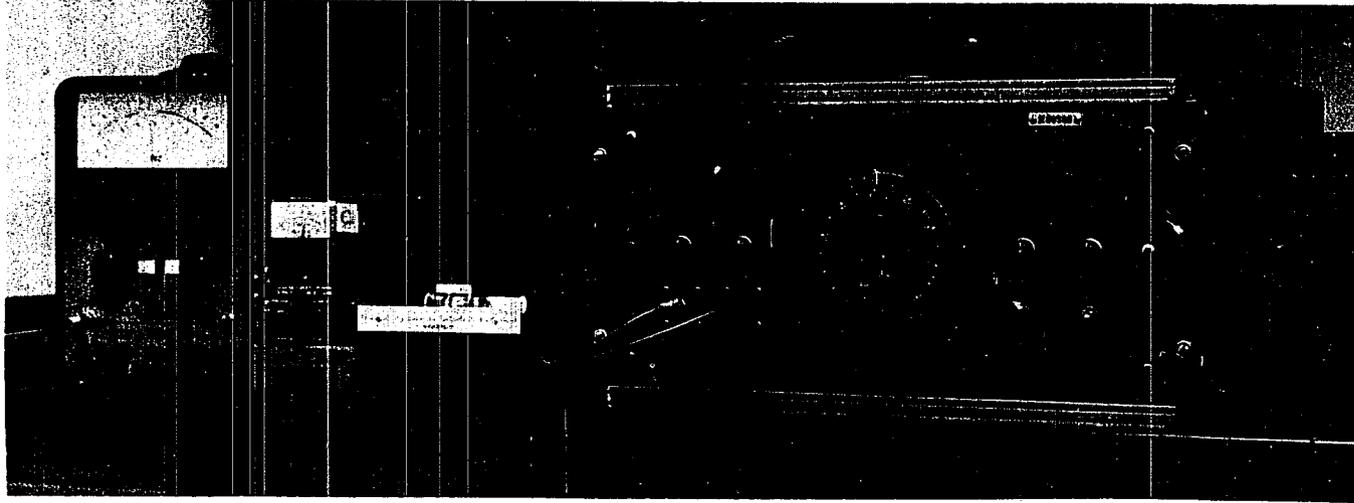
Multiplier Phototube Circuit

Figure 14

sheets were installed covering this hole on the inside and outside surfaces. One-half millimeter holes were pierced in each sheet to form a narrow aperture to the phototube. The light source was a one watt pea bulb, installed seven millimeters from the aperture, and powered by an Electronic Instrument Company, Model 1020, 0 to 30 volt, variable, regulated supply. The small light source and narrow aperture made it possible to examine, essentially, points of the film. The equipment is shown in figure 15.

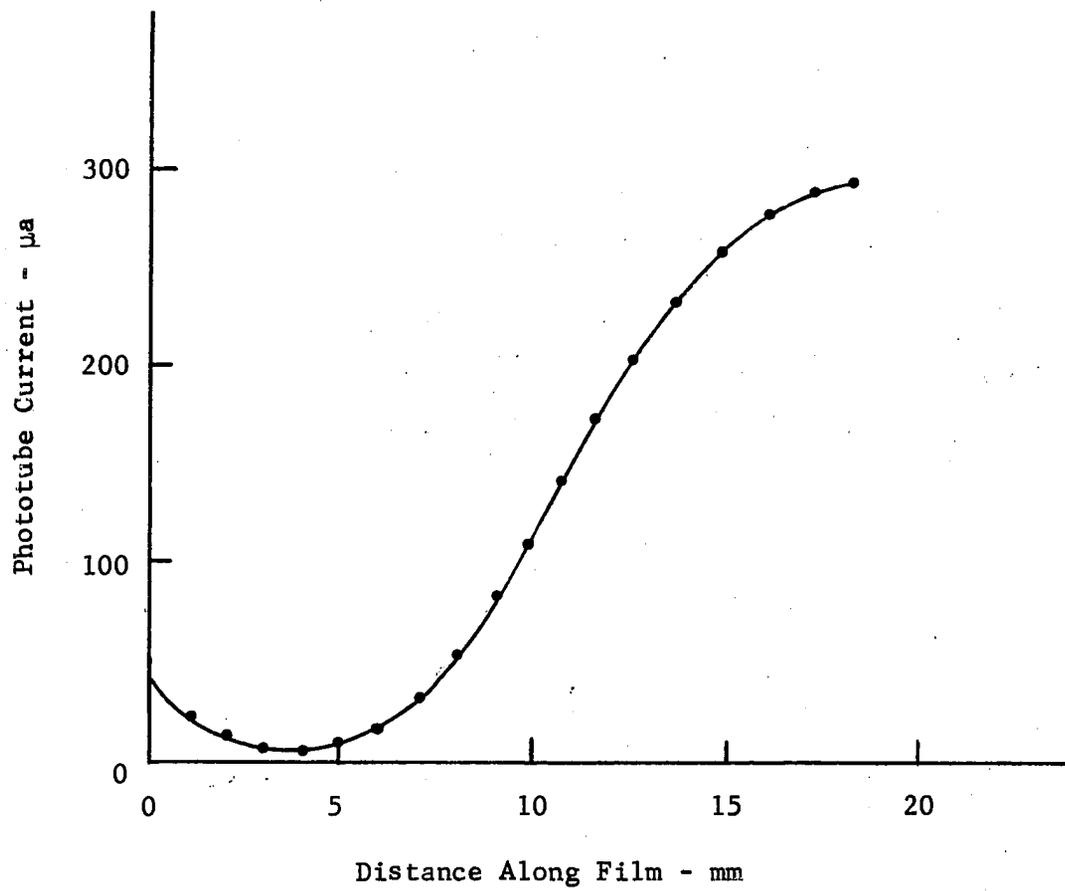
Films were examined as follows. The light source and phototube power were adjusted to give a fixed anode current, with no obstruction over the aperture. The light source was inserted into the film-coated, glass thimble. Current readings were taken as the thimble was moved in one millimeter increments. Since the anode current is linearly proportional to light intensity, these data showed the relative light intensity transmitted by the film segments. A second method consisted of setting a fixed anode current, with the aperture open. The film was then inserted and the tube supply voltage adjusted to give the original anode current. Since the anode current varies exponentially with supply voltage, and the light intensity varies exponentially with film thickness, these data showed the relative thickness of the film segments. The above data are shown in figures 16 and 17.

The above measurements showed only relative thicknesses, while actual thicknesses were desired. To this end, copper films were produced in a Veeco, Model VE-400, vacuum system and vaporizer. The film thickness was measured with a Sloan deposit thickness monitor, Model DTM-2A. The metal evaporated was from the same copper specimen which was used for the sputter cathodes. Tantalum boats of 0.005 inches thickness, and approximately 90



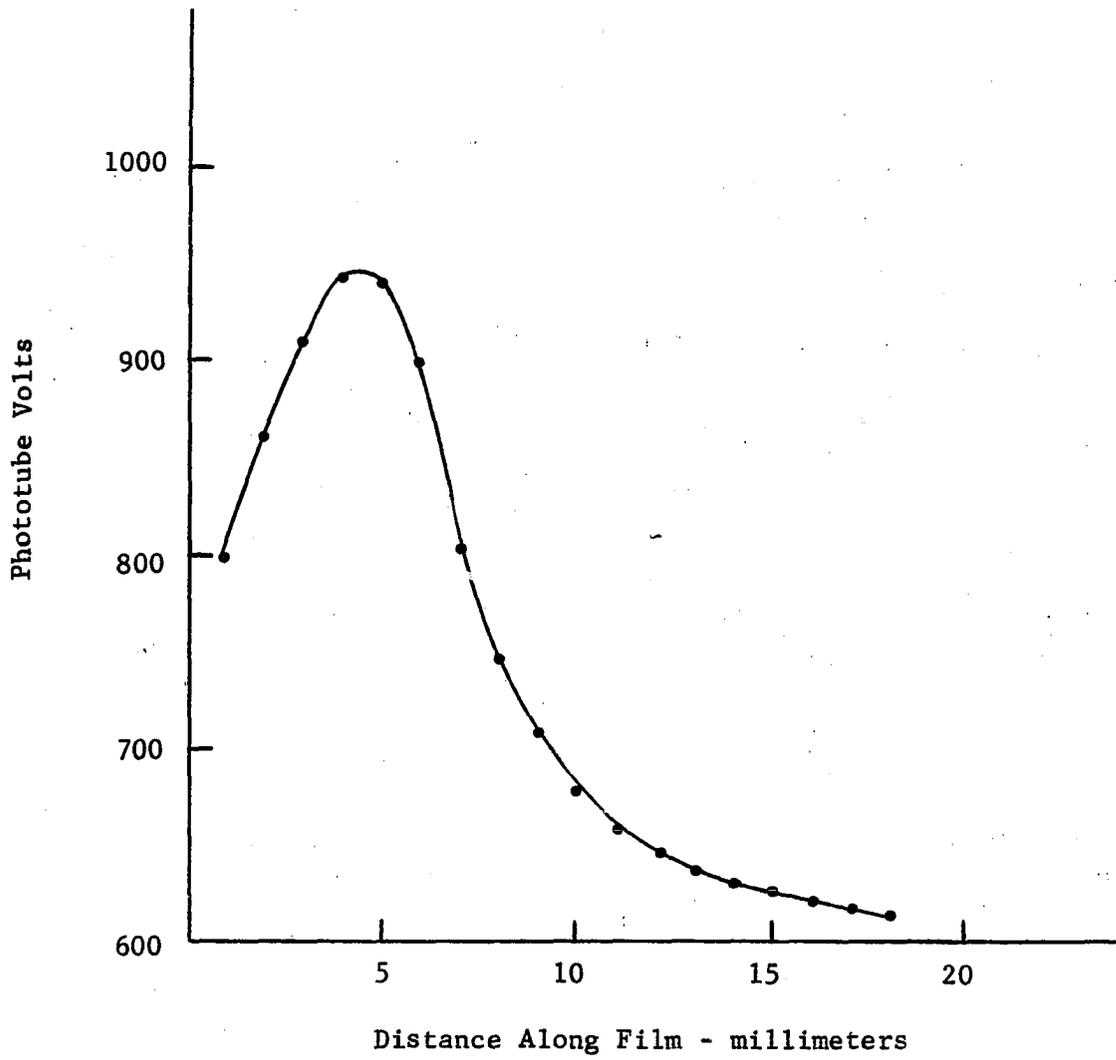
Equipment for Optical Analysis of films

Figure 15



Phototube Current vs. Distance Along Film

Figure 16

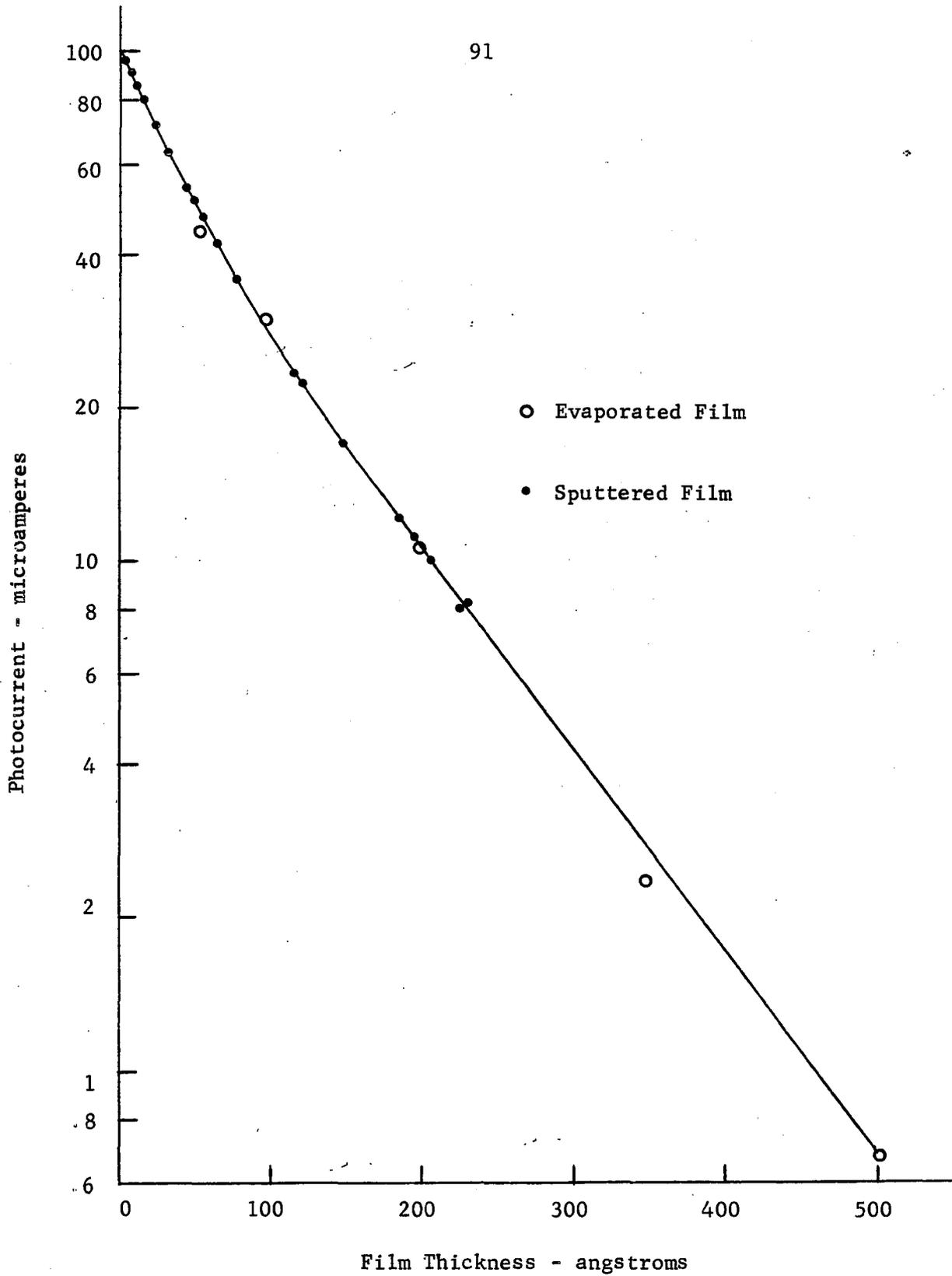


Phototube Voltage vs. Distance Along Film

Figure 17

amperes of current, were employed in evaporation. Five films, varying in thickness from 56 to 1000 angstroms, were made and their light-transmission characteristics were measured on the phototube. These measurements provided five points on the light-transmission curve for copper, as shown in figure 18. The thickness of the sputtered film segments could then be determined by plotting their light-transmission values on the curve.

The results of measurements made in this section are analyzed in chapter V.



Light Transmission Characteristic of Copper Film

Figure 18

CHAPTER V

RESULTS

Comparison of Formula with Laboratory Data

Forty timed sputter runs were made in the laboratory, using copper electrodes in argon gas. The parameters of current, voltage and pressure were fixed and closely monitored for each run. Small increases, of a few microns of mercury, were sometimes required to maintain constant current but these changes were hardly detectable on the pressure gauge. Such adjustments were required to maintain a constant gas density with rising temperature. The parameters varied over the following range in different runs:

pressure, p , from 0.07 to 10 millimeters of mercury

cathode fall voltage, V_c , from 460 to 2500 volts

current, i , from 0.15 to 33 milliamperes

time, t , from 1 to 60 minutes.

The required length of each run was controlled by the physical appearance of the sputtered film, as experience permitted the approximate determination of the amount of sputter by this means.

The cathode was carefully polished and weighed before each run and then comparatively weighed after the run to determine the loss of weight by sputtering. Weighing techniques enabled cathode loss of weight to be determined to 0.05 milligrams with ± 0.025 milligrams accuracy, giving a

possible error of 25 per cent for 0.1 milligrams loss and less than 8 per cent for more than 0.3 milligrams. The experimental loss of sputtered material was found in milligrams and designated as W^* . The expected quantity of sputter, as calculated from the equation derived in the theoretical analysis,

$$W = 2.2(10)^{-5} (V_c - 380)ti, \quad (29)$$

was then computed. The results of the laboratory data and the computations are tabulated in tables 1 and 2. In twenty-four of the forty experiments the computed value of sputter was within thirty per cent of the measured value, to give ratios of W/W^* from 0.7 to 1.3. The data for these runs are displayed in table 1. Fourteen experiments showed computed values ranging from one-half to one and eight-tenths of the measured values. These are listed in table 2. Two runs were not used because they gave values of V_c less than 380, hence the formula is not applicable. This condition will be discussed later.

The above discussion and table 1 show that in a majority of cases the synthesized formula predicted laboratory results with an accuracy of thirty per cent. This result greatly exceeded preliminary expectations. Other workers have developed formulas which gave the amount of sputter to be expected only to an order of magnitude. All authorities agree that the glow discharge is an extremely complicated mechanism, composed of many processes which are quite complex themselves and which are interrelated in a manner which very nearly defies analysis. The fact that these processes could be logically evaluated to produce an expression with this degree of accuracy confirms the success of the program of work undertaken. It is believed that the success of this derivation is due to several factors.

TABLE 1
 MEASURED AND COMPUTED SPUTTER VALUES WITH
 THIRTY PER CENT CORRELATION

Run Date	p mm of Hg	V _c volts	i ma.	t min.	W*mg meas.	W mg calc.	$\frac{W}{W^*}$
8 Dec	0.1	1500	0.31	60	0.45	0.42	0.94
10 Dec	0.1	2500	0.59	20	0.7	0.5	0.72
10 Aug	0.2	775	2.35	20	0.4	0.37	0.93
3 Dec	0.2	790	1.22	20	0.2	0.2	1
17 Jun	0.2	1160	3.8	10	0.6	0.6	1
29 Jun	0.2	1550	4.6	5	0.6	0.54	0.9
6 May	0.3	560	4.0	40	0.6	0.58	0.96
15 Jun	0.3	915	8.4	10	0.7	0.9	1.29
8 Jun	0.3	1125	7.4	10	1.0	1.1	1.1
8 May	0.3	570	2.8	40	0.6	0.43	0.71
15 Jun	0.3	1110	9.2	10	1.0	1.3	1.3
11 May	0.4	550	4.5	40	0.7	0.61	0.88
18 May	0.4	560	3.9	40	0.55	0.56	1.02
22 Dec	0.4	915	8.5	1	0.1	0.091	0.091
19 Jan	0.4	920	7.8	10	1.1	0.85	0.77
24 Jun	0.4	1075	12.5	10	1.4	1.74	1.24
17 Jan	0.5	670	12.9	10	1.1	0.76	0.69
22 Jul	0.5	700	10.0	10	0.55	0.64	1.16
5 Jan	0.5	710	8.6	10	0.45	0.57	1.26
7 Jan	0.5	730	6.8	10	0.2	0.164	0.82
29 May	0.5	860	13.6	10	1.2	1.3	1.1
20 Dec	0.5	865	13.5	10	1.3	1.3	1
5 Jun	0.5	1070	13.0	10	2.35	1.8	0.77
3 Jul	10.0	460	33.6	5	0.2	0.27	1.34

TABLE 2

MEASURED AND COMPUTED SPUTTER VALUES VARYING
BY MORE THAN THIRTY PER CENT

Run Date	p mm of Hg	V _c volts	i ma.	t min.	W*mg meas.	W mg calc.	$\frac{W}{W^*}$
15 Dec	0.07	2500	0.15	30	0.3	0.19	0.6
6 Dec	0.1	1500	0.36	30	0.15	0.24	1.6
20 Jul	0.2	770	2.8	10	0.15	0.22	1.45
3 Jun	0.2	980	2.2	10	0.4	0.26	0.66
8 Jul	0.2	1460	4.3	5	0.75	0.46	0.62
10 Jun	0.3	1155	4.6	10	0.4	0.71	1.8
13 May	0.4	550	5.0	40	0.4	0.68	1.7
24 Jun	0.4	890	11.2	10	0.7	1.14	1.62
21 Jan	0.4	950	4.8	10	1.0	0.55	0.55
4 Jan	0.4	1130	7.25	10	1.7	1.09	1.55
20 May	0.5	530	6.7	40	0.45	0.8	1.8
22 May	0.5	530	7.3	40	0.4	0.7	1.75
3 Jan	0.5	700	10.4	10	0.95	0.66	0.69
1 Jul	2.0	460	14.3	20	0.25	0.46	1.8

In this analysis the part played by the phenomenon of charge exchange was fully exploited. Recent precise data on this process was available. Also, these data came from several separate sources and they all agreed remarkably well. This is frequently not true of data concerning collision processes. Charge exchange cross sections for ions traveling in their own gas are so large, and the effects of this mechanism are so profound, that it is difficult to see how an evaluation of sputtering in the glow could be made without giving full consideration of this process. This attack yields two results: it permits the energy of positive ions to be determined; it also reveals that fast neutral atoms exist near the cathode, hence should be considered in the sputtering process. It has been noted that there is very little information available, in the literature, on the sputtering action of fast neutral atoms but, for reasons previously explained, neutrals must contribute to sputtering in the glow.

The role of photoelectric emission of electrons was also carefully evaluated. Many analyses of the glow discharge can be completed without differentiating between the processes which cause electron emission from the cathode. The result is that there is a dearth of information on the detailed evaluation of the individual part played by radiation. The method adapted from von Engel, although it involved several approximations, permitted the effect of the photoelectric process to be evaluated.

The expression for predicted sputter, equation (29), could be refined by using more exact representations for several of the factors involved. Mean values for p_d and Q were taken from figures 3 and 4. Both of these graphs can be approximated by a fixed value; however, a more

correct approximation may be made by treating each of these graphs as a straight line over the portion of interest. Such approximations do give a slightly more accurate formula for sputter but the complications of the resulting expression outweigh the accuracy gained.

The formula derived gives no result for potentials below 380 volts. Normally, this limitation is of no great importance as sputtering values in this range are very small. A different formula would be required for cathode potentials in the vicinity of the normal glow. The difficulty is caused by the behavior of the graph of figure 4. It will be noted that this figure would require selection of a much higher value of pd than the 0.07 which applies at medium and higher voltages.

Determination of Quantity of Sputter

Accurate determination of quantity of sputter produced was of major importance in this work. The measurement of weight loss of the cathode should give reasonably reliable results but better accuracy would have been obtained with a true microbalance. The limitation of the balance used, to fifty micrograms minimum detectable weight, introduced an appreciable error for small quantities of sputter.

Another possible source of error could have been the loss of cathode weight by the liberation of adsorbed gases. This error, also, could be eliminated with suitable degassing apparatus and procedure. Unfortunately, such apparatus was not available. It was noted that when the sputtered material was collected and weighed, the weight exceeded the cathode loss of weight by almost ten per cent. It was thought that the immersion of the sputter chamber in an argon environment might remove this discrepancy, by preventing the leakage of oxygen into the chamber, but this

procedure was not effective.

The second technique for verifying the amount of sputter was by optical measurement of the thickness of the sputtered film. The optically measured thicknesses of the segments of a typical film are shown in figure 18, page 91. The thickness as indicated by the points on the curve represents the average thickness of a one millimeter segment. The weight of the film may be determined by summing these thicknesses and multiplying by the circumference of the collector and the density of copper. For the example shown this gives

$$(1.5\pi)(8.92(10)^3)(1845(10)^{-9}) = 0.15 \text{ milligrams,}$$

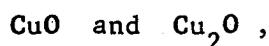
where the three factors are: circumference in centimeters, density in milligrams per cubic centimeter, and average thickness in centimeters. The cathode loss of weight for this film was 0.4 milligrams. Thus the optically measured film weighed approximately 0.4 times the cathode loss of weight. The explanation for this difference in weights is believed to be as follows.

It is known that the sputtered products weighed ten per cent more than the cathode loss of weight. The films showed the characteristics of copper oxide, in that they were non-conducting and exhibited blue and green shades of color. The number of oxygen atoms required to give a ten per cent increase of weight to the sputtered copper atoms may be determined.

$$64N + 16n = 1.1 \times 64N$$

$$n = 0.4N ,$$

where N is the number of copper atoms and n is the number of oxygen atoms. Copper forms two oxides, cupric and cuprous



with approximately equal probability. If it is assumed that these oxides are formed in equal quantities, the average number of copper atoms combining with oxygen atoms would be 1.5, giving

$$N - 1.5 \times 0.4N = 0.4N \text{ atoms of copper}$$

remaining in the pure metallic state. The oxides are transparent, so the optically absorbent film is effectively only 0.4 of the thickness of a true copper film. Any slight discrepancies could be accounted for by a variation in the proportional quantities of the two oxides.

The above explanation is believed to account for all observed factors and to satisfactorily explain the difference between the cathode loss of weight and the weight of the sputtered products. It is obviously not of sufficient precision to verify the amount of sputter but it does give an interesting insight into the actions taking place in a sputtering experiment.

BIBLIOGRAPHY

1. Allen, H. S. Photo-Electricity. London: Longmans, Green and Co., 1925.
2. Anderson, G. S. "Atom Ejection in Low Energy Sputtering of Single Crystals of fcc Metals and of Ge and Si," J. Appl. Phys., 33 (1962), 2017.
3. Aston, F. W. "The Distribution of Electric Force in the Crookes Dark Space," Proc. Roy. Soc., A84 (1911), 526.
4. _____. "Experiments on the Length of the Cathode Dark Space with Varying Current Densities and Pressures in Different Gases," Proc. Roy. Soc., A79 (1907), 80.
5. _____. "On the Influence of the Nature of the Cathode on the Length of the Crookes Dark Space," Proc. Roy. Soc., A87 (1912), 437.
6. _____ and Watson, H. E. "On the Relation between the Current, Voltage, Pressure and the Length of the Dark Space in Different Gases," Proc. Roy. Soc., A86 (1911), 168.
7. Baum, T. Z. "Atomic Deposition," Zeits. f. Phys., 40 (1927), 686.
8. Boast, W. B. Illumination Engineering. New York: McGraw-Hill Book Company, Inc., 1953.
9. Bradley, R. C. "Sputtering of Alkali Atoms by Inert Gas Ions of Low Energy," Phys. Rev., 93 (1954), 719.
10. Brenner, Lum, and Riley. High Temperature Plastics. New York: Rheingold Publishing Corp., 1962.
11. Brose. Ann. d. Phys., 58 (1919), 731.
12. Brown, S. C. Basic Data of Plasma Physics. Cambridge, Mass.: Technology Press, M.I.T., 1959.
13. Bush, V. and Smith. "Explosive Sputter," J. Am. Inst. E.E., 41 (1922), 627.

14. Chaudri, R. M. and Oliphant, M. L. "The Energy Distribution among the Positive Ions at the Cathode of the Glow Discharge through Gases," Proc. Roy. Soc., 137 (1932), 662.
15. Cobine, J. D. Gaseous Conductors. New York: Dover Publications, Inc., 1958.
16. Compton, K. T. and Morse, P. M. "The Theory of Normal Cathode Fall in Glow Discharges," Phys. Rev., 30 (1927), 305.
17. _____ and Langmuir. "Electrical Discharge in Gases," Rev. Mod. Phys., 2 (1930), 122.
18. _____ and _____. "Electrical Discharge in Gases," Rev. Mod. Phys., 3 (1931), 191.
19. Cramer, A. W. H. "Elastic and Inelastic Scattering of Low Velocity Ions," J. Chem. Phys., 30 (1959), 641.
20. Darrow, K. K. Electrical Phenomena in Gases. Baltimore: Williams and Wilkins Co., 1932.
21. Drummond, J. E. Plasma Physics. New York: McGraw-Hill Book Co., 1961.
22. Druyvesteyn, M. J. and Penning, F. M. "The Mechanism of Electrical Discharges in Gases at Low Pressure," Rev. Mod. Phys., 12 (1940), 87.
23. Dushman, S. "High Vacuum," Gen. Elec. Rev., Schenectady, New York: 1922.
24. Engstrom, R. W. and Huxford, W. S. "Time Lag Analysis of the Townsend Discharge in Argon with Activated Caesium Electrodes," Phys. Rev., 58 (1940), 67.
25. Fowler, R. G. "Ionic Conduction of Highly Ionized Plasma," Phys. Rev., (1960).
26. _____. "Investigations on Constriction of the Positive Column Using Glow Discharges of Limited Duration," J. Appl. Phys., 34 (1963), 1401.
27. Francis, G. "The Glow Discharge at Low Pressure," Hand. d. Phys., 22 (1956), 53.
28. _____. Ionization Phenomena in Gases. New York: Academic Press, Inc., 1960.
29. Fraser, R. Molecular Beams. London: Methuen and Co., Ltd., 1937.
30. Gartenhaus, S. Elements of Plasma Physics. New York: Holt, Rinehart, and Winston, Inc., 1964.

31. Glocker and Lind. The Electrochemistry of Gases and Other Dielectrics. New York: John Wiley and Sons, Inc., 1939.
32. Güntherschultze, A. "Kathodenzerstäubung," Zeits. f. Phys., 36 (1926), 563.
33. _____ . "Neue Untersuchungen über der Kathodenzerstäubung," Zeits. f. Phys., 119 (1942), 79.
34. _____ . "Elektronenablösung durch den Aufprall der Positiven Ionen auf die Kathode einen Glimmerentladung," Zeits. f. Phys., 111 (1938), 208.
35. _____ . "Der Kathodenfall der Glimmenladung in Abhängigkeit von der Stromdichte," Zeits. f. Phys., 59 (1930), 433.
36. _____ . "Die Elektronenablösung durch den Stoss positiven Ionen bei Geringen Gasdrucken," Zeits. f. Phys., 62 (1930), 600.
37. Haas, G. (ed.) Physics of Thin Films. New York: Academic Press, 1963.
38. Hagstrum, H. D. "Effects of Monolayer Adsorption on the Ejection of Electrons from Metals by Ions," Phys. Rev., 104 (1956), 1516.
39. _____ . "Auger Ejection of Electrons from Tungsten by Noble Gas Ions," Phys. Rev., 104 (1956), 317.
40. _____ . "Auger Ejection of Electrons from Molybdenum by Noble Gas Ions," Phys. Rev., 104 (1956), 672.
41. _____ . "Metastable Ions of the Noble Gases," Phys. Rev., 104 (1956), 309.
42. Harrison, D. E. "Theory of the Sputtering Process," Phys. Rev., 102 (1956), 1473.
43. Hasted, J. B. "The Exchange of Charge Between Ions and Atoms," Proc. Roy. Soc., A205 (1951), 421.
44. Haworth, F. E. "Electrode Reactions in the Glow Discharge," J. Appl. Phys., 22 (1951), 606.
45. Haydon, S. C. (ed.) Discharge and Plasma Physics. Armitage, Australia: University of New England, 1964.
46. Healea and Chaffee. "Secondary Electron Emission from a Hot Nickel Target Due to Bombardment by Hydrogen Ions," Phys. Rev., 49 (1936), 925.
47. Heavens, O. S. Optical Properties of Thin Films. New York: Dover Publications, Inc., 1965.

48. Hemenway, Henry and Gaulton. Physical Electronics. New York: John Wiley and Sons, Inc., 1962.
49. Henschke, E. B. "New Collision Theory of Cathode Sputtering of Metals at Low Ion Energies," Phys. Rev., 106 (1957), 737.
50. Holland, L. Vacuum Deposition of Thin Films. London: Chapman and Hall Ltd., 1963.
51. Holm, R. Electric Contacts. Stockholm: Almqvist and Wiksells, 1946.
52. Honig, R. E. "Sputtering of Surfaces by Positive Ion Beams of Low Energy," J. Appl. Phys., 29 (1958), 549.
53. Hornbeck, J. A. "The Mobilities of Molecular and Atomic Rare Gas Ions in the Parent Gases: Helium, Neon and Argon," Phys. Rev., 80 (1950), 297.
54. _____. "Microsecond Transient Currents in the Pulsed Townsend Discharge," Phys. Rev., 83 (1951), 374.
55. _____. "The Drift Velocities of Molecular and Atomic Ions in Helium, Neon and Argon," Phys. Rev., 84 (1951), 615.
56. _____. "Cross Sections for Ion-Atom Collisions in Helium, Neon and Argon," Phys. Rev., 82 (1951), 458.
57. Hudson, R. G. Engineers' Manual. New York: John Wiley and Sons, Inc., 1917.
58. Huxford, W. S. "Townsend Ionization Coefficients in Cs-Ag-O Photo-Tubes Filled with Argon," Phys. Rev., 55 (1939), 754.
59. Janananda, S. High Vacua. New York: D. Van Nostrand Co., 1947.
60. Kendall, J. Smith's College Chemistry. New York: D. Appleton-Century Co., Inc., 1935.
61. Kenty, C. "Photoelectric Yields in the Extreme Ultraviolet," Phys. Rev., 44 (1933), 891.
62. _____. "Photoelectric and Metastable Atom Emission of Electrons from Surfaces in the Rare Gases," Phys. Rev., 43 (1933), 181.
63. Keywell, F. "Measurement and Collision-Radiation Damage Theory of High Vacuum Sputtering," Phys. Rev., 102 (1956), 1473.
64. _____. "A Mechanism for Sputtering in the High Vacuum Based upon the Theory of Neutron Cooling," Phys. Rev., 87 (1952), 160.

65. Kingdon and Langmuir. "Removal of Thorium from the Surface of a Thoriated Tungsten Filament by Positive Ion Bombardment," Phys. Rev., 22 (1923), 148.
66. Laegreid, N. and Wehner, G. K. "Sputtering Yields of Metals for Argon and Neon Ions with Energies from 50 to 500 e.v.," J. Appl. Phys., 32 (1961), 365.
67. _____ Document 6463, ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., 1961.
68. Lafferty and Vanderslice. "The Interplay of Electronics and Vacuum Technology," Proc. IRE, 49 (1961), 56.
69. Lamar and Compton. Science, 80 (1934), 541.
70. Lenard, P. Ann. d. Phys., (4) 12 (1903), 714.
71. Levine, S. N. Quantum Physics of Electronics. New York: The Macmillan Co., 1965.
72. "Light," Encyclopaedia Britannica, 14th ed., vol. 14, (1932), 57.
73. Lion. K. S. Instrumentation in Scientific Research. New York: McGraw-Hill Book Co., Inc., 1959.
74. Little, P. F. "Secondary Effects," Hand. d. Phys., 21 (1956), 573.
75. _____ and von Engel, A. "The Hollow-cathode Effect and the Theory of Glow Discharges," Proc. Roy. Soc., 224 (1954), 209.
76. Llewellyn-Jones, F. Ionization and Breakdown in Gases. New York: John Wiley and Sons, Inc., 1957.
77. Loeb, L. B. Fundamental Processes of Electrical Discharge. New York: John Wiley and Sons, Inc., 1939.
78. _____. Basic Processes of Gaseous Electronics. Berkeley: University of California Press, 1960.
79. _____. The Kinetic Theory of Gases. New York: Dover Publications, 1961.
80. Loeb, L. B. "Electrical Breakdown of Gases with Steady or Direct Current Impulse Potentials," Hand. d. Phys., 22 (1956), 53.
81. _____ and Meek. The Mechanism of the Electric Spark. Stanford, Cal.: Stanford University Press, 1941.
82. _____, Kip and Hudson. "Pulses in Negative Point-to-Plane Corona," Phys. Rev., 60 (1941), 714.

83. Massachusetts Institute of Technology, Department of Electrical Engineering. Applied Electronics. New York: John Wiley and Sons, Inc., 1947.
84. Massey, H. S. W. "Excitation and Ionization of Atoms by Electron Impact," Hand. d. Phys., 36 (1956), 335.
85. _____ and Burhop. Electronic and Ionic Phenomena. Oxford: Clarendon Press, 1952.
86. Maxfield and Benedict. Theory of Gaseous Conduction and Electronics. New York: McGraw-Hill Book Co., Inc., 1941.
87. McClung, R. K. Conduction of Electricity Through Gases. Philadelphia: J. A. Blakiston's Sons and Co., 1909.
88. McDaniel, E. W. Collision Phenomena in Ionized Gases. New York: John Wiley and Sons, 1964.
89. Molnar, J. P. "Form of Transient Currents in Townsend Discharges with Metastables," Phys. Rev., 83 (1951), 933.
90. _____. "Studies of Gamma Processes of Electron Emission Employing Pulsed Townsend Discharges on a Millisecond Time Scale," Phys. Rev., 83 (1950), 940.
91. Morey, G. W. Properties of Glass. New York: Rheinhold Publishing Co., 1938.
92. Morse, M. "A Theory of the Electric Discharge Through Gases," Phys. Rev., 31 (1928), 1003.
93. Newman, F. H. Production and Measurement of Low Pressure. London: Ernest Benn Ltd., 1925.
94. Newton, R. R. "Transients in Townsend Discharges," Phys. Rev., 73 (1948), 570.
95. Oliphant, M. L. E. "The Action of Metastable Atoms of Helium on a Metal Surface," Proc. Roy. Soc., A124 (1929), 228.
96. Penning, F. M. Electrical Discharges in Gases. New York: Macmillan Co., 1957.
97. Proceedings of the First International Congress on Vacuum Techniques. New York: Pergamon Press, 1960.
98. Proceedings of the Fifth International Conference on Ionization Phenomena in Gases. Amsterdam: North Holland Publishing Co., 1962.

99. Report of the International Symposium on Electrical Discharges in Gases. The Hague: Martinus Nijhoff, 1955.
100. Rostagni, A. "Untersuchungen über Langsame Ionen und Neutralstrahlen," Zeits. f. Phys., 88 (1934), 55.
101. Seeliger, R. Einführung in die Physik der Gasentladungen. Leipzig: Johann Barth.
102. _____ and Sommermeyer. "Remarks on the Theory of Cathode Sputtering," Zeits. f. Phys., 93 (1935), 692.
103. Shuler, K. (ed.) "Ionization in High Temperature Gases," Technical Papers of the American Rocket Society Symposium. New York: Academic Press, 1963.
104. Smith, A. W. The Elements of Physics. New York: McGraw-Hill Book Co., 1932.
105. Sproull, R. L. Modern Physics. New York: John Wiley and Sons, Inc., 1963.
106. Starr, C. "Sputtering," Phys. Rev., 56 (1939), 216.
107. Thomson, Sir J. J. Rays of Positive Electricity. London: Green and Co., 1921.
108. Thomson, Sir J. J. "Conduction of Electricity in Gases," Encyclopaedia Britannica. 14th ed., vol. 8, p. 238.
109. _____ and Thomson, G. P. Conduction of Electricity Through Gases. Cambridge: Cambridge University Press, 1933.
110. Thomson, J. Electron Physics and Technology. London: Universities Press Ltd., 1959.
111. Timoshenko, G. "Sputtering and Secondary Electron Emission of Metals Bombarded by Argon Ions," J. Appl. Phys., 12 (1941), 69.
112. Townes, C. H. "Theory of Cathode Sputtering in Low Voltage Gaseous Discharges," Phys. Rev., 65 (1944), 319.
113. Transactions of the Eighth Vacuum Symposium. 1961.
114. Urquhart, J. W. Electro-Plating. London: Crosby Lockwood and Son, 1920.
115. von Hippel, A. "Zur Theorie der Kathodenzerstäubung," Ann. d. Phys., 81 (1926), 1043.
116. von Engel, A. Ionized Gases. Oxford: Clarendon Press, 1955.

117. _____ . "Ionization in Gases by Electrons in Electric Fields," Hand. d. Phys., 21 (1956), 504.
118. _____ und Steenbeck. Elektrische Gasentladung. 2 vols., Berlin: Julius Springer, 1934. Reproduced by Edwards Brothers, Inc., Ann Harbor, Michigan, 1944.
119. Walker, Wainfan and Weissler. "Photoelectric Yields in the Vacuum Ultraviolet," J. Appl. Phys., 26 (1955), 1369.
120. Ward and Jones. "Electrical Breakdown in Hydrogen at Low Pressures," Phys. Rev., 122 (1961), 376.
121. Wehner, G. K. "Controlled Sputtering of Metals by Low Energy Mercury Ions," Phys. Rev., 102 (1956), 690.
122. _____. "Threshold Energies for Sputtering and the Sound Velocity in Metals," Phys. Rev., 93 (1954), 633.
123. _____. "Momentum Transfer in Sputtering by Ion Bombardment," J. Appl. Phys., 25 (1954), 270.
124. _____ and Medicus, G. "Sputtering at Low Ion Velocities," Phys. Rev., 89 (1953), 339.
125. _____ and Rosenberg, D. "Sputtering Yields for Low Energy He, Kr and Xe Ion Bombardment," J. Appl. Phys., 33 (1962), 1842.
126. _____ and Stuart, R. V. "Sputtering Yields at Very Low Bombarding Ion Energies," J. Appl. Phys., 33 (1962), 2345.
127. Weissler, G. L. "Photoionization in Gases and Photoelectric Emission from Solids," Hand. d. Phys., 21 (1956), 304.
128. Weidner and Sells. Elementary Modern Physics. Boston: Allyn and Bacon, Inc., 1962.
129. Wheatcroft, E. L. Gaseous Electrical Conductors. Oxford: Clarendon Press, 1938.
130. Windred, G. Electric Contacts. New York: D. Van Nostrand and Co., 1940.

APPENDIX A

SOURCES OF INITIAL ELECTRON-ION PAIRS

This appendix presents a detailed, quantitative analysis of the number of electron-ion pairs which may be expected to be available to initiate a gas discharge. The subject was introduced briefly under Glow Discharges in chapter II, but the ramifications were reserved for this appendix.

There is one phase of gaseous conduction which is of major importance but which is frequently neglected, or treated very casually. This is the starting phase, and it primarily involves a quantitative analysis of the source of the original electron-ion pairs. Many authors list several possible sources of these aboriginal pairs and then postulate that some source has produced some unknown quantity of these conductors in the gaseous discharge device being studied. These authors then examine in great detail the processes which ensue under various conditions of fields and pressures. At other times authors specify one initiating source but ignore the effects of other sources. Ultraviolet radiation of the cathode and X-ray radiation of the gas are two sources commonly employed.

Many phenomena which are investigated in gas discharges are primarily concerned, although sometimes not obviously, with the exact conditions existing in the gas at the initial point. These conditions, therefore, warrant detailed study and understanding. Also, the artificial sources which are most commonly recommended frequently involve equipment of much greater complexity than the basic equipment being used. Many smaller laboratories do not possess the necessary source equipment and hence must rely on other means for producing starting pairs. For all of the above reasons, the following paragraphs will explore the detailed, quantitative status of ion pairs in a natural gas.

Theories concerning the conductivity of gases-mainly air-go back at least to a paper published by Coulomb in 1785 (108). Prior to this time it was well-known that the best insulated, charged bodies lost their charge very slowly. Some physicists believed that such leakage was due to unavoidable defects in the insulation, while others believed it was

caused by dust particles in the air striking the charged body and carrying off small charges. Coulomb made some very careful investigations of leakage from well-insulated, charged bodies, the results being published in the paper referred to above. His conclusion was that air molecules striking the charged body absorbed a charge of like sign and were then repelled away from the body, carrying their charge with them. Investigations over the next 100 years added very little to the explanation of the leakage phenomena, other than Matteucci's findings that it varied directly with gas pressure and was approximately the same for all gases.

Rutherford achieved a major step forward in 1903 when he found that the leakage was decreased 30% by surrounding the charged body with thick sheets of lead. The rate was not decreased any further, however, no matter how thick the lead shield was made. This indicated that the loss was partly due to some kind of emanation which could not penetrate a thick lead shield. M'Clennan, in 1912, corroborated Rutherford's finding by measuring the rate of leakage on land and in the middle of the ocean. The rate over water was again 30% less than that measured on land. The conclusions drawn from these experiments, and similar experiments performed by others, were the following.

The conductivity of air is caused by the presence of conducting electron-ion pairs. These pairs are formed by the ionization of the molecules of the air. The energy sources producing this ionization are: extremely high energy cosmic rays from the sky, and the radiation produced by radioactive sources which exist in minute quantities in the atmosphere and in the soil. Different investigators have arrived at different results on the amount of ionization produced by each source. Also, ionization

varies considerably under different test conditions and in different parts of the world. The best average results obtainable show the ion pairs produced per cubic centimeter per second, in air at atmospheric pressure, to be: radioactive materials in the air, 5; radioactive materials in the soil, 3; cosmic rays, 1.5. Thus the average rate of production is approximately ten pairs per cubic centimeter per second. This result can vary both upward and downward by a factor of two to three.

Atmospheric ions are being produced at the rates given above but, at the same time, they are recombining to form neutral atoms and molecules. The equation governing the equilibrium condition for production and recombination is:

$$q = an^2 + bn$$

with q = the rate of production

a = the rate of recombination of electrons and ions

n = ion pairs, hence number of electrons or ions

b = a decay factor accounting for removal of ions by clustering, attachment to dust particles and other causes.

The factor a has been determined in the laboratory to be approximately $1.6(10)^{-6}$. The factor b varies with conditions from $6(10)^{-3}$ to $20(10)^{-3}$ and is essentially an empirical factor. When these values are introduced into the equilibrium equation the value of n varies from 450 to 1240 ion pairs per cubic centimeter. This is generally in agreement with measured values, most of which run from 500 to 1000 pairs, giving an average of 750 pairs.

The figure of 750 electron-ion pairs applies only under normal temperature and pressure conditions. This number varies inversely as pressure so that at one millimeter of mercury pressure, the approximate

pressure for glow investigation, there exist only $1/760$ of 750 or one pair per cubic centimeter. Furthermore, if the initial one pair per cubic centimeter is withdrawn from the gas by a slowly increasing electric field, the replenishing rate of production will be only $1/760$ of 10 (rate of production at atmospheric pressure) or 0.013 pairs per cubic centimeter per second. Thus there is one pair per cubic centimeter available to initiate a discharge upon a sudden application of field but only 0.013 per cubic centimeter per second available by the time a slowly increasing field reaches the point of field intensification of ionization.

It will next be demonstrated that the above, naturally-produced pairs are the only conductors available to initiate a discharge unless specific steps are taken to provide additional sources. One phenomenon which is commonly assumed as a natural source of ionization is the photoelectric effect. There are three factors involved in the photoelectric effect: a source of photons of requisite energy; a photoelectric material; and a conducting path between the first two. These factors will be discussed in the order given.

Common photon sources would be sunlight, incandescent lights, and fluorescent lamps. The sun has a broad spectrum; however, the atmosphere absorbs all photons having wavelengths below 3000 angstroms (104, p. 636). Also, common window glass will not pass any wavelength less than 3500 angstroms (72). Incandescent lamps have a cut-off at 3000 angstroms (83, p. 105). Fluorescent lights do generate, internally, wavelengths of 2500 angstroms but this energy is converted to wavelengths longer than 3800 angstroms by the emitting phosphor coating. The combination of phosphor coating and glass bulb effectively absorbs the higher energy, internal

photons. Figure 19 gives a typical fluorescent light spectrum (105, p. 370). From the above it can be seen that no photons of energy greater than about 3000 angstroms would be likely to be present in a glass-windowed room.

The next factor to be considered is the photoelectric emission of electrons from materials. The materials normally involved in a gas discharge are the electrodes, the gas, and the glass envelope. The latter may be eliminated since glass does not exhibit the photoelectric effect. The electrodes are most likely to be electron emitters when bombarded with photons, their emission threshold being controlled by the Einstein relation

$$h\nu = ew,$$

where

h = Planck's constant

ν = threshold frequency for electron emission

e = electron charge

w = work function of the metal.

This expression may be converted to

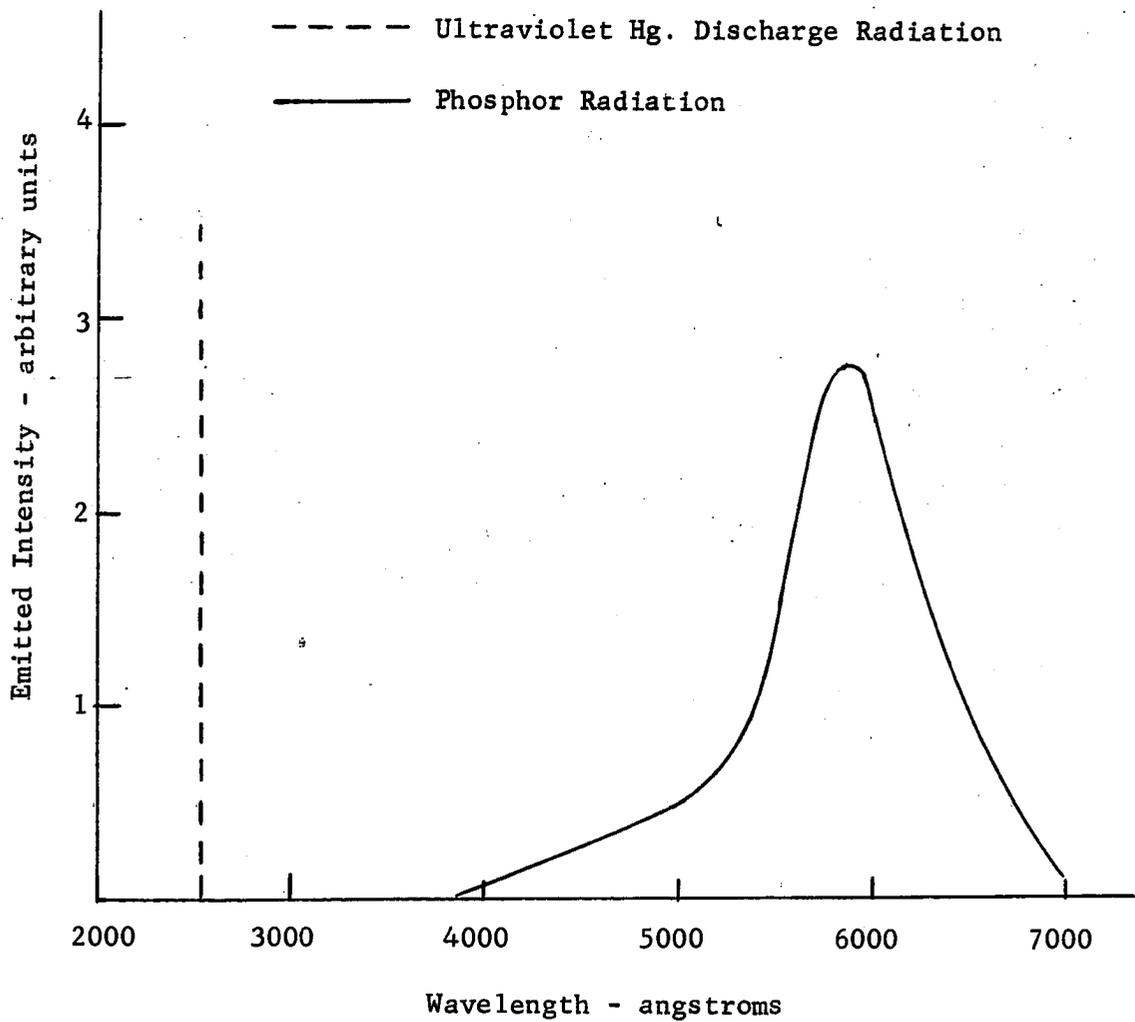
$$\lambda = 12400/w,$$

with

w = volts

λ = maximum wavelength in angstroms

for electron emission. The work function will vary from about one to five volts for most materials exhibiting the photoelectric effect, giving wavelengths from 2467 to 12,336 angstroms. A negligible number of electrons can be ejected from the material by photons of less energy than that corresponding to the threshold wavelength (48, p. 57). Some specially prepared compounds of Cesium have very low work functions and most of the alkali metals have threshold values between 4900 and 6400 angstroms, as



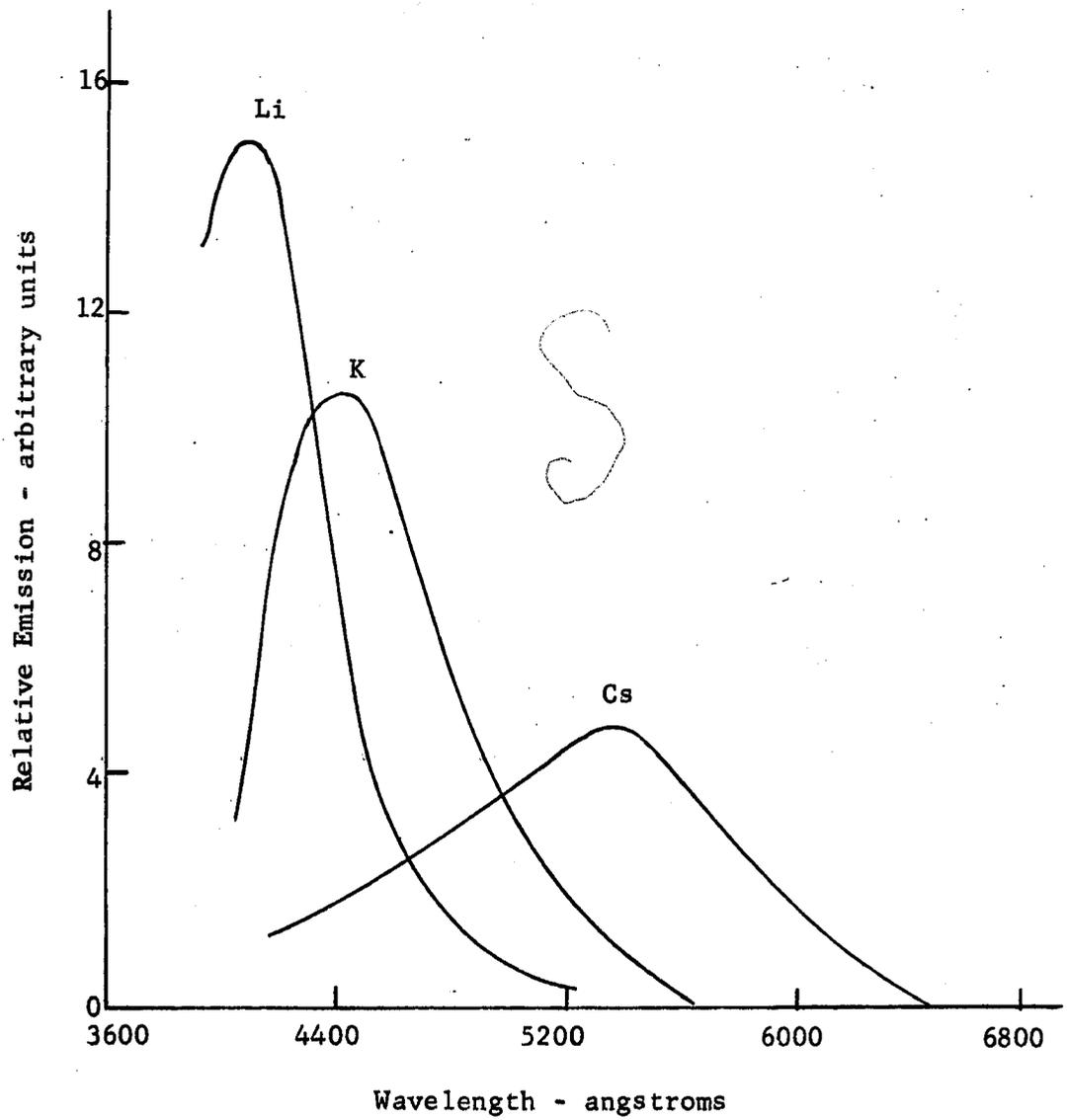
Radiation Characteristic of Fluorescent Lamp

Figure 19

shown in figure 20, but the more common metals, such as copper, aluminum and iron; which would normally be used as electrodes in gas discharge tubes; have thresholds between 2850 and 2950 angstroms, as shown in figure 21. It will be noted from this figure that the threshold for copper is 2850 angstroms.

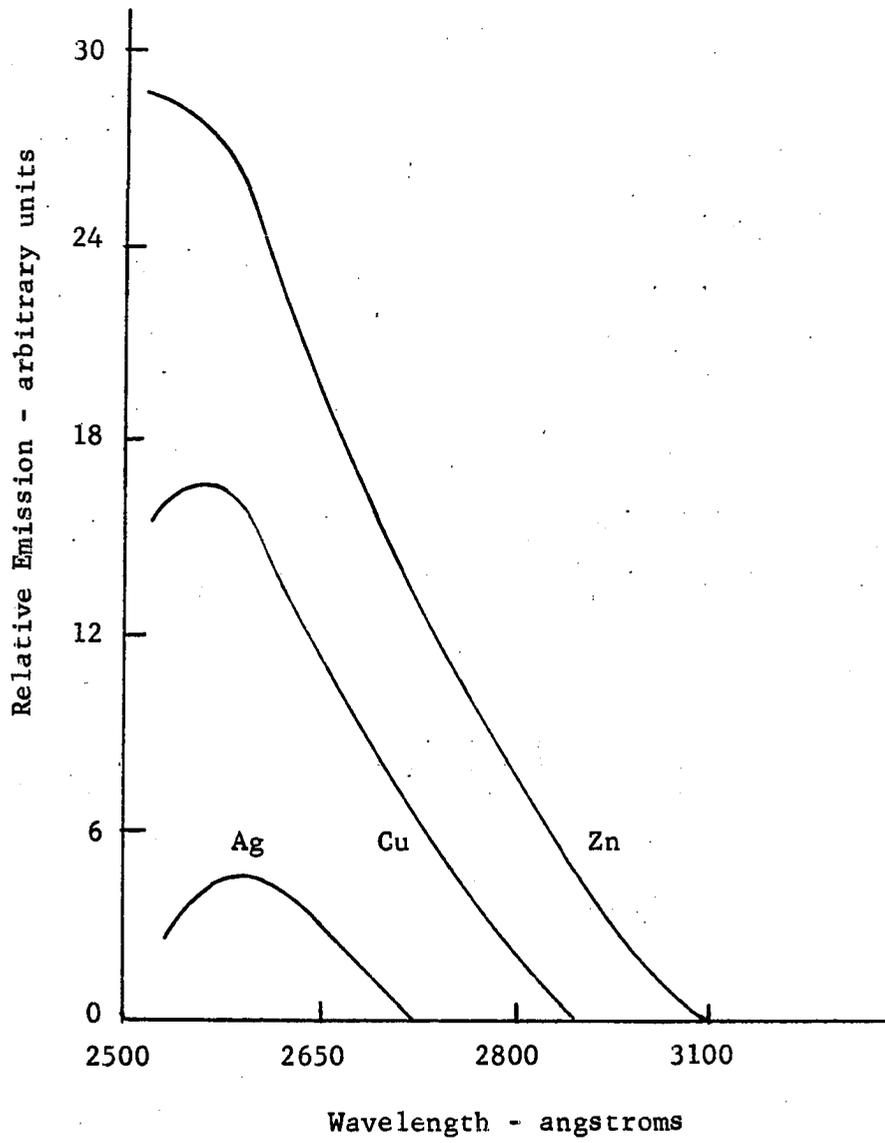
The final material present in the tube is the gas. Gas can be ionized by high energy particles and rays, as was demonstrated earlier in connection with cosmic ray and radioactive ionization of the air. The phenomenon of photoionization of gases is quite complex and depends on, among things, whether the gas is atomic or molecular and on the resonance and ionization potentials of the gas. In all cases, it is safe to say that the ionizing photon must possess at least the energy to excite the gas to resonance, and this energy corresponds to a wavelength in the far ultraviolet, or less than 2600 angstroms (88, p. 345).

The source of photons and the photoelectric emitters having been discussed, there remains only the connecting path to complete the cycle. The path--or better, the photon absorbers which obstruct the path--have necessarily been mentioned in connection with sunlight passing through windows, and artificial illumination passing through the enclosing bulb. The last absorber between the photons and the emitters is the discharge tube itself. This tube is invariably made of Pyrex glass, of at least one millimeter thickness, the transmission characteristic of which is illustrated in figure 22. It will be noted that Pyrex passes no wavelength less than 2700 angstroms; less than five per cent at 2800 angstroms; and thirty-five per cent at 3000 angstroms.



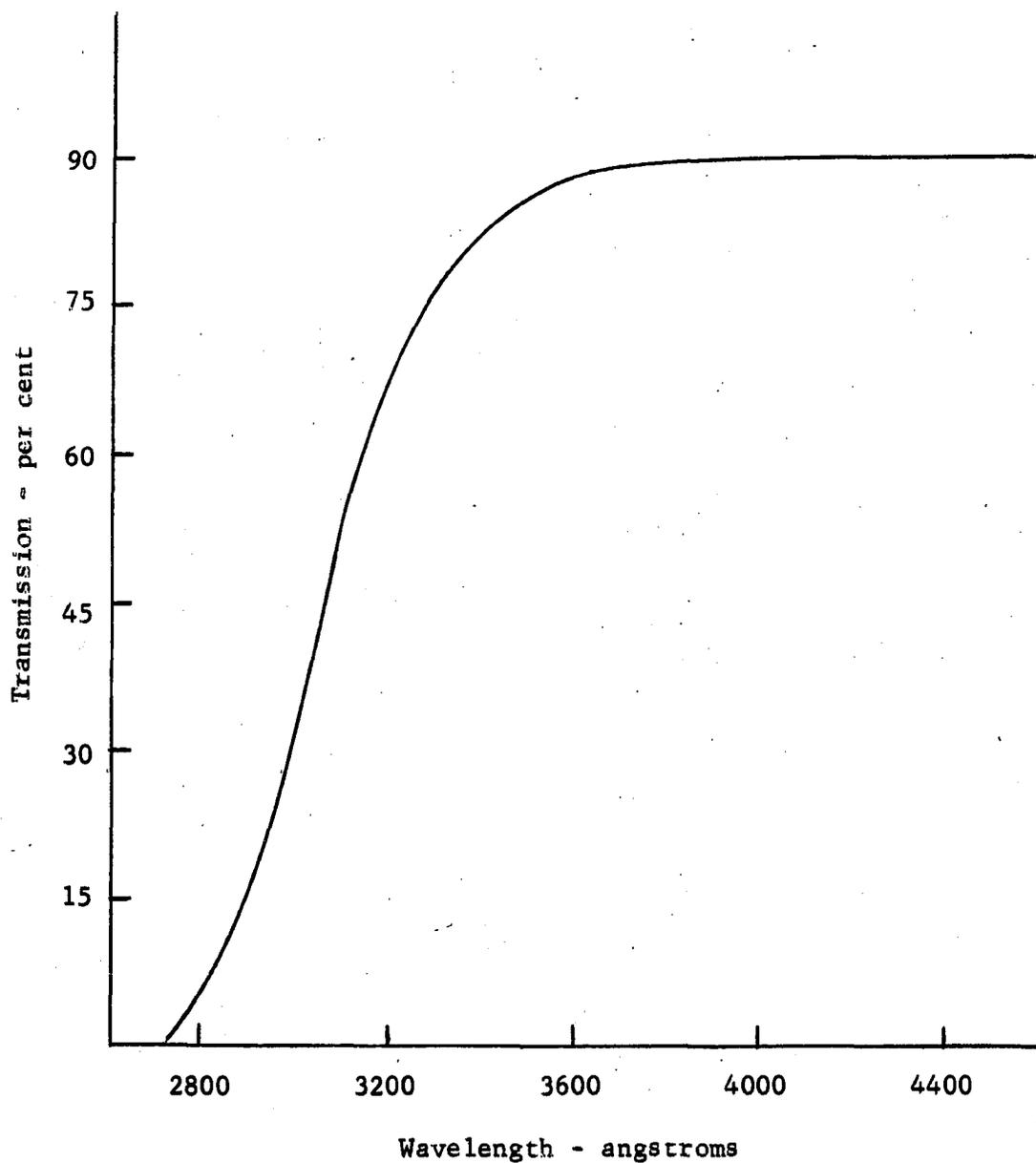
Photoelectric Response of Alkali Metals

Figure 20



Photoelectric Response of Metals

Figure 21



Light Transmission Characteristic of Pyrex

Figure 22

A summary of the values derived in the preceding paragraphs shows that:

- a. Photons of wavelength shorter than 3000 angstroms are unlikely to be present.
- b. The gas will not be ionized by any wavelength greater than 2600 angstroms.
- c. Copper, or any less active material, requires a wavelength of at least 2850 angstroms to cause photoelectric emission of electrons.

The conclusion which may be drawn is that there would be no effective creation of charge carriers in the tube due to photoelectric action.

The above discussion of photoelectric action is admittedly general and not rigorous. The various phenomena were treated as if they had specific, finite values, whereas they are really statistical averages, derived generally from exponential functions. Thus they have small, exponentially decreasing values well beyond the so-called cut-off points. Even a very small photon intensity might be sufficient to produce a number of electrons comparable to the also small number of ion pairs produced by cosmic rays and radioactivity. Really meaningful results could only be determined by a detailed analysis under specific conditions.

Another source of ionization is thermal energy. Thermal energy is capable of ionizing either the gas or the electrodes of a discharge tube; however, it will be shown that room temperature is insufficient to provide any such ionization. First, the Saha equation (15, p. 92) for partial pressures of gases will be used:

$$X^2 p / (1 - X^2) = 3.16(10)^{-7} T^{2.5} \exp(-eV/kT),$$

where $X = n_i/n = n_e/n =$ fraction of ionized atoms

$n_i = n_e =$ ionized pairs

$n = 3.54(10)^{16} =$ atoms per cubic centimeter at one millimeter of mercury

$p =$ pressure in atmospheres, assumed as $1/760$ or $1.32(10)^{-3}$

$T =$ absolute temperature

$V =$ ionization potential.

For very small ionization fractions, $1 - X^2$ may be replaced with 1 and Saha's equation may be rewritten

$$\log_{10} n_i^2 = -5050V/T + 2.5\log_{10} T + \log_{10} n^2/p - 6.5.$$

If it is assumed that

$$T = 300 \text{ degrees Kelvin}$$

and

$$V = 14 \text{ volts,}$$

then

$$\begin{aligned} \log_{10} n_i^2 &= -5050 \times 14/300 + 2.5\log_{10} 300 + \log_{10} 9.5(10)^{35} - 6.5 \\ &= -236 + 6.2 + 36 - 6.5 = -200 \end{aligned}$$

$$\text{and } n_i = (10)^{-100}$$

This, of course, is a totally negligible, almost ridiculous figure. In order to show that the Saha equation does give reasonable results under other conditions, consider sodium vapor, with

$$V = 5.14 \text{ volts}$$

$$T = 5050 \text{ degrees Kelvin}$$

$$p = 1 \text{ atmosphere.}$$

$$\text{Then } \log_{10} n_i^2 = -5.14 + 9.2 + 30.4 - 6.5 = 28$$

$$\text{and } n_i = (10)^{14} \text{ ion pairs per cubic centimeter, a}$$

very appreciable degree of ionization. The tremendous difference in the two cases is primarily due to the exponential factor

$$eV/kT \approx (10)^4 V/T$$

Thermal energy may also cause the emission of electrons from metallic electrodes, but this action, also, is negligible at room temperature. The actual degree of electron emission may be shown by the use of Richardson's equation (105, p. 438). The equation for no electric field will be used, since even very high fields modify the results only to a minor degree,

$$j = AT^2 \exp(-w/kT)$$

or
$$n_e = j/e = (AT^2/e) \exp(-w/kT),$$

where j = amperes per square centimeter

A = 60 amperes per square centimeter per degree Kelvin squared, an empirical constant

T = absolute temperature, assumed as 300 degrees

w = metal work function, assumed as 4.5 volts, an average value for many metals

n_e = electrons emitted per square centimeter per second.

Substitution of these values gives

$$\begin{aligned} n_e &= \left(60(300)^2 / 1.6(10)^{-19} \right) \exp \left(-(10)^4 4.5/300 \right) \\ &= 3.37(10)^{-40} \text{ electrons per square centimeter per} \end{aligned}$$

second, again a trivial figure. Richardson's equation is very similar to that of Saha, especially in the exponential factor; and, similarly, gives radically different results for small changes in w/T , the variable factor in the exponential. In both cases the exponential is eX/kT , with X representing either work function or ionization potential. Small variations in X or T give extremely large variations in the value of the function. Most gases show negligible ionization below about 5000 degrees Kelvin and most metals below 1000 degrees.

The next ionization source to be considered is high electric field emission from metal electrodes. This type of emission becomes appreciable for electric fields greater than 10^9 volts per meter but is trivial for fields less than 10^8 . A field of 10^9 would require a supply of 100 kilovolts and an electrode gap of 0.1 millimeter. Such a combination would probably not be used unless the specific objective was to investigate high field emission. A more probable maximum field would consist of a potential source of several tens of kilovolts and a gap of several tenths of a millimeter, giving a field of

$$X(10^4)/X(10)^{-4} = (10)^8 \text{ volts per meter.}$$

The Fowler-Nordheim equation (105, p. 453) governs this type of electron emission,

$$n_e = j/e = \left(1.6(10)^{-10} E^2/ew \right) \exp \left(-7(10)^9 w^{3/2}/E \right),$$

where E is the field in volts per meter and other symbols are as previously defined. A field of 10^8 volts per meter and work function of 4 volts give

$$n_e = \left(1.6(10)^{-10} E^2/ew \right) \exp \left(-7(10)^9 8/(10)^8 \right) = (10)^{-220} \text{ electrons per centimeter squared per second.}$$

This, again, is a trivial, ignorable quantity.

Other possible sources of ionization are flames and X-rays, but these will not normally be present in any form and will not, therefore, be discussed.

Summarizing the entire discussion of the presence of charge carriers in a laboratory discharge tube, under normal conditions, it is seen that:

- a. Flames, X-rays, thermal energy and high electric fields will produce no such carriers.

- b. Photoionization of the gas is highly unlikely, as it requires photon wavelengths of less than 2600 angstroms, and only wavelengths greater than 3000 angstroms are likely to be present.
- c. There would be some probability of photoemission from some metals; such as zinc, with a work function of 3.5 volts; in intense, natural or artificial light. Less active metals with work functions greater than four volts, not exposed to intense lighting, would be very unlikely to emit photoelectrons.
- d. Other than those produced as in c above, the only carriers present at one millimeter of mercury are the one pair per cubic centimeter produced by average radioactivity and cosmic ray action.

APPENDIX B

LIST OF SYMBOLS

The meaning of symbols used throughout the paper are shown in this list. Symbols with more than one meaning will be clarified when used. Also, the specific meaning will frequently be indicated by the use of subscripts and superscripts. Some symbols used for limited purposes are not included in the list but are explained in legends when used.

Symbol	Description
A	Area, constant
a	Constant
B	Constant
b	Constant
C	Constant
D	Diffusion coefficient, photoelectric ionization factor
d	Length, length of Crookes dark space
E	Electric field, energy
e	Charge of electron, natural logarithm base
F	Constant
f	Fraction
H	Heat of evaporation
h	Planck's constant
i	Current
J	Sputtered atom current
j	Current density
K	Thermal conductivity
k	Boltzmann constant
K.E.	Kinetic energy
L	Mean free path
M	Mass of atom
m	Mass of ion
N	Number, specific meaning indicated when used
n	Number, specific meaning indicated when used
P	Photoelectric ionization factor

Symbol	Description
p	Pressure
Q	Macroscopic charge exchange cross section at one millimeter of mercury pressure
q	Rate of electron-ion pair production
s	Ionization coefficient
T	Temperature
t	Time
V	Potential
V_c	Cathode fall potential
V_n	Normal glow cathode fall potential
v	Velocity
W	Weight, power
w	Work function
x	Variable
y	Variable
Y	Sputter yield
γ	Electron emission coefficient
λ	Wavelength
ν	Frequency