CONCLUSIONS

The present study of the dispersion of microwaves due to rotational spectra of this bimolecule has provided very useful information. Most important is the resolution of K lines, which has led to the exact determination of rotational constants, the knowledge of which can be used to determine exactly the O-H—O bond length in the gas phase. Susceptibility measurements have been used for the first time to determine the molecular structure. The large moment of inertia of this bimolecule has been a serious handicap, as it reduces the population of levels involved in the transitions; but it has also been useful as the reduction in population density has resulted in a small value of $\Delta\nu$, which is responsible for the resolution of the spectrum. It is hoped that further studies with isotopic species will provide information on the entropy change ΔS in the bimolecular reaction, and that they will also be of interest for internal-rotation studies.

ACKNOWLEDGMENTS

We are greatly indebted to Professor R. C. Majumdar, head of the Department of Physics and Astrophysics, University of Delhi, for his interest in the work and persistent encouragement. We are thankful to Dr. P. C. Mathur for his valuable help in the preparation of the manuscript, and to the Council of Scientific and Industrial Research for financial assistance.

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Calculation of Ion Bombarding Energy and Its Distribution in rf Sputtering

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The energy distribution of bombarding ions in typical rf sputtering conditions has been calculated. The Mathieu-type equations of motion of ions and electrons in the cathode-fall region are numerically integrated by a computer with various initial and boundary conditions. The self-biased dc component V_{dc} is found to be 0.999928 of one-half the peak-to-peak rf potential applied across the cathode dark space, which is in agreement with the value obtained from mobility considerations. The ion energy distribution is found to depend on rf voltage and frequency, dark-space distance, and $e/$(ion mass) ratio. Physical explanations are provided for the fact that a large percentage of the ions possess energies greater than eV_{dc}. The effect of high electron temperature on the ion-energy distribution has been studied and found to be very small. Trajectories of both the ion and electron in the cathode-fall region have also been calculated.

I. INTRODUCTION

THE technique of radio-frequency (rf) sputtering, as first described by Anderson, Mayer, and Wehner[1] has gained popularity in applications such as dielectric thin-film deposition and ion etching.[2] Many investigations[3,4] on the properties of sputtered film have been reported. In order to achieve an understanding of the sputtering and etching mechanisms, it is necessary to know the bombarding energy of the ion and its distribution.

It is known[5,6] that in a low-pressure abnormal glow discharge the application of an rf sinusoidal potential onto a dielectric insulated electrode results in a dc voltage on the surface of the dielectric which is biased negatively with respect to the plasma. As a result of this dc bias, a cathode-fall region or Crookes dark space is formed around the cathode. The magnitude of the dc component is determined by the boundary condition that no charge can pass through the dielectric and hence the net charge at its surface must be zero in one complete rf cycle. Butler and Kino[6] have measured this dc bias and mathematically described the rectification effect. Their theoretical treatment is based on some experimentally measured parameters and no attempt has been made to determine the energy distribution of the ions. The effect of superimposing a rf field on a dc glow discharge has been studied by Severin.[7] In this case, the amplitude of the rf field is assumed to be small compared to that of the dc field in the cathode-fall region. Hence, it can be treated as a perturbation, i.e., the alternating field does not depend on ion displacement.

[1] G. S. Anderson, W. N. Mayer, and G. K. Wehner, J. Appl. Phys. 33, 2991 (1962).

[2] See, for instance, First and Second Symposia on the Deposition of Thin Films by Sputtering, sponsored by University of Rochester and Consolidated Vacuum Corporation, 1966 and 1967 (unpublished).

[3] G. V. Jorgenson and G. K. Wehner, J. Appl. Phys. 36, 2672 (1965).

[4] P. D. Davidse and L. I. Maissel, J. Appl. Phys. 37, 574 (1966).

[5] P. A. Sturrock, Microwave Laboratory Report No. 638, W. W. Hansen Laboratories of Physics, Stanford University, Stanford, Calif., 1958 (unpublished).

[6] H. S. Butler and G. S. Kino, Phys. Fluids 6, 1346 (1963).

[7] P. J. W. Severin, Philips Res. Rept. Suppl. No. 2 (1965).

The present paper is an attempt to calculate the magnitude of the dc bias potential and the ion bombarding energy and its distribution in typical rf sputtering conditions. The assumptions under which this calculation is valid and the mathematical formulations are given in Sec. II, the results and discussions are presented in Secs. III and IV, respectively.

II. GENERAL FORMULATION

In order to facilitate a discussion of this work, a brief outline of assumptions and the method of calculation is given here. The forces acting on both ions and electrons in the cathode-fall region consist of a dc and an applied rf potential. Since the magnitude of the dc force is not known, an estimated value[8] is used to calculate the ion and electron velocities at the cathode for a large number of initial conditions. Knowing those velocities, the dc value can be obtained from the boundary conditions. This new dc value is used to calculate the velocities and still another value of the dc potential is obtained. This process is iterated until the input and output values of the dc component are equal. Once this is known, the energies and trajectories of ions and electrons are then calculated. The ion-energy distribution is obtained by a graphical method from the curves of ion velocity versus injection phase angle (see Figs. 2–4).

There are three assumptions made in this calculation:

(1) No collision term: The majority of ions do not suffer collisions when traveling across the cathode-fall region. This condition will be satisfied or partially satisfied if the mean free path of gas molecule-molecule collision is large or at least comparable to the dark-space distance, which is the case in typical rf sputtering conditions, i.e., pressure equal to 2 to 20 mTorr.

(2) Linear field distribution: The electric field $\mathcal{E}(x)$ is assumed to be a linear function of distance inside the cathode-fall region and does not extend into the plasma. This linear relationship has been verified by Langmuir probe measurements, electron-beam deflection techniques, and Stark effect of the emitted spectral lines, at least in dc glow discharges, for the condition that the size of the cathode is large compared to the dark-space distance. The recent results of Crawford and Cannara[9] have also affirmed this assumption.

(3) Origin of ions: It is assumed that both ions and electrons originate from the plasma with a Maxwellian velocity distribution. This is in accordance with findings of Davis and Vanderslice.[10] From their measurements of ion-energy distribution in a dc discharge, it is clear that at the pressure of 2 to 20 mTorr, the majority of ions originate at the ion-sheath–plasma interface.

A. Equations of Motion

If the cathode dimension is large compared to the cathode-fall distance, the motions of ions and electrons can be treated as an ideal one-dimensional case as shown in Fig. 1. From the second assumption, the electric field can be written as

$$\mathcal{E}(x)=\mathcal{E}_0(x/d)\,, \tag{1}$$

where x is the distance from the sheath-plasma boundary which is located at $x=0$ with the cathode situated at $x=d$, and $\mathcal{E}_0$ the field at $x=d$. Clearly, the potential $V(x)$ distribution is parabolic,

$$\begin{aligned} V(x) &= V_0(1-x^2/d^2) \\ &= (\tfrac{1}{2}\mathcal{E}_0 d)(1-x^2/d^2)\,. \end{aligned} \tag{2}$$

The V_0 here is the potential difference across the dark space. If a rf potential of frequency $f=\omega/2\pi$ is applied to the cathode, the equations of motion of ion and electron can be written as

$$(d^2x/dt^2)-(eV_0/Md^2)(\epsilon+2\cos\omega t)x=0\,, \tag{3}$$

$$(d^2x/dt^2)+(eV_0/md^2)(\epsilon-2\cos\omega t)x=0\,, \tag{4}$$

where M and m are the masses of ion and electron, respectively, e is the electronic charge, and ϵ is a dimensionless parameter representing the dc bias and is to be determined from the boundary condition $0<\epsilon<1$.

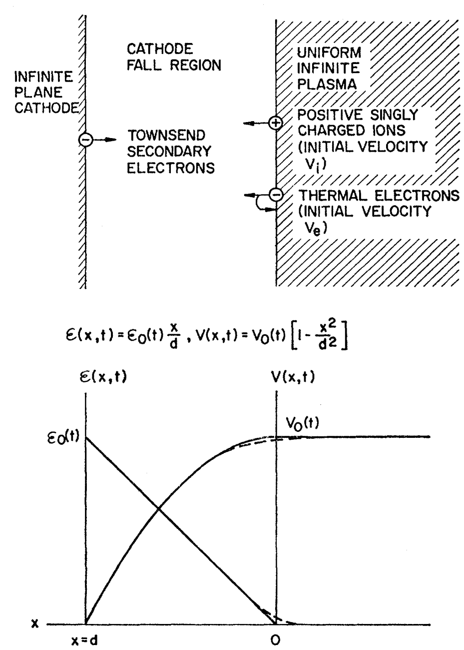

FIG. 1. Idealized one-dimensional model of the cathode-fall region in rf sputtering.

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[8] It has been shown (Refs. 1 and 6) that the magnitude of the dc force is almost equal to one-half the peak-to-peak rf potential. Hence, an arbitrary estimated value of 0.95 has been used to initiate the iteration process. A different value, say 0.5, can be used but will require more steps in the iteration process. The final result will remain unchanged.

[9] F. W. Crawford and A. B. Cannara, J. Appl. Phys. 36, 3135 (1965).

[10] W. D. Davis and T. A. Vanderslice, Phys. Rev. 131, 219 (1963).

It should be noted that V_0 here indicates the peak-to-peak voltage of the applied rf signal and the majority of the ions under consideration are assumed to be singly charged positive particles. Both Eqs. (3) and (4) are in the form of the Mathieu equation. To conform to its standard form,[11] a change of variable $\omega t=2z$ is made,

$$(d^2x/dz^2)-a_i(\epsilon+2\cos 2z)x=0\,, \tag{5}$$

$$(d^2x/dz^2)+a_e(\epsilon-2\cos 2z)x=0\,, \tag{6}$$

with

$$a_i=4eV_0/Md^2\omega^2\,, \tag{7}$$

$$a_e=4eV_0/md^2\omega^2\,. \tag{8}$$

In the Mathieu stability diagram[11] the operating points for Eqs. (5) and (6) will lie on the straight lines through the origin of the diagram with slopes ϵ and $-\epsilon$ for ion and electron, respectively. The effect of varying the e/mass ratio, the rf voltage or frequency or the cathode-fall distance is merely to shift the operating points along the straight lines. However, this is only true if ϵ is not dependent on those parameters, which, as it will be shown in Sec. III, is generally true for rf sputtering. The solutions of the equations of motion are, therefore, characterized by the values of a_i and a_e. In the case of the ion, the operating point falls in the unstable region because the dc term is negative. The solutions are essentially exponential functions. As for the electron, the nature of the solution will depend on the value of a_e. Because of its small mass the magnitude of a_e is much greater than unity. Hence, the operating point will generally lie also in the unstable region. No bounded solutions, therefore, exist. Although Eqs. (5) and (6) possess only divergent solutions, it is plausible physically since these two equations are valid only in the cathode dark space. As soon as the ions and electrons strike the cathode or cross the ion-sheath–plasma interface into the plasma, the equations are no longer valid. Numerical integration techniques have to be used to calculate the final velocities and the trajectories of ions and electrons in the cathode-fall region not only because of the divergent nature of the solutions but also because of the iteration process in order to determine the parameter ϵ.

B. Boundary Conditions

The boundary condition is defined by Eq. (9) that in every rf cycle, the net change of electric charge at the dielectric cathode surface must be zero.

$$\sum_i Q_i=0\,, \tag{9}$$

where Q_i stands for charges from ions and electrons (including secondary electrons). If τ is the period of the rf cycle, we have from (9)

$$-eN_e\langle\nu_e\rangle\Delta t+eN_i\langle\nu_i\rangle(\tau-\Delta t)(1+\gamma)=0\,, \tag{10}$$

where N_i and N_e are the numbers of ions and electrons per unit volume in the dark space; $\langle\nu_i\rangle$ and $\langle\nu_e\rangle$, their average final velocities at the cathode; Δt, the time period when the cathode is positive or anodic with respect to the plasma; and γ, the second Townsend secondary emission coefficient. It is shown[12] that u_i and u_e, the number of ions and electrons passing the plasma-sheath interface per unit area per unit time, can be written as

$$u_i\cong\tfrac{1}{4}(3kT/M)^{1/2}n_i\,, \tag{11}$$

$$u_e\cong\tfrac{1}{4}(3kT/m)^{1/2}n_e\,, \tag{12}$$

hence,

$$\begin{aligned}(N_i/N_e)&\cong(u_i/d)(\tau-\Delta t)/(u_e/d)\Delta t\\ &\cong(m/M)^{1/2}(\tau-\Delta t)/\Delta t\,,\end{aligned} \tag{13}$$

where kT has the usual meaning (assuming the plasma is at thermal equilibrium, $T_i\cong T_e$) and $n_i=n_e$ is from the fact that the plasma is approximately neutral. The approximate signs in Eqs. (11) and (12) arise because the relation $(\langle\nu^2\rangle)^{1/2}\cong\langle\nu\rangle$ has been used. Equation (10) can then be reduced to

$$\Delta t=\tau/[1+(M/m)^{1/4}(\langle\nu_e\rangle/\langle\nu_i\rangle)^{1/2}(1+\gamma)^{-1/2}]\,. \tag{14}$$

The parameter ϵ is related to Δt by the simple relationship

$$\epsilon=\cos(\tfrac{1}{2}\Delta t)\,. \tag{15}$$

C. Initial Conditions

In order to find $\langle\nu_i\rangle$ and $\langle\nu_e\rangle$, one must determine the dependence of ν_i and ν_e as a function of the initial velocities (dx/dt at $x=0$) and also the phase angle at which the particles cross the boundary $x=0$ into the field region. It is generally true that the probability of an ion or electron entering the dark space is equal for all phases of the rf cycle. Therefore, the number of ions and electrons entering the field region will be linearly proportional to the time period of the cathodic and anodic part of each cycle, respectively [this has been assumed in Eq. (10)], which will, in turn, depend on ϵ. Since the anodic part is very short compared to the cathodic part of each cycle, it is assumed in the computer calculation, that ions enter the dark space at a uniform rate during the entire rf period. Electrons will enter only in the anodic period which varies according to the value of ϵ.

In the one-dimensional case, only the positive x component of the initial velocities is considered which is assumed to have a Maxwellian distribution,[13]

$$f(\nu)=A\exp(-m\nu^2/2kT)\,, \tag{16}$$

[11] See, for example, N. W. McLachlan, *Theory and Application of Mathieu Functions* (Oxford University Press, London, 1951); or E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1950), 4th ed.

[12] R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill Book Co., New York, 1958).

[13] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958).

where A is a normalization constant, T is the plasma or electron temperature, and ν refers to the positive x component of the initial velocities. The final average velocities of ions $\langle\nu_i\rangle$ and electrons $\langle\nu_e\rangle$ can then be written as

$$\langle\nu_i\rangle=\left[\int_0^\infty f(\nu_i)\{(1/N)\sum_{j=1}^N \nu_{ij}\}d\nu_i\right]\Big/\int_0^\infty f(\nu_i)d\nu_i, \quad (17)$$

$$\langle\nu_e\rangle=\left[\int_0^\infty f(\nu_e)\{(1/N)\sum_{j=1}^N \nu_{ej}\}d\nu_e\right]\Big/\int_0^\infty f(\nu_e)d\nu_e. \quad (18)$$

The averaging of the phase factor is indicated by $(1/N)\sum_{j=1}^N \nu_j$ at certain ν_i or ν_e values. The integrals do not extend to $-\infty$, since negative values of the initial velocity do not add any particles into the cathode-fall region.

III. RESULTS

The numerical integration of Eqs. (5) and (6) was carried out on computer by the fourth-order Runge-Kutta method similar to the one used by Lever.[14] The input values of ϵ, a_i, and a_e are 0.95, 2.64×10^{-3} to 0.526, and 1.94×10^2 to 3.87×10^4, respectively. Those values of a_i and a_e correspond to a variation of V_0 from 0.2 to about 40 kV (with $f=13.56$ MHz) or a variation of f from 2.2 to 30 MHz (with $V_0=1$ kV). The other parameters have been chosen to be M = mass of argon and $d=1$ cm (which is equivalent to the pressure of about 10 mTorr and zero magnetic field). The experimental value of γ is available for Ge, Si,[15] and other materials[16] ($\gamma=0.04$ is used in the computer calculations). The electron temperature of the plasma is assumed to be no less than 500°K, at which most calculations were performed. Several runs have been made at $T=10\,000$°K, which is probably typical if the electric field extends slightly into the plasma region (Fig. 1). The effect of the large T value on the ion-energy distribution is very small as it will be shown later.

A. Self-Biased dc Term

When the initial input is 0.95 the convergence of the ϵ value occurs after three or four iterations. With various values of a_i, a_e, and plasma temperature, the final value of ϵ remains essentially constant at 0.999928 $\pm$0.000002 which is almost identical to the value obtained from assuming that the mass ratio m/M is equal to the ratio of the areas of the anodic and cathodic parts of the applied rf cosine signal. Physically it would seem reasonable to observe this agreement since the ions and electrons are under the influence of identical forces and their mobilities will then depend only on the masses involved. For all practical purposes, therefore, the dc bias voltage determined from the mass-ratio consideration can perhaps be used reliably for an estimate of the bombarding energy of the ions in rf sputtering.

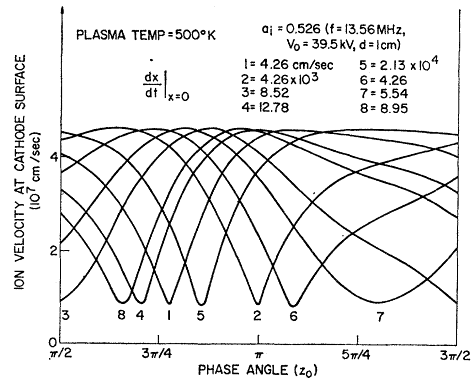

FIG. 2. Ion energy as a function of injection phase angle with a distribution of initial velocity $a_i=0.526$.

B. Ion-Energy Distribution

Knowing the dc voltage V_{dc}, which is equal to $\frac{1}{2}\epsilon V_0$, one would expect the maximum bombarding energy of the ions to be no greater than $\frac{1}{2}eV_0$. This, however, turns out not to be the case. This dc potential serves only as an approximate average value of the ion energy. There is an energy distribution which is determined by many factors. Figures 2–4 show the ion velocity (or energy) at cathode ($x=d$) as a function of the phase angle Z_0, at which the ion enters the dark space with various initial velocities (dx/dt at $x=0$). At $a_i=0.526$ ($V_0=39.5$ kV, $f=13.56$ MHz, and $d=1$ cm), it is shown in Fig. 2 that large percentages of ions arrive at the cathode with maximum final velocity. There are one or more minima in each curve, which seem to shift to larger values of Z_0 in a cyclic fashion as the ion-injection velocity is increased. As a_i becomes smaller

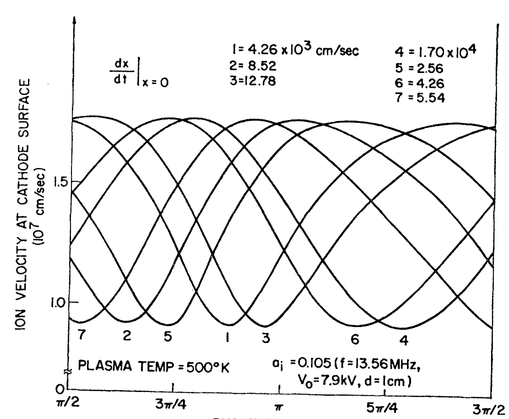

FIG. 3. Ion energy as a function of injection phase angle with a distribution of initial velocity $a_i=0.105$.

[14] R. F. Lever, IBM J. Res. Develop. **10**, 26 (1966).
[15] H. D. Hagstrum, Phys. Rev. **119**, 940 (1960).
[16] H. D. Hagstrum, Phys. Rev. **96**, 325 (1954); **104**, 317 (1956); **104**, 672 (1956).

(Figs. 3 and 4), the percentage of ions with high velocity decreases and the curves become more sinusoidal in shape. It is noted that the spread in ion velocity is also reduced as a_i decreases. The actual distribution at different values of a_i is shown in Fig. 5. These distribution curves were obtained by graphic techniques. Starting with the curves shown in Figs. 2–4, one can divide the rf period into N equal elements of phase angle, each with corresponding velocity (or energy) value. Every element is equivalent to the same number of ions entering the cathode-fall region from the plasma. After all the curves which cover the entire spectrum of initial velocity are divided; the number of phase-angle elements with the same energy are summed up. During this summing process, each element is weighted by the Maxwellian distribution factor corresponding to the initial velocity. Thus, an energy distribution curve at a certain a_i value is obtained. The distributions are plotted as the percent

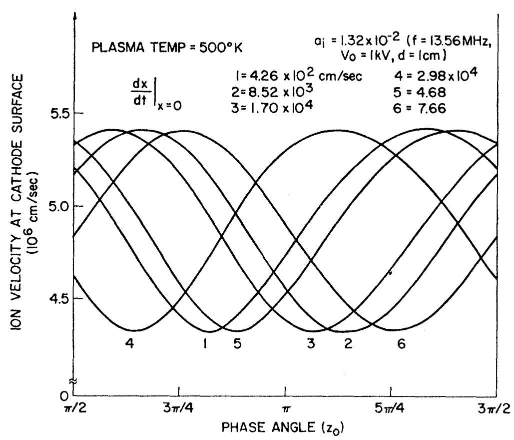

FIG. 4. Ion energy as a function of injection phase angle with a distribution of initial velocity $a_i = 1.32\times 10^{-2}$.

of ions versus the normalized energy in Fig. 5. The E_{dc} used in normalization is the energy derived from $E_{dc} = eV_{dc} = \frac{1}{2}\epsilon V_0$.

Some of the ions attain energies greater than E_{dc}. The physical interpretation is the following: At large values of a_i, which means large V_0 or small f or d, the ions require a short transit time, about 3 to 4 rf periods, to cross the cathode-fall region. If an ion enters the region at t_1 and reaches the cathode at t_2, as illustrated in Fig. 6, it is accelerated by a voltage greater than V_{dc} during the time intervals Δt_1 and Δt_2 and, therefore, attains an energy greater than E_{dc}. The excess in energy is indicated by the doubly shaded areas in Fig. 6. It is conceivable that some ions will gain energy less than E_{dc} from the field simply because of this same phase factor. As a_i decreases, the ions will have a longer transit time and the equivalent number of rf periods will increase. The maximum duration in which the ions are being accelerated at voltages greater than V_{dc} will,

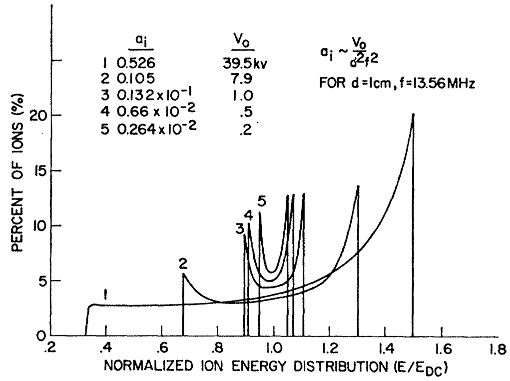

FIG. 5. Ion-energy distributions at different values of a_i (note: each curve with different density in data points used in the averaging process).

however, remain constant and, therefore, become a smaller percentage of the total energy gained from the field. The energy spread will then be reduced with decreasing values of a_i (Fig. 5). In order to demonstrate that the number of rf cycles for the ions to traverse the dark space varies with a_i, the ion velocity at $x=d$ is plotted as a function of the initial injection velocity as shown in Fig. 7. At $a_i = 0.526$, and assuming all the ions enter the field at $Z_0 = \frac{1}{2}\pi$, when the cathode is at its maximum negative voltage, the curve indicates two minima which means two rf cycles. The number of minima or cycles, increasing as a_i becomes smaller, is in good agreement with the average time interval the ions require to cross the cathode-fall distance. The distribution in Fig. 5 shows a concentration of high-energy ions at large values of a_i. This may be attributed to the fact that at large a_i, more ions arrive at the cathode during the second half of the cathodic part than in other portions of the cycle.

Several computer runs have been made with the electron temperature of the plasma set equal to 10 000°K. The objective is to study the effect on ion bombarding energy distribution if the electric does not vanish at $x=0$ as assumed, but extends into the plasma. This small extension is believed to increase the initial

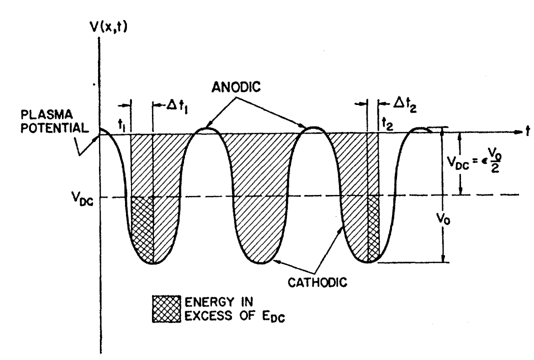

FIG. 6. Illustration of ion energy in excess of $E_{dc} = eV_{dc}$.

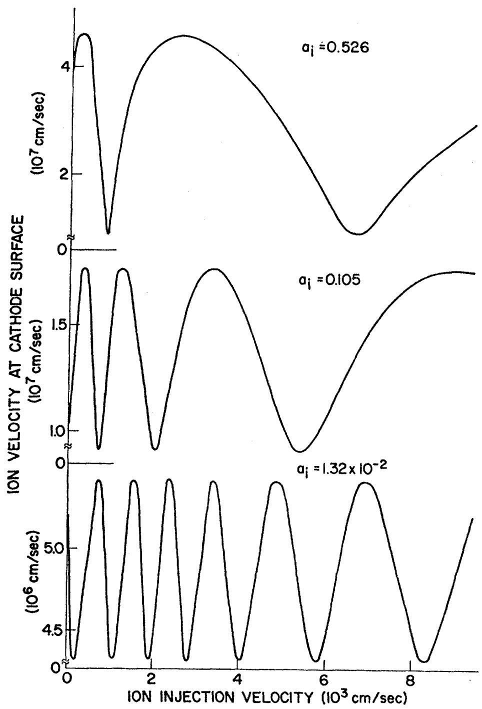

FIG. 7. Ion final velocity as a function of initial velocity at three values of a_i and $Z_0=\frac{1}{2}\pi$.

velocities of ions and electrons to the value corresponding to about 10 000°K. It is further assumed that this variation is so small that the $\mathcal{E}=\mathcal{E}_0(x/d)$ assumption is still valid inside the cathode-fall region. The results obtained are practically identical to those shown in Figs. 2–5 with very little change in the energy-distribution curves. Small variations occur only at large values of a_i. It is understandable since the injection velocity even at 10 000°K is still very small indeed when compared to the final velocity of the ions. At small a_i, the ion-velocity–phase-angle curves (Fig. 4) do not vary with increasing injection velocity. At large a_i, the curves do change in shape but the variation is cyclic (see Fig. 2). Since the energy distribution is obtained from an averaging process, the effect of large injection velocity is very small.

C. Ion and Electron Trajectories

At $a_i=0.526$, the ions will take on the average 3 to 4 cycles to traverse the dark space depending on the initial velocity. During every cycle the ions receive a retarding kick whenever the cathode becomes positive with respect to the plasma. Hence, there will be two points of inflexion in the second time derivative of x for each anodic period. This is shown in Fig. 8. The eight trajectories represent ions injected into the field at eight equally spaced phases spanning over an entire rf period. The origin of each curve is shifted by an equal amount (9.23×10^{-9} sec) for the sake of clarity. All trajectories demonstrate the characteristics of an exponential increase in x with periodic modifications due to the rf term in the Mathieu equation.

The trajectory of electrons is shown in Fig. 9. The predicted solution of the equation of motion is a sinusoidal function with exponentially increasing amplitude. Because of the large numerical value of a_e, the exponential factor is very large. Since the cathode is only at a relatively small distance, d, away, the electrons will take a very small fraction of the rf period to arrive. The trajectory is therefore almost purely exponential.

IV. DISCUSSION AND CONCLUSION

The solutions of the Mathieu-type equations of motion for ions and electrons in rf sputtering have a strong dependence on the parameters V_0, f, d, etc. In the case of the ion, the operating point of the equation lies on a straight line with slope ϵ in the third quadrant of the stability chart.[11] As V_0 decreases [or f, d increases, note $a_i\sim(df)^{-2}$] the operating point will move towards the origin of the stability diagram and the rf modification will become very large in amplitude, resulting in negative values of x, which is not acceptable physically. It thus poses the lower bond for the operating V_0, f, and d. On the other hand, as a_i is increased, the operating point will reach an area in which stable periodic solutions can be found. The ions may then oscillate inside the dark space and never reach the target. In practice, the upper limit with $a_i>2$ will be encountered only in extreme cases such as very small f or d. Similar boundary values exist also for a_e. In practice, the electron transit time in crossing the dark space is probably the factor in deciding how large f can be.

In a conventional rf diode-type sputtering system, the plasma is mainly sustained by the Townsend secondary electrons. Although the reported experimental values of γ are very small, i.e., $\gamma=0.04$ for Si with 1-kV Ar ions, they will give rise to a large number of ionizations in the plasma because of their high energy. The ion energy distribution will generally not depend on the cathode target material. Unless the value of γ becomes comparable to unity, the cathode material

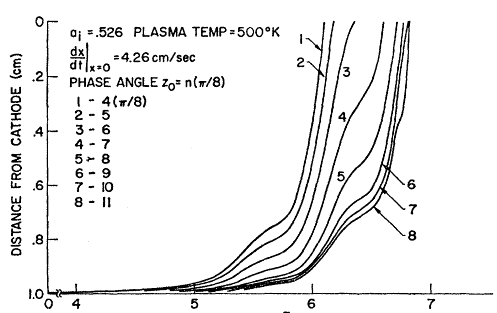

FIG. 8. Typical ion trajectories in the dark space.

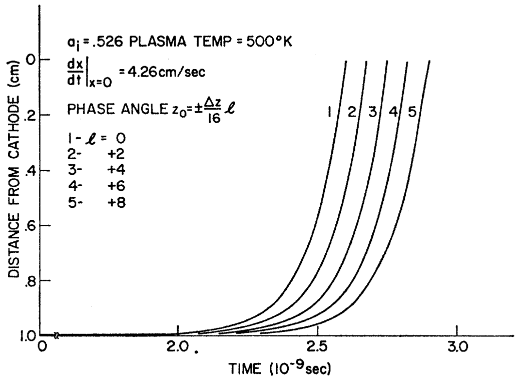

FIG. 9. Typical electron trajectories in the dark space.

will have very little effect on ϵ as can be seen from Eqs. (14) and (15).

No secondary electron due to electron bombardment is considered in this calculation. These secondaries will occur only in the anodic part of the cycle and will be driven right back to the cathode contributing no net change in the process.

The ion energy distribution, as shown in Sec. III, is attributed mainly to the phase factor and the initial velocity distribution. In order to obtain ions with relatively uniform energy, it is advisable to use large f, d, or M but small V_0. The value of M and V_0 will, however, be determined from the sputtering yield considerations and f will be limited by the electron transit time. The d value will depend on the minimum pressure one can use to sustain a glow discharge and also from ion etch or sputtering rate considerations. As for the condition of large percentage of impact ions with the largest energy, the large value of a_i indicates small f, d, and M but large V_0. Again, the choice of the values of M and V_0 is dictated by the sputtering mechanisms. The factors determining the minimum value of f are given elsewhere[1] and the limits on d may be the back-diffusion of the sputtered material onto the cathode and also some considerations on the property of the sputter-deposited films. No attempt has been made to include in this calculation the fact that electrons and ions with large initial injection velocities may enter the field region against a repulsive force. This occurs when an ion (or electron) diffuses into the dark space at the end of the anodic (or cathodic) part of the cycle with enough kinetic energy to carry it far into the field region until it is accelerated by the attractive force in the next part of the cycle. This is believed to have little effect on the values of the dc biasing potential and its effects on ion-energy distribution have been compensated for by the assumption that ions are injected into the field region at a constant rate during the entire cycle.

Another factor which may have some effect on the ion-energy distribution is the electron-ion recombination. When an ion comes close enough to the cathode's surface for the electronic wave functions of the ion and the solid to overlap, the incoming ion may be neutralized by an electron tunneled into its ground state. Bombarding ions may also be neutralized by Auger electrons.[15] The neutralized ion will then have a final velocity that depends on the time and place of neutralization. This recombination effect is considered to be small since electron tunneling occurs only when the ion is very close to the cathode and the ion–Auger-electron recombination usually has a small cross section. At the same time there are very few Auger electrons to neutralize the incoming ions because of the small γ value.

Other factors, such as ionization of sputtered particles, charge exchange between ions, and neutral gas molecules or sputtered species, etc. will all have small effects on the results of this work. It would, however, be unduly complicated to include all these effects in the present calculation.

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