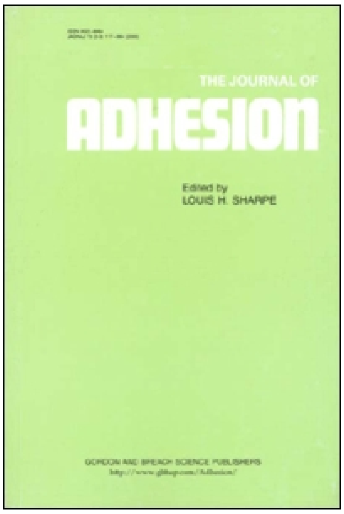

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Adhesion of Ion Plated Films and Energies of Deposition

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Adhesion of Ion Plated Films and Energies of Deposition[†]

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Expressions for the energy distribution of ions in a glow discharge first derived by Davis and Vanderslice are related to the ion plating process and used to derive expressions for the energy distributions of the neutral atoms. These expressions indicate that in ion plating, the majority of the depositing particles arrive at the substrate with energies of the order of 100 eV. The mechanism of adhesion is discussed in the light of these results.

INTRODUCTION

The concept of improving the grain structure and film/substrate adhesion by evaporation in a glow discharge with the substrate as cathode is not new. In 1938, Berghaus[1] described the technique and coating apparatus in some detail, claiming "a perfect structure and adhering strength" even for thicker layers. In 1963, Mattox, in a paper describing the apparatus, methods of deposition and results obtained, named the technique "ion plating" and this title now seems to have gained general acceptance. Since then, many papers [2,3] describing the technique and the results obtained have been published. The main advantage claimed for ion plating is the very good adhesion obtained between films and substrate, even when the film and substrate materials are mutually insoluble (incompatible pairs). Other advantages are the improvement in grain structure that can be obtained,[4, 5] and the good throwing power leading to improved coating uniformity.[3, 6, 7] In ion plating the specimen is held at a high negative voltage, typically 2–5 kV, and a glow

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discharge is struck between the earthed parts of the apparatus and the specimen in an inert gas atmosphere, typically argon at a pressure between 10^{-2} torr and 5×10^{-2} torr. The discharge causes sputter cleaning of the specimen surface and this is continued until the specimen surface is clean. The coating material is then evaporated into the discharge and deposits on the specimen surface and other parts of the apparatus, the discharge being maintained during deposition. The reasons for the good adhesion obtained, have been discussed[2] but no convincing explanation has yet emerged. In the present paper, the known facts on ion plating that are considered to be relevant are presented and discussed, and the energies of particles in a glow discharge are considered and related to the ion plating process.

FACTORS AFFECTING ADHESION

Mattox[2] has considered the factors affecting adhesion in some detail. Following his approach we can state that for good adhesion we require a clean substrate surface so that contaminating films do not form a weak interlayer between film and substrate. Also adhesion will be improved if the film material can penetrate into the substrate material or *vice versa* by diffusion or by some other mechanism. This penetration into the substrate will also be more likely if the substrate is clean. When diffusion between coating material and substrate is possible, high temperatures will aid diffusion as will defects (vacancies) in the subsurface layers. Penetration of coating material into the substrate not only improves the adhesion directly, but by forming a gradation of composition across the interface, it reduces damaging stress gradients across the interface caused for instance, by differences in thermal expansion coefficients.

ION PLATING AND ADHESION

Numerous comparisons of the adhesion of films produced by ion plating and those produced by other techniques have indicated the superiority of ion plated films in this respect.[2, 6] Figure 1 shows two mild steel tensile specimens which have been pulled to failure. Both specimens were coated with silver, about 3 μ thick. The coating produced by vacuum evaporation has peeled from the steel whereas the ion plated film is adherent up to the point of tensile failure. Figures 2a and b, are scanning electron micrographs of vacuum evaporated and ion plated silver films on a steel substrate after rubbing a hemispherically ended pin (radius 0.25 inch) across the surface under a load of 100 g. The superiority of the ion plated film is obvious.

Experiments performed by the author have never succeeded in causing an adhesion failure of ion plated films, and it must be accepted that such films have extremely high adhesion to the substrates.

Let us now consider the reasons for the high adhesion. Firstly, in ion plating the substrate is cleaned prior to plating and is maintained clean during plating by the ion bombardment. The cleanliness is a necessary condition for good adhesion but it is doubtful whether it is a sufficient condition when the coating material and substrate material are incompatible. Results from many experiments show that specimens prepared by vacuum evaporation, immediately after ion bombardment cleaning do not show good adhesion (Figure 2a). It seems probable, therefore, that the deposition in the discharge is essential. The most widely supported reason for the improved adhesion has been that the vapour atoms are ionised and arrive at the substrate with high energies, thus penetrating the lattice of the substrate.

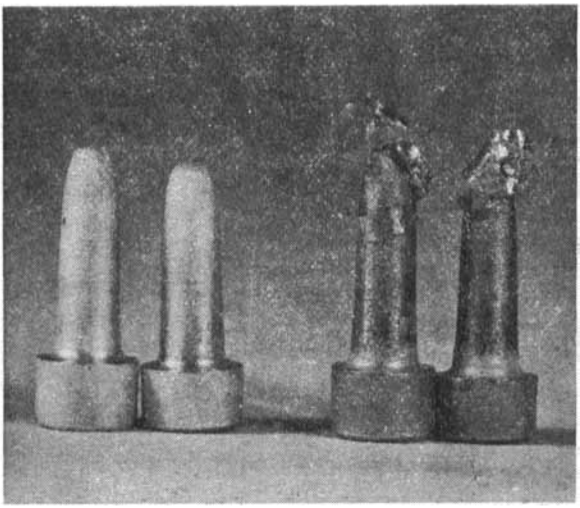

FIGURE 1 Steel tensile specimens plated with silver prior to pulling to failure. The specimen on the left is ion plated and the coating is adherent. That on the right is vacuum evaporated and the coating has pulled away completely.

However, if the ions arrived at the substrate with the maximum possible energy, i.e. 5 keV in a 5 kV discharge, the maximum depth of penetration would be small, about 50 A[8] whereas penetration depths of several microns have been reported.[9] Also, we must enquire what fraction of the vapour atoms are ionised. Several estimates have appeared in the literature.[10, 11] One estimate of about 30% ionisation was based on the assumption that the deposition on the back surfaces of substrates was due to ions following the field lines to the back of the specimen. However it has been shown[5] that

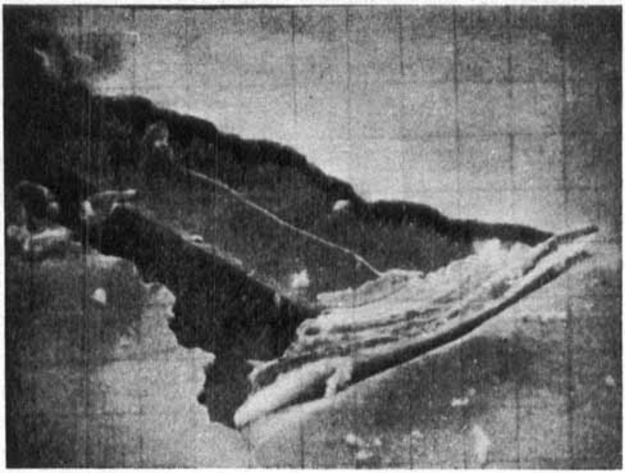

Figure 2a
Vacuum deposited

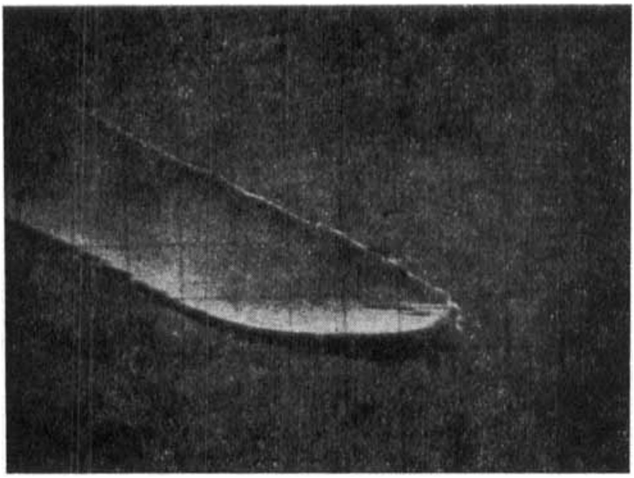

Figure 2b
Ion plated

FIGURE 2. Silver coatings on steel substrates after rubbing with a hemispherically ended steel pin under a load of 100 g.

deposition on the back surfaces can be attributed to gas scattering effects alone.

In ion plating experiments at University of Salford, typical conditions are pressure of argon 10^{-2} torr, bias voltage 3 kV. Under these conditions the current through the discharge can be measured, and if it is assumed that this current is due entirely to ion current at the cathode, a typical ion current density is 0.5 mA/cm^2. This indicates that about 3×10^{15} ions are impinging on 1 cm^2 of specimen surface per second. However at 10^{-2} torr about 4×10^{18} atoms are impinging on 1 cm^2 per second. This indicates that in the argon discharge less than 1 argon atom in a 1,000 is ionised.

An alternative approach is to consider the number of coating atoms arriving at 1 cm^2 of specimen surface per second and comparing this with the ion current density at the specimen. This indicates an ionisation efficiency of less than 1%. These calculations are crude but do indicate that ionisation efficiencies are low. Further evidence in favour of low ionisation efficiencies can be obtained by considering sputtering yields, that is the number of atoms ejected per incident ion. For discharges in argon, between 2 kV and 5 kV, most metals have a sputtering yield greater than unity.[12] Therefore in order to obtain a rate of film growth during ion plating, that is greater than the rate of film removal by sputtering, either the ionisation efficiency must be low or the ions must be of low energy. Direct experimental evidence is available on this point. Williams[13] reports on a coating system using an arc as the vapour source and with a negative bias on the specimen. The arc source can give ionisation efficiencies as high as 50% but in this case it was necessary to reduce the bias voltage to low values, or otherwise the removal rate by sputtering was greater than the deposition rate.

Accepting then that the ionisation rate is low, it must be asked how a small number of high energy ions can affect the adhesion of the total number of depositing atoms. In all probability the answer is that they cannot affect the overall adhesion significantly.

It has been shown[11] that the throwing power of the ion plating process is due to gas scattering effects and not to ionisation and field effects. The mean free path at 10^{-2} torr is about 5 mm, and typical vapour source to specimen distances in ion plating are over 100 mm. Therefore an ion leaving the source will have over 20 collisions before reaching the specimen, and energy will be transferred from ions to neutral atoms. The energy distribution of ions in a glow discharge has been calculated by Davis and Vanderslice,[14] and their theory will be used to obtain expressions for the energy distribution of both ions and neutrals, under typical ion plating conditions.

ION ENERGIES IN A GLOW DISCHARGE

After making certain simplifying assumptions Davis and Vanderslice[14] have derived an expression for the distribution of ion energies in a glow discharge. The theory has been tested experimentally by Davis and Vanderslice,[14] Houston and Uhl[15] and Ahmed,[16] whose results indicate that the theory can explain the main features of the measured energy distributions. The

Davis and Vanderslice approach is followed exactly below, but different boundary conditions are chosen so that equivalent, but simpler expressions are obtained.

The assumptions are that all ions originate in the negative glow, that the electric field varies linearly from the cathode to the edge of the negative glow, that symmetrical charge transfer collisions only are responsible for the energy spectrum and that the collision cross section does not change with energy. These assumptions are discussed by Davis and Vanderslice.[14]

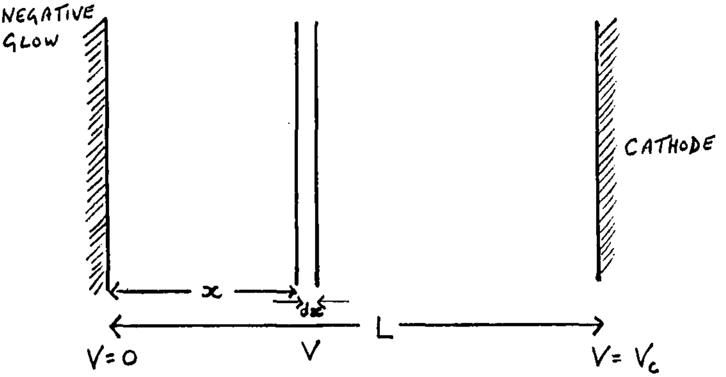

FIGURE 3 Representation of cathode dark space used in the calculation of ion energies.

Referring to Figure 3, the boundary conditions are

$V = 0, \quad x = 0$ at the edge of the negative glow
$V = V_c, x = L$ at the cathode.

The field strength varies linearly

$$\therefore \qquad \frac{dV}{dx} = \frac{Kx}{L}, \qquad V = \frac{Kx^2}{2L} + A$$

From boundary conditions $A = 0$ and $K = 2V_c/L$

$$\therefore \qquad V = V_c \frac{x^2}{L^2} \tag{1}$$

If N_0 is number of ions leaving negative glow, number of collisions between x and $x + dx$ is $N_0\, dx/l$.

The probability of any of the ions resulting from collisions between x and $x + dx$, reaching the cathode without further collisions is given by exp $[-(L-x)/l]$, where l is the mean free path for charge transfer collisions.

$\therefore$ Number of ions arriving at cathode with energy $V_c - V$ is

$$dN = \frac{N_0}{l} \exp\left[-\frac{(L-x)}{l}\right] dx$$

Substituting from eq. (1),

$$dN = \frac{N_0L}{2l\sqrt{V_cV}}\exp\left[-\frac{(L-L\sqrt{V/V_c})}{l}\right]dV$$

This is equivalent to the expression derived by Davis and Vanderslice.

The total ion energy arriving at the cathode is given by

$$\int_0^{V_c}(V_c-V)\,dN$$

This can be evaluated and is equal to

$$N_0V_c\left[\frac{2l}{L}-\frac{2l^2}{L^2}+\frac{2l^2}{L^2}e^{-\frac{L}{l}}-e^{-\frac{L}{l}}\right]$$

If no collisions occurred, the total energy arriving at the cathode would be N_0V_c and it is apparent that if l/L is small the ion energy loss is large.

The energy lost by the ions is transferred to neutral atoms. Not all the energy gained by the neutrals will be transferred to the cathode, but as the collisions are small angle a significant proportion of this energy will reach the cathode and measurements indicate that about 70% of the energy transferred to the neutrals is absorbed by the cathode.

ENERGY DISTRIBUTION OF THE NUMERALS

It is much more difficult to calculate an expression for the energy distribution of the neutrals arriving at the cathode than it is to calculate the comparable expression for the ions. If certain simplifying assumptions are made such an expression is obtainable, and represents the required energy distribution in a qualitative manner. Further, the major errors involved are apparent and sufficiently accurate quantitative estimates of the important parameters can be made.

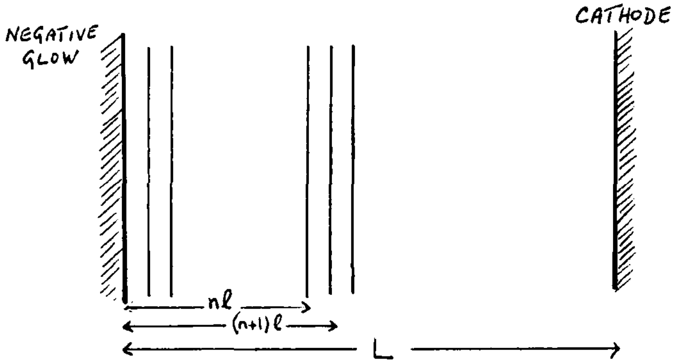

FIGURE 4 Representation of cathode dark space used in the calculation of neutral energies.

Referring to Figure 4, we assume that the space between the negative glow and the cathode is divided into L/l equal regions and that charge transfer collisions occur only at the boundaries between these regions, i.e. all collisions take place after an ion has travelled a distance l, the mean free path. We further assume at this stage that all energetic neutrals so formed travel to the cathode without further collision. (This is seriously in error, but does not effect the total energy of neutrals reaching cathode, which can be estimated from experimental measurements.)

$$\text{Voltage at} \quad nl = V_c \frac{n^2 l^2}{L^2}$$

$$\text{Voltage at } (n+1)l = \frac{V_c l^2}{L^2}(n^2+2n+1)$$

$$\therefore \text{ energy of ions at } (n+1)l = \frac{V_c l^2(2n+1)}{L^2}$$

These ions undergo charge transfer collision at $(n+1)l$ producing neutrals of equal energy. The number of collisions at each plane is N_0 and therefore there are N_0 neutrals formed at $(n+1)l$ with energy $V_c l^2(2n+1)/L^2$ and this gives the energy distribution of the neutrals.

$$\text{Total energy in neutrals} = \frac{N_0 V_c l^2}{L^2} \sum_{0}^{(L/l)-2} (2n+1) = N_0 V_c \left[1 - \frac{2l}{L} + \frac{l^2}{L^2}\right]$$

Before considering the expressions obtained for the total energy and energy distribution of the neutrals it is worthwhile to consider the energies of the ions, assuming that all collisions take place after a path length l, i.e. the same assumption as was made in considering neutrals. In this case all the ions arrive at cathode after travelling distance l. Their energy is found from Eq. (1) and is

$$V_c\left[\frac{2l}{L} - \frac{l^2}{L^2}\right]$$

and total energy of ions arriving at cathode is

$$N_0 V_c\left[\frac{2l}{L} - \frac{l^2}{L^2}\right]$$

which when added to the total energy of neutrals equals $N_0 V_c$.

Consider now the energy of the neutrals. The maximum possible energy of a neutral from the above expression is obtained by substituting $n = (L/l) - 2$ and equals

$$\frac{V_c l^2}{L^2}\left(\frac{2L}{l} - 3\right)$$

However, this is clearly incorrect as it depends on the arbitrarily chosen origin, i.e. the final plane where collisions occur has been arbitrarily chosen as being distance l from the cathode, but of course collisions can occur, and energetic neutrals formed, at any plane up to the cathode surface. Therefore, it can be seen that the maximum possible energy of a neutral is equal to the maximum possible energy of an ion. However, the choice of origin has little effect on the total energy of neutrals arriving at the cathode.

Let us now assume that l/L equals 1/20; it is probable that the ratio is less than this for ion plating.

The total energy in the ions is approximately $\frac{N_0 V_c}{10}$

and the total energy in the neutrals is $\frac{9\,N_0 V_c}{10}$

Measurements indicate that about 70% of the energy in the neutrals reaches the cathode and therefore we find that under these conditions the neutrals carry six times as much energy to the cathode as do the ions.

Now consider the number of particles involved. The number of ions arriving at the cathode is N_0, but the number of energetic neutrals formed is $N_0(L/l)$, typically at least 20 N_0.

Using the approximate theory for neutrals, those formed at distance l from the negative glow, i.e. those with lowest energy, have an energy of $V_c/400$, i.e. 10 eV for 4 kV bias.

The highest energy neutrals (using approximate theory) have energy

$$\frac{V_c l^2}{L^2}\left(\frac{2L}{l}-3\right),$$

i.e. for $L/l = 20$, about 0.1 V_c, 400 eV if the bias voltage is 4 kV.

The mean energy of the neutrals is

$$\frac{l}{L}V_c\left[1-\frac{2l}{L}+\frac{l^2}{L^2}\right]$$

which typically equals 200 eV for a bias voltage of 4 kV.

ENERGIES OF EVAPORATED ATOMS

In the previous section the energies of the argon ions and neutrals were considered. We are primarily interested in the energies of the metal atoms evaporated into the argon glow discharge. Unfortunately, little is known about the energies of metal ions in a discharge. In the following section we assume that the energy distribution for metal ions and neutrals are similar to those of the argon ions and neutrals. Results obtained by Ahmed[16] indicate that this assumption is reasonable.

ADHESION AND ION PLATING

We are now in a better position to discuss the reasons for the adhesion achieved in ion plating. The process that now emerges is one where the substrate is coated with a small number of energetic ions and a larger number of energetic neutrals and the majority of the depositing particles are of high energy. The energies of most of these particles is of the order of 100 eV rather than 1000 eV. We now no longer need to ask how a small number of very high energy particles affects the adhesion of all particles. The energy has been shared.

The depth of penetration of the coating ions and neutrals cannot be more than a few Angstrom units at these energies and the reported graded interfaces[9, 17] must be explained on a different basis. The actual bombardment of the specimen does however increase the surface temperature, promoting diffusion. Diffusion will also be increased due to the bombardment causing the formation of vacancies close to surface.

Ion plating is probably unique in this respect, as diffusing particles (i.e. the coating atoms) cause the vacancies to form and diffusion will occur before the vacancies are removed by annealing. The results of Swaroop and Adler[9] can be taken as evidence of enhanced diffusion as can results obtained by Sherbiney[19] who ion plated indium on to copper and found the copper–indium eutectoid with constant composition to a depth of 30 microns. This result will be reported more fully later.

No deep graded interfaces have been reported for incompatible pairs although the adhesion of such pairs is excellent. Ahmed[16] detected interpenetration of lead and copper over a depth of 40 A using SIMS. Although diffusion of nonsoluble materials would not normally be expected it is possible that some diffusion could take place in a highly defected surface.

An alternative explanation for the formation of graded interfaces is as follows. The ion and neutral bombardment of the substrate causes the surface atoms to be sputtered from the substrate. A significant proportion of the sputtered atoms will return to the substrate surface[18] due to gas scattering, as the mean free path is less than 5 mm. Therefore the atoms of coating material arriving first at the substrate, will be mixed or co-deposited with the returning sputtered atoms. This process can lead to significant depths of graded interfaces, especially at the higher gas pressures used (50 μ), as has been demonstrated by comparing sputtering and deposition rates.[5]

Some preliminary observations of the nucleation of ion plated and vacuum evaporated films[17] indicate that the vacuum evaporated atoms diffuse over the surface much more than do the ion-plated atoms, and therefore it is doubtful if surface diffusion is the cause of high adhesion in ion plated films.

During deposition an ion plated film is continually subjected to energetic particle bombardment. It is probable that any poorly adherent atoms that are deposited (possibly the ions and neutrals of minimum energy) will be preferentially sputtered from the surface. The removal of such particles will enhance the overall adhesion of the film.

CONCLUSIONS

The exact reason why high energy depositing particles should adhere more strongly than low energy particles is still unanswered. However, it now appears that ion plating is the deposition of particles, both ions and neutrals, the majority of which have energies of the order of 100 eV. These particles might adhere well due to:

a) Penetration into the substrate lattice to a depth of a few Angstroms.

b) Physical mixing of the depositing atoms and sputtered substrate atoms.

c) Preferential removal of any poorly adherent particles by sputtering during deposition.

d) Diffusion enhanced by high surface temperatures.

e) Diffusion enhanced by the bombardment induced subsurface defects.

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