

ELECTRICAL CHARGE EFFECTS IN THIN FILM ADHESION

by

Hanno Graf von Harrach

A thesis submitted for the
Degree of Doctor of Philosophy
in the University of London

Department of Electrical Engineering
Imperial College of Science and Technology
London

April 1973

Abstract

The adhesion of a thin film is normally attributed to physical and chemical interactions of the film with its substrate. In this work an electrostatic contribution to the adhesion due to the presence of electrical charges at the film-substrate interface is considered; the importance of the electrostatic adhesion is assessed.

The theories of physical (van der Waals) and electrostatic adhesion are discussed in detail. The calculations for metal films on insulating substrates show that the electrostatic component can contribute significantly to the adhesion of the film.

The electrostatic adhesion is determined by the electrical charge at the film-substrate interface. The mechanisms of charge generation at interfaces are discussed and a model is proposed for the electronic processes at metal-insulator interfaces.

The adhesion of thin films has been measured by a method which allows a quantitative comparison with the theories of adhesion. The electrostatic adhesion has been deduced from measurements of the electrical charge generated at the film-substrate interface. For the materials investigated in these experiments, the electrostatic component is a small percentage of the total adhesion of the film.

'Give to those who ask
and do not force those
who do not care to receive'

Bapak

Acknowledgements

I wish to thank The Clothworkers' Company for providing me with a grant for three years, and the Science Research Council for the financial support of this project.

For numerous discussions and suggestions I am deeply indebted to Professor J. C. Anderson, to my supervisor, Dr. Brian N. Chapman and to my colleagues in the Materials Section.

It gives me pleasure to thank sister Kate and brother Dave for their help in preparing the final manuscript.

INDEX

CHAPTER I	INTRODUCTION	page 9
1.1	Theoretical Description of Adhesion	9
1.2	Adhesion Measurements	10
CHAPTER II	THEORIES OF ADHESION	12
2.1	Van der Waals Forces	13
2.1.1	Interaction between Isolated Atoms	13
2.1.1.1	Dispersion	13
2.1.1.2	Polar Molecules	16
2.1.1.3	Repulsion	17
2.1.2	Adsorption on Solid Surfaces	18
2.1.2.1	Adsorption Calculations	23
2.1.3	Adhesion between Solids	43
2.1.3.1	Summation over adsorption energies	43
2.1.4	Macroscopic Theory of Adhesion	46
2.1.5	Summary	50
2.2	Electrostatic Adhesion	52
2.2.1	Definition of Electrostatic Adhesion	53
2.2.2	Electrostatic Work of Adhesion	55
2.2.2.1	Electrostatic force	55
2.2.2.2	Separation under equilibrium conditions	57
2.2.2.3	Separation at constant surface charge	61
2.2.2.4	Separation of a metal-insulator contact	62

CHAPTER III	ELECTRICAL CHARGES AT INTERFACES	67
3.1	Charges on Solid Surfaces	68
3.2	Contact Charging	71
3.2.1	Mechanisms of Contact Charging	72
3.2.1.1	Transfer of electrons across interfaces	74
3.2.2	Separation of Interfaces	79
3.2.2.1	Thermionic emission and tunneling	80
3.2.2.2	Discharge	84
3.2.3	Contact between Metals	89
3.2.4	Metal - Semiconductor Contact	90
3.2.4.1	Theoretical description	90
3.2.4.2	Experimental evidence	98
3.2.5	Metal - Insulator Contact	100
3.2.5.1	Electron transfer models	101
3.2.5.2	Ionic effects	113
3.2.5.3	Experiments of contact charging	115
3.3	Summary	120
CHAPTER IV	THE MEASUREMENT OF ADHESION	121
4.1	Methods involving Separation of Interfaces	122
4.1.1	Mechanical Methods	123
4.1.2	Acceleration Methods	127
4.2	Nucleation Methods	129

CHAPTER V	EXPERIMENTAL DETAILS	133
5.1	Film Stripping	134
5.2	Charge Measurement	140
5.2.1	Theory	141
5.2.2	Apparatus	144
5.3	Procedure	149
5.3.1	Substrate Preparation	149
5.3.2	Film Deposition	152
5.3.3	Film Stripping	152
5.3.4	Charge Measurement	154
CHAPTER VI	RESULTS AND DISCUSSION	155
6.1	Adhesion of Metal Films to Glass	155
6.1.1	General Results	156
6.1.1.1	Dependence on deposition parameters	158
6.1.1.2	Dependence on stripping conditions	158
6.1.1.3	Aging of films	160
6.1.2	Repeated Stripping	161
6.1.3	Charge Flow During Stripping	161
6.1.4	Charge Decay Measurements	163
6.1.5	Extraneous Sources of Charging	165
6.1.6	Microscopic Observations	168
6.1.7	Sputtered Films	170

6.2	Discussion: Adhesion to Glass Substrates	172
6.2.1	Reversibility of the Film Stripping Process	172
6.2.2	Charge Transfer across the Film-Glass Interface	175
6.2.3	Geometrical Factors in Adhesion Measurements	181
6.2.4	Comparison between Experimental and Theoretical Adhesion	187
6.2.4.1	Chemisorption	191
6.2.4.2	Comparison with previous experiments	193
6.2.5	Summary	194
6.3	Adhesion to Ionic Crystals	195
6.3.1	Results for Mica Substrates	195
6.3.2	Discussion	197
6.3.3	Adhesion to Rocksalt	201
6.3.4	Discussion	201
6.3.5	Summary	204
CHAPTER VII	CONCLUSIONS	205
CHAPTER VIII	FURTHER WORK	207
8.1	Charge Transfer Mechanisms	207
8.2	Adhesion Measurements	208
	PUBLICATIONS	209
	REFERENCES	210

CHAPTER I

INTRODUCTION

The adhesive properties of materials are applied to a wide range of uses. The applications fall into two broad categories: in the first, 'adhesives' are used to bond two materials together; the second category is concerned with the coating of surfaces for decorative or protective purposes. In all these applications the adhesion between two materials is of prime importance; however, our knowledge of the mechanisms by which materials adhere to each other has remained incomplete.

This work is concerned specifically with the adhesion of thin films, i.e. surface coatings of less than $1\ \mu\text{m}$ thickness. One of the most important applications of thin films is in micro-electronics. In the present semiconductor technology, metal films are used as interconnections on semiconductor devices; the durability of a device depends critically on the adhesion of these films to their substrate. Rather complex procedures are used nowadays (see Anderson 1972) to ensure good adhesion. However, theoretical estimates of thin film adhesion are not in agreement with the experimental values. Clearly, there is therefore a need for fundamental research into the adhesion of thin films.

1.1. Theoretical Description of Adhesion

The adhesion between two materials is the result of the interaction between the atoms or ions of the two materials near the interface.

A distinction can be made between chemical and physical adhesion forces (see Chapter 2): chemical bonding across the interface leads to strong adhesion; the van der Waals' forces are relatively weak, but always contribute to the physical adhesion. In cases where no chemical interactions occur between the adherands, the van der Waals adhesion is normally thought to be the only contribution.

An additional contribution to the adhesion of thin films is considered in this work: the electrostatic adhesion resulting from the presence of an electrical double layer at the interface. This effect follows very simply from classical electrostatics: if the two surfaces in contact are charged to opposite polarities, then there is an electrical attraction between the charge layers, which therefore contributes to the adhesion.

The importance of electrostatic adhesion of thin films on insulating substrates has been investigated in this thesis. It is well-known, that insulator surfaces become electrically charged by contact with other materials. This property often leads to hazards in industry, but is usefully applied, for example, in electrophotography. The mechanisms of charging (static electrification) are little understood at present. The investigation of charging mechanisms by contact between solids (Chapter 3) is therefore of importance for the investigation of the electrostatic adhesion.

1.2 - Adhesion Measurements

The structure of a thin film depends strongly on the adsorption of the atoms of the film to the substrate surface. If the atoms are

adsorbed by physical forces only, then it is possible to define a surface which represents the boundary between the two materials, i. e. the interface. For these cases, where there exists a discrete interface, it is possible, in principle, to measure the adhesion by separation of the interface. The thermodynamic definition of adhesion (Eley 1961) is applicable to this case: the adhesion energy W is defined as the work done in separating unit area of an interface reversibly.

If a film is bound to its substrate by chemical forces, it becomes more difficult to define an interface: the chemical reaction can lead to the formation of a chemical compound in an intermediate layer between the film and substrate. A similar situation arises if the film diffuses (or is implanted) into the substrate. In these cases the adhesion measurements cannot always be interpreted in terms of the thermodynamic adhesion energy.

The only direct way of measuring the adhesion of a thin film is by separation from the substrate (see Chap. 4). However, these experiments give only a measure of the adhesive performance, since the separation of the film normally involves irreversible processes. The adhesion energy as defined above, can only be deduced if the energy dissipated in irreversible processes is small; this condition appears to be satisfied in the method of adhesion measurement used in this work. In addition, the electrostatic adhesion can be assessed from measurements of the charge at the film-substrate interface (throughout this thesis, surface charge densities are given in units of electronic charges per square centimetre, written as $e \text{ cm}^{-2}$). Thus, a comparison can be made of the theoretical and experimental adhesion energies.

CHAPTER II

THEORIES OF ADHESION

The interactions between the atoms or molecules at the interface between two media are essentially the same as those occurring within a medium. It is convenient to classify these interactions according to their range of action. Short-range interactions (attractive or repulsive) are a result of an overlap of the electron distributions around each atom. Depending on the nature of the interacting atoms, a chemical compound may be formed by the sharing or exchange of electrons; the resulting chemical bonds (covalent, ionic or metallic) have strengths of several electron volts.

Long-range interactions, which give rise to the van der Waals' forces of attraction (physisorption), are universal between interacting atoms. These interactions are of primary importance in the adsorption of atoms to solid surfaces in the absence of chemical reactions, leading to bond energies of a few tenths of electron volts per atom.

In Sect. 2.1. the adsorption of atoms to solid surfaces will be discussed in terms of these long-range interactions; the short-range interactions are considered to contribute only a repulsive force as a result of the overlap of the electron wave functions of the interacting atoms.

The adhesion between two solids which do not react chemically, is calculated from the van der Waals forces. The additional contribution due to the electrostatic adhesion, arising from an electrical double layer at the interface between two solids, is considered in Sect. 2.2.

2.1. Van der Waals Forces

A theoretical description of the interactions at the interface between two solids can be approached from two different starting points. We can start by considering the interaction between two isolated atoms at a given separation and assume that these pair interactions can be summed to find the total adhesion between two solids; this method has been used extensively in the past for the calculation of physical adsorption forces. The other approach describes the interaction between two solids in terms of their macroscopic properties, while ignoring completely the microscopic details of the interface. These two approaches will be used to calculate the adhesion of the materials studied in this work.

2.1.1. Interaction between Isolated Atoms

2.1.1.1. Dispersion

The dispersion interaction between two atoms was first described by London (1930) and can be seen to arise as follows: in classical terms, the motion of the electrons around the nucleus of the atom gives rise to a fluctuating dipole moment; the electric field due to this dipole induces an instantaneous dipole on the other atom and causes an attractive force between the two atoms. London (1930) showed that the attractive energy, U_{dd} , between two hydrogen-like atoms (i and j) at a separation r_{ij} , between their nuclei is given by

$$U_{dd} = - \frac{C_{ij}}{r_{ij}^6} \quad (2.1)$$

where C_{ij} is the dispersion constant,

$$C_{ij} = \frac{3}{2} \alpha_i \alpha_j \frac{\hbar \omega_{oi} \omega_{oj}}{\omega_{oi} + \omega_{oj}} \quad (2.2)$$

α is the static electronic polarisability and ω_0 is the frequency of the electron in the ground state.

In the above description, only one electron is considered to contribute to the dispersion interaction. For more complex atoms, this assumption is inadequate, since several of the outer electrons in the atom will contribute to the interaction. These contributions can be taken into account by writing the dispersion constant (Eisenschitz and London 1930) as :

$$C_{ij} = \frac{3 \hbar e^4}{2 m^2} \sum_i \sum_j \frac{f_i f_j}{\omega_{oi} \omega_{oj} (\omega_{oi} + \omega_{oj})} \quad (2.3)$$

where f is the oscillator strength (in classical terms); the summations are taken over all the electronic transitions in each of the two atoms. These transitions are the same as those which determine the optical dispersion properties of the atoms.

In general, Eq. (2.3.) cannot be evaluated; instead, the summations are approximated by a single term with an effective characteristic frequency ω for each atom. The dispersion constant can then be expressed as

$$C_{ij} = \frac{3}{2} \alpha_i \alpha_j \frac{\hbar \omega_i \omega_j}{\omega_i + \omega_j} \quad (2.4)$$

This expression is similar to Eq. (2.2), except that the ground-state frequency ω_0 has been replaced by the characteristic frequency ω . It was suggested by London (1937) that the ionisation energy of the atom should be used for the value of $(\hbar\omega)$. This procedure is used

frequently in adsorption calculations, but it leads to difficulties in the case of condensed media (for example, what is the ionisation energy in an ionic crystal ?). A much better estimate of the characteristic frequency can be made from an analysis of the optical dispersion data of a material (Gregory 1969).

Various modifications of Eq. (2.4) have been introduced (see review by Margenau 1939), mainly to obtain better agreement with experimental values for inert gas atoms. An expression due to Kirkwood and Müller (Müller 1936) which has been used successfully (e.g. see Young and Crowell 1962), introduces the diamagnetic susceptibility, χ , into the dispersion constant :

$$C_{ij} = 6 \pi c^2 \frac{\alpha_i \alpha_j}{\alpha_i/\chi + \alpha_j/\chi} \quad (2.5)$$

Retardation

The London treatment of dispersion forces assumes that the interaction between the fluctuating dipoles is transmitted instantaneously. In fact, the electric field due to a dipole is transmitted at the speed of light, and the characteristic frequency of the interaction lies in the ultra-violet. Therefore, unless the separation between two atoms is much smaller than the characteristic wavelength ($\simeq 100$ nm) of the dispersion spectrum, a phase lag is introduced into the interaction. The "retarded" dispersion energy decreases more rapidly with separation; at separations greater than a few 100 nm the attractive energy is given by (Casmir and Polder 1948)

$$E_r = - \frac{23}{8 \pi^2} h c \alpha_i \alpha_j r_{ij}^{-7} \quad (2.6)$$

At intermediate separations there will be a gradual transition from the normal dispersion, proportional to r_{ij}^{-6} , to the retarded interaction, proportional to r_{ij}^{-7} . The transition has been shown from measurements of the adhesion between mica plates (Tabor and Winterton 1969) to occur at about 20 nm.

Multipole Interactions

So far, only dipole interactions have been discussed. For complex atoms there are additional contributions from several outer electrons to the fluctuation in electron density. These contributions can be taken into account by multipole interactions, in particular dipole-quadrupole interactions which vary with separation as r_{ij}^{-8} , and quadrupole-quadrupole interactions which vary as r_{ij}^{-10} (for the appropriate dispersion constants, see Sect. 2.1.2.)

2.1.1.2 Polar Molecules

The interaction between molecules with permanent dipole moments is often far stronger than the dispersion. In the case of a polar molecule interacting with a non-polar one, the dipole induced on the non-polar molecule (with polarisability α_i) in the electric field (F_j) of the permanent dipole (dipole moment μ_j) gives rise to the induction effect (Debye 1920) with a binding energy,

$$U_I = - \frac{1}{2} \alpha_i F_j^2 \quad (2.7)$$

$$= - \frac{\alpha_i \mu_j^2}{6 r_{ij}^3} \quad (2.8)$$

The induction effect contributes to the adsorption of a non-polar molecule to the surface of an ionic crystal; in this case the electric field F_j in Eq. (2.7) is the net field due to all the ions interacting with the molecule.

The interaction between two polar molecules causes their dipoles to align; this "orientation" effect is counteracted by thermal rotation of the dipoles; by use of classical statistics the net interaction has been calculated by Keesom (1921):

$$U_o = - \frac{2 \mu_i^2 \mu_j^2}{3 kT} r_{ij}^{-6} \quad (2.9)$$

where μ_i and μ_j are the dipole moments of the two molecules. Obviously, the induction and dispersion effects will also contribute to the total interaction between the molecules.

2.1.1.3 Repulsion

Two interacting atoms or molecules will reach an equilibrium separation when the attractive forces between them are balanced by a repelling force. Repulsive forces are consequence of the Pauli exclusion principle which tends to minimise the overlap of the electron distributions of the two particles. From quantum-mechanical considerations, the repulsion is expected to decay exponentially with separation: Born and Mayer (1932) proposed a semi-empirical expression for the repulsion energy, U_R ,

$$U_R = a \exp - \frac{r_{ij}}{\varrho} \quad (2.10)$$

where a and ϱ are adjustable constants.

Lennard-Jones (1931) made use of the empirical expression

$$U_R = C_R r_{ij}^{-12} \quad (2.11)$$

where C_R is the repulsion constant. This is the repulsive part of the well-known Lennard-Jones potential,

$$V(r) = - \frac{C_{ij}}{r^6} \left[1 - \frac{1}{2} \left(\frac{r_0}{r} \right)^6 \right] \quad (2.12)$$

Here, the repulsion constant (C_R in Eq. 2.11) has been expressed in terms of the dispersion constant and the equilibrium separation r_0 . Although less accurate, this property makes Eq. (2.11) far more useful than Eq. (2.10) which contains two constants.

2.1.2. Adsorption on Solid Surfaces

The adsorption energy of an adatom on a solid surface can be calculated simply by adding up the interactions of the adatom with each atom or ion in the solid. This procedure assumes that the pair interactions are additive, such that the adsorption energy, E_i , of an adatom i is given by

$$E_i = \sum_j V(r_{ij}) \quad (2.13)$$

where $V(r_{ij})$ is the interaction energy between the adatom and an atom (ion) j , in the solid at separation, r_{ij} .

For the purposes of this work, the adsorption of a metal atom to the surface of an ionic crystal is of particular interest. The interaction of the adatom with an ion in the crystal at separation r_{ij} can be taken to have the following contributions, as discussed in the previous section:

1. dipole-dipole dispersion,

$$\text{interaction energy, } U_{dd} = -C_{ij} r_{ij}^{-6} \quad (2.1)$$

where the dispersion constant is given by the Kirkwood-Müller expression

$$C_{ij} = 6 m c^2 \frac{\alpha_i \alpha_j}{\alpha_i/\chi_i + \alpha_j/\chi_j} \quad (2.5)$$

2. dipole-quadrupole dispersion,

$$\text{interaction energy, } U_{dq} = -C_{ij}' r_{ij}^{-8} \quad (2.14)$$

where the constant C_{ij}' is given by

$$C_{ij}' = \frac{45 \hbar^2}{8m} \alpha_i \alpha_j \left[\frac{1}{2 \left(\frac{\alpha_i \chi_j}{\alpha_j \chi_i} + 1 \right)} + \frac{1}{2 \left(\frac{\alpha_j \chi_i}{\alpha_i \chi_j} + 1 \right)} \right] \quad (2.15)$$

(see Ross and Olivier 1964)

3. quadrupole-quadrupole dispersion,

$$\text{interaction energy, } U_{qq} = -C_{ij}'' r_{ij}^{-10} \quad (2.16)$$

where

$$C_{ij}'' = \frac{105 \hbar^4}{16 m^3 c^2} \alpha_i \alpha_j \left[\frac{\frac{\alpha_i}{\chi_i}}{3 \left\{ \frac{\alpha_j \chi_i}{\alpha_i \chi_j} + 1 \right\}} + \frac{3}{4 \left\{ \frac{\chi_i}{\alpha_i} + \frac{\chi_j}{\alpha_j} \right\}} + \frac{\frac{\alpha_j}{\chi_j}}{3 \left\{ \frac{\alpha_i \chi_j}{\alpha_j \chi_i} + 1 \right\}} \right] \quad (2.17)$$

4. induction energy,

$$U_I = -\frac{1}{2} \alpha_i F_{ij}^2 \quad (2.18)$$

where F_{ij} is the electric field due to the ion at the centre of the adatom; if the ion has q electronic charges, the field is

$$F_{ij} = \frac{q}{r_{ij}^2} \quad (2.19)$$

5. repulsion energy,

$$U_R = C_R r_{ij}^{-12} \quad (2.11)$$

where C_R is the repulsion constant.

Thus, the total adatom-ion interaction, $V(r_{ij})$, is given by

$$V(r_{ij}) = U_{dd} + U_{dq} + U_{qq} + U_I + U_R \quad (2.20)$$

If the two particles are in equilibrium at a separation r_e , we can derive an expression for the repulsion constant, C_R ; from the condition for the interaction energy,

$$\frac{d V(r_e)}{d r_{ij}} = 0$$

it follows that

$$C_R = \frac{1}{6} \alpha_i q^2 r_e^8 + \frac{1}{2} C_{ij} r_e^6 + \frac{2}{3} C_{ij}' r_e^4 + \frac{5}{8} C_{ij}'' r_e^2 \quad (2.21)$$

The above equations define a set of constants (C_{ij} , C_{ij}' , C_{ij}'' , C_R) for the interaction of the adatom with a given type of ion in the crystal. If the positions of the ions relative to the adatom (r_{ij}) are known, we can determine the adsorption energy E_i by summation of the interactions $V(r_{ij})$. Since the interaction weakens rapidly with increasing separation, r_{ij} , it is sufficient to limit the summation to the nearest ions, up to a separation (r_c) which is much greater than the lattice spacing. The remainder of the crystal may be regarded as a continuous solid, as far as the interaction with the adatom is concerned. We can therefore replace the summation over $r_{ij} > r_c$ by an integration. Ignoring the contributions other than the dipole-dipole dispersion, the adsorption component $E_i(r > r_c)$ is given by (Young and Crowell 1962)

$$E_i(r > r_c) = - \frac{2\pi N_j C_{ij}}{3 r_c^3} \left[1 - \frac{3z}{4r_c} \right] \quad (2.22)$$

where N_j is the number of ions per unit volume of the crystal and z is the adsorption distance of the adatom (i. e., its perpendicular distance from the crystal surface). It should be noted that for

$r_c \geq 10z$, the contribution to the adsorption given by Eq. (2.22)

is normally negligible compared with the summation up to

$r_{ij} = r_c$. The summation is therefore limited to the nearest 10^2 to 10^3 ions (e. g. see Orr, 1939, Hayakawa 1957).

Continuum approximation

The adsorption energy of an atom to a solid surface cannot be determined by the summation method if the positions of the atoms/ions in the solid are not known. For non-crystalline solids, the summation is therefore approximated by an integration of the interaction over the volume of the solid (de Boer 1936, Hamaker 1937). As pointed out above, this procedure is only valid for separations (r_{ij}) which are much greater than the mean atomic (ionic) separations in the solid, i. e. for

$$r_{ij} \gg (N_j)^{-\frac{1}{3}} \quad (2.23)$$

Since the adsorption distance is normally only a few tenths of nanometers, and N_j is typically $\frac{1}{2} \cdot 10^{23} \text{ cm}^{-3}$, this condition is not normally fulfilled. Nevertheless, the continuum approximation leads to some interesting results (see below).

The adsorption energy, E_c , of an adatom to a solid with N_j atoms/ions per unit volume, for this approximation, is given by

$$E_c = \int_v V(r_{ij}) N_j \, dv \quad (2.24)$$

where the integration is taken over the volume v of the solid (regarded as infinite half-space). We shall approximate the interaction energy, $V(r_{ij})$, by using the Lennard-Jones potential,

$$V(r) = -C_{ij} r^{-6} + C_R r^{-12} \quad (2.25)$$

At an adsorption distance z , the adsorption energy is (from Eqs. (2.24) and (2.25))

$$E_c = - \frac{\pi N_j C_{ij}}{6 z^3} + \frac{\pi N_j C_R}{45 z^9} \quad (2.26)$$

At the equilibrium distance $z = z_o$, the adsorption energy has its minimum value (maximum magnitude) thus,

$$\left(\frac{d E_c}{dz} \right)_{z=z_o} = 0$$

Hence, it follows from Eq. (2.26) that

$$C_R = \frac{5}{2} C_{ij} z_o^6 \quad (2.27)$$

From Eqs. (2.26) and (2.27) the adsorption energy is therefore

$$E_c = - \frac{\pi N_j C_{ij}}{6 z^3} \left[1 - \frac{1}{3} \left(\frac{z_o}{z} \right)^6 \right] \quad (2.28)$$

Finally, at the equilibrium position the adsorption energy is

$$E_c = - \frac{\pi N_j C_{ij}}{9 z_o^3} \quad (2.29)$$

The adsorption energy calculated from this equation will be compared with the results from the summation method in the following section.

It is obvious from the limitation of the continuum approximation

(discussed above) that Eq. (2.29) underestimates the contribution

of the surface atoms/ions near the adatom to the adsorption. The interaction

of the adatom with the surface layer has been calculated by Ross and

Olivier (1964). Using the Lennard-Jones potential (Eq. (2.25)), the

adsorption energy E_s to a surface layer containing N_s atoms (ions) per unit area at a distance z_s from the adatom, is given by

$$E_s = \frac{3\pi}{10} N_s C_{ij} z_s^{-4} \quad (2.30)$$

As will be seen below (Sect. 2.1.2.1), this contribution may be larger than the total adsorption energy (E_c) calculated from Eq. (2.29).

2.1.2.1 Adsorption calculations

The methods outlined in the previous section can now be used to calculate the adsorption energies of the materials of interest in this study. The adsorption of the noble metal atoms, gold, silver and copper, to the surfaces of mica and rock-salt has been computed by the summation method. The continuum approximation was used to calculate the adsorption energies of these atoms to the surface of glass. The calculated values will be compared with those deduced from nucleation experiments in Chapter 4 (Sect. 4.2.).

The accuracy of the adsorption calculations is largely determined by the interaction constants, in particular, the dipole-dipole dispersion constant (Eq. (2.5)), the induction, and repulsion constant (C_R). The values of these constants depend on the polarisabilities, the diamagnetic susceptibilities and the radii of the interacting atoms and ions. Unfortunately, the parameters for free atoms of the noble metals have, apparently, not been measured (apart from their radii). However, a semi-empirical expression for the polarisability, α_{th} , of hydrogen-like atoms has been used by London (1937):

$$\alpha_{th} = \left(\frac{Z}{2}\right)^{\frac{1}{2}} \frac{e^2}{m \omega_I^2} \quad (2.31)$$

where Z is the atomic number and ω_I is the ionisation frequency of the atom (m and e are the electron mass and charge respectively). Table 2-1 shows the values of α_{th} for various elements (values of ω_I were taken from Richtmayer et al. 1962). Good agreement with the

Table 2-1

Atomic Polarisability α and Diamagnetic Susceptibility χ
of selected Elements

[α_{exp} from Landolt-Börnstein (1950) in units of
 α_{th} from Eq.(2.31) 10^{24} cm^3
 χ from Landolt-Börnstein (1967) $10^{30} \text{ cm}^3 \text{ atom}^{-1}$]

α_{exp}	27					1.63
α_{th}	Na	-9.8				Ar 1.41
χ						-32.0
α_{exp}	46, 36		[7]	6.1		2.48
α_{th}	K	18.0	Cu	7.04	Zn	4.3
χ				-9.1		-15.2
α_{exp}	50		[9]	7.9		4.32
α_{th}	Rb	27.2	Ag	9.40	Cd	6.7
χ				-32.4		-32.6
α_{exp}	42, 61		[8]	5.1		
α_{th}	Cs	34.6	Au	8.16	Hg	6.4
χ				-46.6		-55.5

measured polarisabilities (α_{exp}) is obtained for the inert gases, but for the alkali metal atoms, α_{th} is far too low. For the elements Zn, Cd and Hg (Group IIB, neighbouring Cu, Ag and Au in the Periodic Table) the agreement is about 30%; similar agreement may therefore be expected between α_{th} and α_{exp} for the noble metals. With this assumption we have proposed likely values for the polarisabilities of Cu, Ag and Au, as shown in brackets [] in Table 2-1; the expected accuracy of these values is about 30%. Thus the induction energy (Eq. (2.18)), which is determined by the adatom polarisability (α_i), will be accurate to only 30%; the error in the dispersion constant C_{ij} due to the error in α_i will be around 15%.

The diamagnetic susceptibility (χ) of solid Cu, Ag and Au have been measured to a high degree of accuracy (Henry and Rogers 1956). But, again, for the free metal atoms no data has been published; therefore the values for the solid metals were used in the adsorption calculations. Since the atomic susceptibility (and the dispersion properties) depend on the wave functions of the outer electrons of an atom, one would expect a large change in the susceptibility when metal atoms are condensed into a solid (it is well-known that the overlap of electron wave functions lead to the formation of continuous bands in metallic solids). For this reason, our calculations are more appropriate to a description of the adhesion between a metallic and an ionic solid. Since this study is concerned primarily with the adhesion between solids, these calculations are of immediate relevance.

Sodium Chloride

The adsorption of metal atoms to the (100) cleavage surface of sodium chloride has been calculated by the summation method. The optical properties of alkali halide crystals have been investigated extensively in the past. The polarisability can be derived from refractive index data; it is found that the contributions of the two types of ion to the polarisability (α) of alkali halide crystals are almost exactly additive (Mayer 1933, Tessman et al. 1953), i. e.,

$$\alpha = \alpha^{+} + \alpha^{-} \quad (2.32)$$

where α^{+} and α^{-} are the positive and negative ion polarisabilities respectively. Pirenne and Katheuser (1964) have fitted a set of self-consistent values for the ionic polarisabilities of 20 alkali halide crystals to a mean deviation of only 3% (0.3% for NaCl). The values required for the adsorption calculations are the ionic polarisabilities extrapolated to zero frequency (see Eq. (2.5)); these values have been derived from optical data by Tessman et al. (1953) and are shown in the Table 2-2 for NaCl.

The diamagnetic susceptibility of alkali halide crystals shows similar features: the contributions due to the two types of ion are additive (Brindley and Hoare 1935), though not to the same degree of accuracy as in the case of the polarisabilities; the ionic susceptibilities for Na^{+} and Cl^{-} ions are shown in Table 2-2.

The adsorption energy of Au, Ag and Cu to the (100) surface of NaCl was computed by summation of the interaction with the ions in the 500 nearest lattice cells (i. e., up to a separation (r_{ij}) of

Table 2-2

Adsorption on Rocksalt (100) SurfaceData:

	Au	Ag	Cu	Na ⁺	Cl ⁻
polarisability, α (10^{24} cm ³)	[8]	[9]	[7]	0.22 ⁽¹⁾	3.00 ⁽¹⁾
susceptibility, χ (10^{30} cm ³)	46.6 ⁽³⁾	32.4 ⁽³⁾	9.1 ⁽³⁾	10.1 ⁽²⁾	40.2 ⁽²⁾
radius, r (Å)	1.44	1.44	1.28	0.95	1.81
dispersion constant C_{i-Na^+}	44.8	32.5	9.4		
(10^{12} erg Å ⁶) C_{i-Cl^-}	481.6	376.4	119.3		

References: (1) Tessman et al. (1953), (2) Brindley and Hoare (1935),
(3) Henry and Rogers (1956)

Calculated adsorption parameters: adsorption energy E_i , distance z_o

Adatom:	Au		Ag		Cu		Au (m.s.)*
	E_i (eV)	z_o (Å)	E_i (eV)	z_o (Å)	E_i (eV)	z_o (Å)	E_i (eV)
Surface site 1	0.36	2.7	0.27	2.8	0.15	2.5	0.58
2	0.33	2.8	0.24	2.9	0.12	2.6	0.48
3	0.23	3.2	0.16	3.3	0.06	3.2	0.26
4	0.19	3.5	0.14	3.5	0.05	3.5	0.19
5	0.18	3.5	0.13	3.6	0.05	3.6	0.18
6	0.31	2.8	0.22	2.9	0.09	2.8	0.43
7	0.25	3.0	0.18	3.2	0.07	3.1	0.28
8	0.24	3.1	0.17	3.2	0.06	3.2	0.24
9	0.20	3.4	0.14	3.4	0.05	3.4	0.20
Average values	0.25	3.1	0.18	3.2	0.08	3.1	0.31
Diffusion							
Energy, E_d (eV)	0.11		0.09		0.08		0.30

Continuum Approximation:

E_c (eV)	0.26	0.18	0.07
z_o (Å)	2.7	2.8	2.5

* Adsorption on NaCl with displaced surface ions (see p. 32)

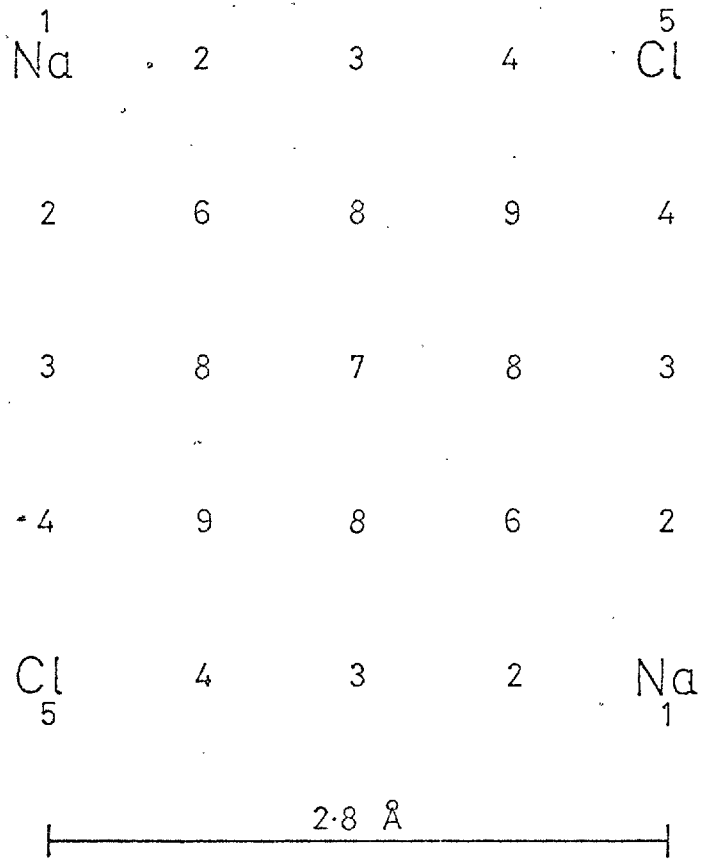


Fig. 2-1 Adsorption Sites on the NaCl (100) Surface

about 3 nm). A computer programme (D. Colven, private communication) was used to calculate the adsorption energy of an adatom at a specified site above the NaCl surface: nine different surface sites were considered, as shown in Fig. 2-1 (sites numbered 1 to 9). For each surface site the computation is carried out at successively decreasing heights, z , of the adatom above the surface. A plot of the adsorption energy as a function of z is shown in Fig. 2-2; the minimum of each curve gives the equilibrium adsorption energy ($E_1(z_0)$) and distance (z_0) of the adatom at a surface site. The variation of the equilibrium adsorption energy across the NaCl surface is illustrated by the contour map of Fig. 2-3; the adatom (Ag in Fig. 2-3) is most strongly bound above the sodium ion (0.27 eV) and least strongly above the chlorine ion (position 5, 0.13 eV). This result is in qualitative agreement with the adsorption calculations of Hayakawa (1957) for gases on NaCl; it is interesting to note that Hayakawa's experimental studies of gas adsorption on alkali halide crystals show adsorption energies which are within 10% of the calculated values at the strongest adsorption site.

In Table 2-2 a summary of the data and our computed results for the adsorption of Au, Ag and Cu on rock-salt is given. The three metals behave very similarly, the adsorption at any given surface site being strongest for Au, weakest (about one-third) for Cu. A metal atom impinging on the surface is most likely to nucleate at a sodium ion site (adsorption energy E_a). The energy required for an atom to diffuse between Na^+ sites (i. e., the diffusion

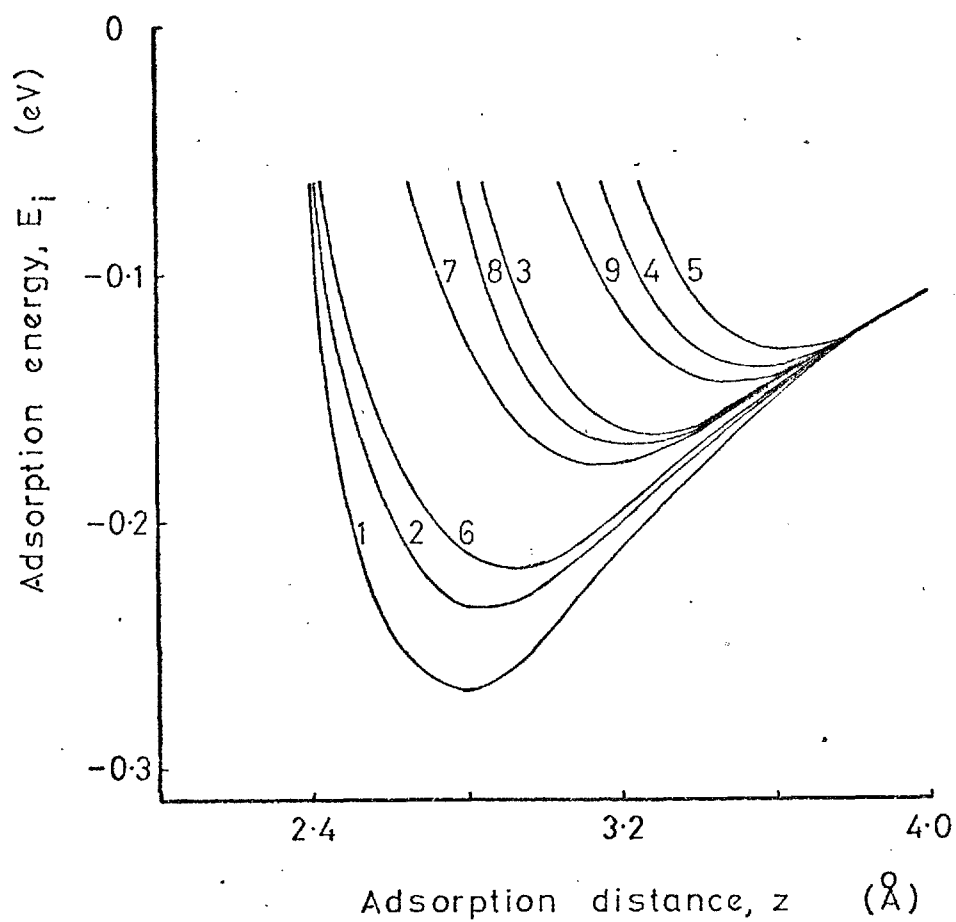


Fig. 2-2 Adsorption of Ag atom at nine different sites on NaCl (100) surface.
(surface sites as shown in Fig. 2-1)

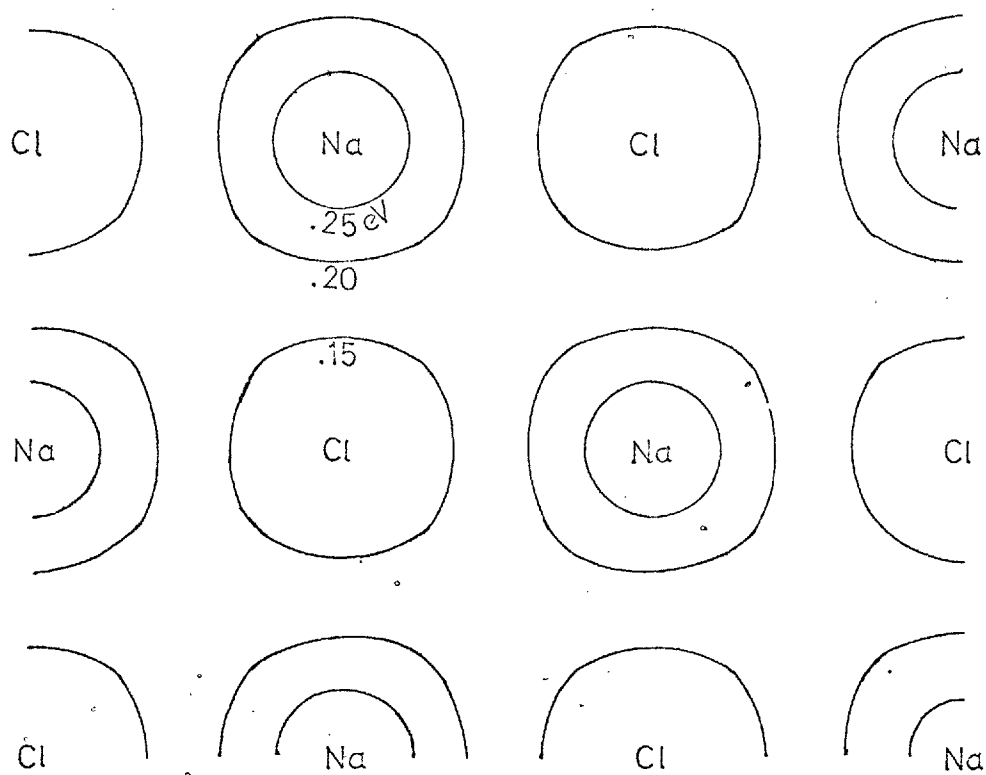


Fig. 2-3 Contours of constant Adsorption Energy
for Ag on NaCl (100)

energy E_d) is about 0.1 eV for the three metals. The values of E_a and E_d can be compared with the parameters derived from nucleation experiments (see Sect. 4.2).

It is interesting to compare these results with the adsorption energies obtained from the continuum approximation. The same parameters have been used in the evaluation of E_c (Eq. (2.29)) as for the computer calculation; the value of the adsorption distance (z_o) was taken from the computed value at the Na^+ site. This procedure leads to values of E_c , as shown in Table 2-2, which are very close to the mean adsorption energies derived from the computer results at the nine adsorption sites.

The results discussed so far are based on the assumption that the NaCl surface is ideal, i. e., that the surface ions occupy the same positions as the ions in the bulk of the crystal. However, when a crystal is cleaved, the surface ions relax into positions which are slightly displaced from the normal lattice sites (thereby tending to minimise the surface energy). Recent calculations (Benson and Claxton 1968) have shown that the surface Na^+ ions are displaced inwards by about 5% of the Na-Cl distance ($2.79 \text{ \AA}$), the surface Cl^- ions are displaced outwards by 2%; the displacements were found to decrease over five layers below the surface.

A calculation of the adsorption energy Au on the modified NaCl surface was carried out, using displacements of $0.15 \text{ \AA}$ (inwards) for the surface Na^+ ions, $0.05 \text{ \AA}$ for Cl^- ions. The results are shown in Table 2-2; the adsorption energies of Au are increased

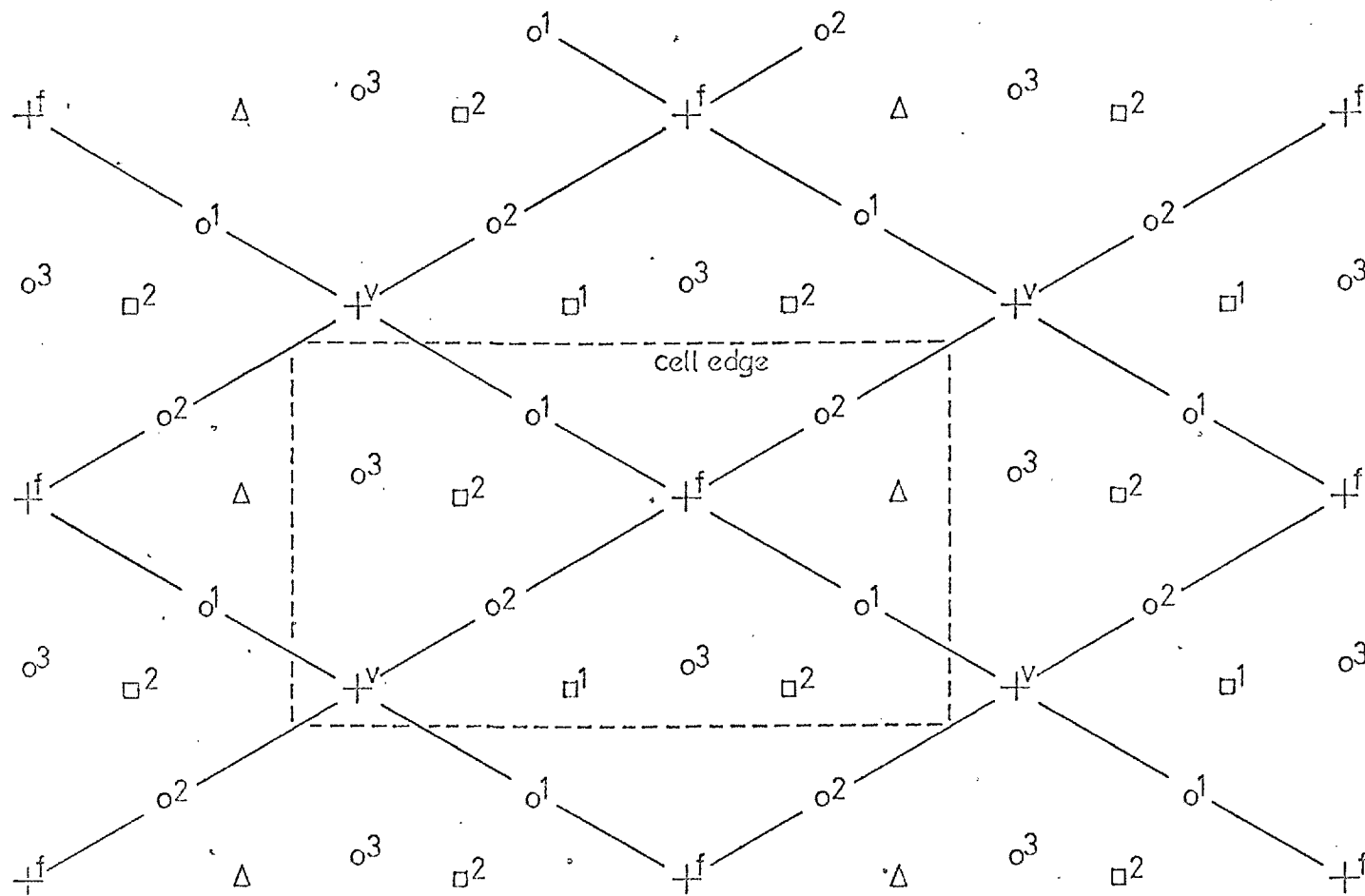
(due to a large induction component) to 0.58 eV at the Na^+ adsorption site, but are unchanged at the Cl^- site; the diffusion energy (E_d) is increased to 0.3 eV.

The surfaces of real crystals are far from ideal; apart from cleavage steps, there are defects, such as vacancies, adsorbed impurities, and grain boundaries and dislocations emerging on the surface. Generally, the adsorption will be increased at a defect site; for example, at a vacancy site, the strong electric fields result in an adsorption energy of several electron volts, according to calculations similar to those above (D. Colven, private communication). Surface defects will therefore have a strong influence on the nucleation properties of atoms on ionic crystals. The preferential deposition of evaporated metals at defect sites on ionic crystals (known as the decoration effect) is commonly observed in nucleation studies (e. g. see Bethge 1969, Robins et al. 1966).

Mica

Muscovite mica, $\text{KAl}_2(\text{Si}_3\text{Al})_0\text{}_{10}(\text{OH})_2$, is a monoclinic silicate crystal with a complex layer structure (see Wyckoff 1962). A layer consists of two parallel sheets of silicate tetrahedra (SiO_4), arranged in hexagonal rings with every fourth Si^{4+} ion replaced by Al^{3+} ; pairs of sheets are bonded by OH^- and Al^{3+} ions at octahedral sites (i. e., at the centre O^- octahedra). The layers are bonded by K^+ ions at the centre of hexagons formed by O^- ions on the (001) plane. The bonding between the layers is relatively weak, so that cleavage occurs preferentially along the (001) plane, surfaces being electrically neutral if half of the surface K^+ sites are occupied. The arrangement of the surface ions at the (001) cleavage surface of mica is shown in Fig. 2-4.

The adsorption energy of Au, Ag and Cu on the (001) surface of mica was computed by summation over the nearest 32 lattice cells (there are 76 ions per cell). The largest part of the interaction is due to the K^+ , O^- and OH^- ions in mica (Si^{4+} and Al^{3+} have very small polarisabilities). The data for the K^+ ion (α_{K^+} and χ_{K^+}) were estimated from measurements on potassium halides; for the O^- ion, the polarisability of which depends on the solid containing the ion (see Tessman et al. 1953), the data was taken from measurements on crystalline silica (SiO_2); for OH^- values were chosen, in the absence of reliable data, to be a little higher than those for O^- . A summary of the data for all the ions is shown in Table 2-3; estimated values are shown in brackets.



Surface sites:

- + K⁺ (f - filled
v - vacant)
- o O⁼ (types 1,2,3)
- Si⁴⁺ (types 1,2)
- Δ Al³⁺

1 Å

Fig. 2-4 Adsorption Sites on the Mica (001) Surface

Table 2-3

Adsorption on Mica (001) SurfaceData:

Crystal ions (j)	K ⁺	O ⁼	Si ⁴⁺	Al ³⁺	OH ⁻
α (10^{24} cm ³)	1.0	1.7	0.02	0.03	[2]
χ (10^{30} cm ³)	24.2	[18]	[4]	[5]	[20]
r (Å)	1.33	1.40	0.41	0.50	[1.5]

Dispersion constants:

C _{Au-j} (10^{12} erg Å ⁶)	184	250	4.4	6.6	289
C _{Ag-j}	139	202	3.1	4.7	234
C _{Cu-j}	42	67	0.9	1.3	78

Adsorption values (Summation method)

Adatom (i) :	Au		Ag		Cu	
Surface site	E _i (eV)	z _o (Å)	E _i (eV)	z _o (Å)	E _i (eV)	z _o (Å)
(1) K ⁺ (vacant)	0.80	1.0	0.75	1.1	0.55	0.9
(2) K ⁺ (occupied)	0.27	3.0	0.24	3.0	0.18	2.9
(3) O ⁼ ₁	0.70	3.4	0.65	3.4	0.54	3.2
(4) O ⁼ ₂	0.51	3.6	0.45	3.6	0.39	3.3
(5) O ⁼ ₃	0.25	3.8	0.20	3.7	0.08	4.1
(6) Si ⁴⁺ ₄₊	0.67	3.7	0.61	3.7	0.48	3.4
(7) Si ⁴⁺ ₁	0.54	3.8	0.48	3.8	0.31	3.8
(8) Al ³⁺ ₂	0.74	3.7	0.71	3.7	0.53	3.6
Average	0.61	3.6*	0.49	3.6*	0.35	3.0*
Diffusion energy						
E _d (eV)	0.3		0.3		0.16	

* Surface site (1) excluded in average.

The adsorption energies were calculated at eight different surface sites as indicated in Fig. 2-4. The results, shown in Table 2-3, indicate a very strong adsorption site above the vacant K^+ ion (for Au, $E_a = 0.80$ eV). The diffusion energy E_d between vacant K^+ sites is about 0.3 eV for Au and Ag, 0.16 eV for Cu. The mean adsorption energies have been calculated by averaging over the values at twelve surface sites (the eight sites considered and four sites resulting from the symmetry of the crystal structure - see Fig. 2-4).

Generally, the adsorption energies are somewhat larger than expected for van der Waals forces. This is because there is a large induction component due to the surface electric fields; at the equilibrium position the induction energy is of the same order as the dipole dispersion energy. Above the empty K^+ site (for Au, $z_0 = 0.1$ nm above that site) the electric field is particularly strong so that the induction component is very large (0.6 eV for Au). If all the K^+ sites on the mica surface are assumed to be vacant the adsorption energy of Au at that site is increased to about 1.5 eV, where the induction component is some ten times greater than the dipole dispersion energy (a similar result is obtained if all K^+ sites are assumed to be filled). However, our calculations probably overestimate the induction energy, since the electric field is assumed to be uniform over the volume of the adatom (see Eq. (2.19)). At small adsorption distances this assumption becomes inaccurate (see Lenel 1933); the electric field acting on the outer electrons of the adatom should be taken as the average over the cross-section

of the adatom. At the vacant K^+ site the induction energy should therefore be reduced by 10 to 20%.

For comparison, the adsorption on mica has been calculated by the continuum approximation, using the data of Table 2-3. The interaction with each type of ion in the crystal was calculated from Eq. (2.29). The results, shown in Table 2-4, indicate very low adsorption energies ($E_C < 0.05$ eV) for all three metals. As already mentioned, this is because the continuum approximation underestimates the contribution due to the ions closest to the adatom. We have, therefore, calculated the contribution E_s of the surface layer of potassium and oxygen ions from Eq. (2.30). Using the adsorption distances determined by the summation method, the adsorption due to the surface ions is found to be an order of magnitude greater than the values of E_C (see Table 2-4), and about 20% of the mean adsorption energy calculated by the summation method. It thus appears that, even by taking into account the contribution of the surface layer, the continuum approximation gives somewhat lower values than the summation method. Since the continuum approximation does not take the induction effect into account and the summation method overestimates the induction energy, the difference in the two results is not surprising.

Glass

The adsorption of metal atoms on glass has been investigated by Benjamin and Weaver (1959), and more recently by Chapman (1969). The continuum approximation was used in both these publications to

Table 2-4Adsorption on Mica - Continuum Approximation

Adsorption energy E_c calculated from Eq. (2.29); surface contribution E_s from Eq. (2.30)

		Crystal ions (j)					
		K^+	O^{2-}	Si^{4+}	Al^{3+}	OH^-	Total
no. of ions $N_j (10^{-20} \text{ cm}^3)$		4.3	43	12.9	12.9	8.6	81.7
no. surface ions $N_s (10^{-14} \text{ cm}^3)$		2.1	12.8	4.2	2.1		
nearest neighbour distance ($\text{\AA}$)		2.77	2.6	1.61	1.69	1.93	
<u>Au</u>	$z_o (\text{\AA})$	2.82	2.74	2.24	2.29	2.41	
	$E_c (\text{meV})$	0.8	11.4	.01	.01	3.9	16.1
	$z_s (\text{\AA})$	3.0	3.6	2.7			
	$E_s (\text{meV})$	28	110	350			138 (378)
<u>Ag</u>	$z_o (\text{\AA})$	2.83	2.75	2.25	2.30	2.42	
	$E_c (\text{meV})$	0.6	9.1	.01	.01	3.1	12.8
	$z_s (\text{\AA})$	3.0	3.6	2.8			
	$E_s (\text{meV})$	21	90	246			111 (267)
<u>Cu</u>	$z_o (\text{\AA})$	2.66	2.58	2.08	2.13	2.25	
	$E_c (\text{meV})$	0.2	3.3	.01	.01	3.1	4.8
	$z_s (\text{\AA})$	2.9	3.3	2.6			
	$E_s (\text{meV})$	7.3	43	110			50 (117)

calculate the adsorption energies, using the dipole dispersion component for the interaction with the oxygen ions only. The adsorption distance (z_o) was taken as the mean of the interatomic distance in the metal (solid) and the shortest inter-ion separation in the glass (separation $O^- - O^-$ is 2.6 Å). Using the Kirkwood-Müller expression (Eq. (2.5)) for the dipole dispersion constant, Chapman (1969) found values of several tenths of electron volts (see Table 2-5) for the adsorption energies of Au, Ag and Cu [using the London expression for the dispersion (Eq. (2.1)) Benjamin and Weaver reported rather lower adsorption energies] .

The procedure used by the above workers does not appear to be very satisfactory, especially since only the attractive part of the interaction was taken into account, and that only for the oxygen ions. Both these defects are avoided in our calculations: the repulsive part of the interaction is included by using the Lennard-Jones potential (Eq. (2.25)); the interaction with all the ions in the glass is calculated, and the contribution due to the surface ions is considered.

The adhesion of metals to borosilicate glass (Corning 7059) has been investigated in this work. The adsorption energies of Au, Ag and Cu have been calculated for this glass; from the chemical composition of Corning 7059 glass (see Brown 1970), the number of each type of ion can be deduced. Obviously, the strongest interaction with the adatom is due to the oxygen ions; the values used for $\alpha_o =$ and $\chi_o =$ therefore have a strong influence on the accuracy of the adsorption calculation. Unfortunately, the value of α has been found to vary in different oxides (Tessman et al. 1953); it is therefore

insufficient to take the value for α_0 in silica, since about half the oxygen ions in Corning 7059 glass are co-ordinated by positive ions other than silicon. Instead, we have therefore used the available data for the oxides in the glass (see Table 2-5); the total interaction is then found by adding up the contributions from the oxides.

The results of these calculations are shown in Table 2-5; the adsorption distance was taken as the sum of the adatom radius and one-half of the oxygen ion separation ($2.6 \text{ \AA}$). The adsorption energies of all three metals are below 0.1 eV ; i.e. rather lower than obtained by previous workers (Chapman 1969, Benjamin and Weaver 1959); the difference is primarily a result of the high value for the number of oxygen ions in glass chosen by previous workers.

As in the case of the adsorption on mica, the contribution due to the surface ions can be calculated from Eq. (2.30). However, we need to make some assumptions about the structure of glass surface in order to deduce the density of surface ions. Theoretical descriptions of the structure of glasses have ranged from random networks (Zachariasen 1932) to microcrystallites (Lebedev 1940). The silicon ions will, in any case, be surrounded by oxygen tetrahedra; some of the oxygen ions (called bridging ions) form the links between two tetrahedra. As in mica, the silicate tetrahedra at the glass surface may be arranged in hexagonal rings. A structure of this kind has been considered by Benjamin and Weaver (1959). The density of oxygen ions at the surface can thus be deduced from the hexagonal structure, assuming the nearest neighbour distance between oxygen ions is $2.6 \text{ \AA}$.

Table 2-5

Adsorption on Borosilicate Glass (Corning 7059)

[Polarisability α (10^{24} cm³), susceptibility χ (10^{30} cm³), no. of adsorbent units N_j (10^{-22} cm⁻³), dispersion constant C_{ij} (10^{12} erg Å⁶), adsorption distance z_o (Å), energy E_c (meV)]

	α	χ	N_j	<u>Au</u>			<u>Ag</u>			<u>Cu</u>		
				C_{Au-j}	z_o	E_c	C_{Ag-j}	z_o	E_c	C_{Cu-j}	z_o	E_c
SiO ₂	2.85 ¹	40 ²	0.92	460	2.74	43.3	360	2.75	35.4	115	2.58	13.3
BaO	4.96 ¹	48.3 ²	0.18	710		12.7	575		11.3	193		4.4
Al ₂ O ₃	4.03 ¹	61.4 ²	0.12	663		8.5	519		6.6	163		2.5
As ₂ O ₃		68.5 ²	0.001			.1			.1			.1
B ₂ O ₃	[3.9] ³	64.2 ²	0.21	656		14.7	508		11.4	159		4.2
<u>Total</u>						<u>79.2</u>			<u>64.7</u>			<u>24.4</u>
O ⁼	1.7 ¹	[18] ⁴	3.01	249		74.8	201		64.3	67		26.0
Chapman ⁵	3.88	23	6.05	455	2.74	440	393	2.75	370	142	2.58	160
Benjamin and Weaver ⁶				94		90	117		120	112		130
Surface contribution (O ⁼ ions, $N_s = 12.8 \cdot 10^{22}$ cm ⁻³)						334			265			114
Total adsorption energy E_t (meV)						<u>350</u>			<u>280</u>			<u>120</u>

References: 1 Tessman et al. (1953); 2 Landolt-Börnstein (1967); 3 estimated from Ref.1;

4 estimated from Ref. 2; 5 Chapman (1969); 6 Benjamin and Weaver (1959)

The adsorption due to the surface oxygen ions has been calculated from Eq. (2.30), using the data of Table 2-5. The resulting values of E_s for the three metals are about four times larger than the corresponding values of E_c . The adsorption due to all the ions other than those in the surface layer is only about 20% of the value of E_c ; thus the total adsorption energy E_t is given approximately by

$$E_t \approx E_s + 0.2 E_c$$

The values of E_t are about 0.35 eV for Au, 0.28 for Ag and 0.12 eV for Cu (see Table 2-5).

2.1.3. Adhesion between Solids

2.1.3.1 Summation over adsorption energies

The values of the adsorption energies calculated in the previous section can now be used to determine the adhesion energy between two solids. The simplest procedure is to multiply the adsorption energy by the density of (metal) adatoms at the interface, thus neglecting the contribution due to the metal atoms below the interface. In the adsorption calculations the parameters for the metal solid were used; as discussed in Sect. 2.1.2., these parameters are more appropriate for the adhesion between two solids. However, the dispersion interaction with metals contains a large contribution due to the conduction electrons; the estimated values of the polarisability used above may therefore be too small.

The adhesion energies of Au, Ag and Cu (solids) on NaCl and mica calculated by this method are shown in Table 2-6; the adatom density at the interface has been deduced from the lattice parameters

Table 2-6Adhesion of Metals to Ionic Solids

	<u>Au</u>	<u>Ag</u>	<u>Cu</u>	
<u>Rock-salt</u> - (111) surface of metal on NaCl (100)				
no. surface atoms				Au (m.s.)*
(metal) N_s (10^{-18} m^{-2})	13.9	13.9	17.7	13.9
adsorption energy (mean)				
(Table 2-2) E_i (eV)	0.25	0.18	0.077	0.31
adhesion energy				
W (mJ m^{-2})	<u>555</u>	<u>406</u>	<u>218</u>	<u>680</u>
<u>Mica</u> - (111) surface of metal on mica (001)				
adsorption energy (mean)				
(Table 2-3) E_i (eV)	0.61	0.49	0.35	
adhesion energy				
W (mJ m^{-2})	<u>1360</u>	<u>1090</u>	<u>970</u>	
<u>Borosilicate glass</u> (Corning 7059)				
no. metal atoms	5.90	5.85	8.47	
N_i (10^{-28} m^{-3})				
adhesion distance				
z_o (10^{10} m)	2.74	2.75	2.58	
adsorption energy				
(Table 2-5) E_t (eV)	0.35	0.28	0.12	
adhesion energy				
W (mJ m^{-2})	<u>390</u>	<u>310</u>	<u>185</u>	

* NaCl with displaced surface ions (see Table 2-2)

assuming the (111) plane of the metal is parallel to the insulator surface. The adhesion on NaCl, calculated from the average adsorption energy, is several hundred mJm^{-2} (erg cm^{-2}); on mica the adhesion is more than twice as strong (i.e. above 1Jm^{-2}). If the metal were deposited in such a way that the metal atoms were adsorbed at the strongest surface sites (the Na^+ site on NaCl, the K^+ site on mica) the adhesion should be raised considerably; however there is generally a lattice misfit of a few per cent, which makes it energetically less favourable for the atoms to be adsorbed at the strongest site. Nevertheless, the adhesion energy should depend on the orientation of the metal lattice on the insulator surface.

2.1.3.2. Hamaker method

The continuum approximation has been used by Hamaker (1937) to determine the adhesion energy between two solids. Using the dispersion contribution only, the adhesion energy, $W(z)$, was found by integration of adsorption energy,

$$W(z) = \int_z^{\infty} \frac{\pi N_i N_j C_{ij}}{6 z^3} dz = - \frac{A_{ij}}{12\pi z^2} \quad (2.34)$$

where N_i is the number of atoms per unit volume of solid i , and A_{ij} is the Hamaker constant given by

$$A_{ij} = \pi N_i N_j C_{ij} \quad (2.35)$$

If the repulsion term is included (as in the Lennard-Jones expression) then using Eq. (2.28) for the adsorption energy, E_c , the adhesion energy is

$$W(z) = \int_z^{\infty} - \frac{\pi N_j C_{ij}}{6 z^3} \left[1 - \frac{1}{3} \left(\frac{z_0}{z} \right)^6 \right] N_i dz$$

$$W(z) = \frac{\pi N_i N_j C_{ij}}{12 z^2} \left[1 - \frac{1}{12} \left(\frac{z_0}{z} \right)^6 \right]$$

$$\text{at } z = z_0 \quad W = \frac{11 \pi}{144} \frac{N_i N_j C_{ij}}{z_0^2} \quad (2.36)$$

$$\text{from Eq. (2.29)} \quad W = \frac{11}{16} z_0 N_i E_c \quad (2.37)$$

Thus, by including the repulsion term, the adhesion is changed by a factor $\left(\frac{11}{12}\right)$ from the Hamaker expression (Eq. (2.34)).

The adhesion of the metals Au, Ag, and Cu on glass has been calculated from Eq. (2.37), using the values of adsorption energies shown in Table 2-5. The resulting adhesion energies (see Table 2-6) are below 200 mJ m^{-2} . However, if the surface contribution is taken into account [Eq. (2.30)] the adhesion energy is raised to 390 mJ m^{-2} for Au, 310 mJ m^{-2} for Ag and 185 mJ m^{-2} for Cu.

2.1.4. Macroscopic Theory of Adhesion

The most important shortcoming of the microscopic theories of dispersion is the assumption of complete additivity of pair interactions. A rigorous approach to the problem, however, involves the solution of quantum-mechanical many-body problems - a task which at present is far too complex, except for the very simplest atoms (Dalgarno 1967, Margenau and Kestner 1968).

A completely different approach, based entirely on the macroscopic properties of the interacting media, was proposed by Lifshitz (1956). The spontaneous polarisations of the atoms or ions

in a solid give rise to local electric fields - as was argued by London (1930). According to Lifshitz, these fields are at least partially coherent over distances of the order of k^{-1} , where k is the adsorption co-efficient. Between two bodies separated by a small distance, the fluctuating fields have a phase correlation, which leads to an attractive force. For two semi-infinite bodies separated by a constant gap width, z_0 , the resulting attractive force, P , per unit area of interface is given by

$$P = \frac{\hbar \bar{\omega}_{ij}}{8\pi^2 z_0^3} \quad (2.38)$$

$$\text{and the interaction energy, } W = \frac{1}{2} z_0 P \quad (2.39)$$

$$\text{where } \bar{\omega}_{ij} = \int_0^\infty \frac{\epsilon_i(i\xi) - 1}{\epsilon_i(i\xi) + 1} \frac{\epsilon_j(i\xi) - 1}{\epsilon_j(i\xi) + 1} d\xi \quad (2.40)$$

the integration being taken over the complex frequency plane ω ($= \omega' + i\xi$) along the imaginary frequency axis ($i\xi$). The complex dielectric constant, $\epsilon(\omega) = \epsilon + i\epsilon''$ is related to $\epsilon(i\xi)$ by the Kramers-Kronig relation

$$\epsilon(i\xi) - 1 = \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon''(\omega)}{\omega^2 + \xi^2} d\omega \quad (2.41)$$

If values of $\epsilon''(\omega)$ are available from optical absorption and reflection measurements, the value of $\bar{\omega}$ can be found by numerical integration of Eqs. (2.40) and (2.41); the details of this method have been reviewed by Krupp (1967).

The range of validity of this theory is similar to that of the continuum approximation (Sect. 2.1.2): the separation between the

interacting bodies must be greater than atomic dimensions and smaller than the characteristics wave lengths of the interaction. At separations greater than about 100 nm the retardation effect must be taken into account.

Krupp (1967) has calculated the values of $\bar{\omega}$ for various materials from their optical dispersion data; further results have been published by Böhme et al. (1969). There are, however, no values available for the interaction between two different materials. It is often assumed that the dispersion constant for two materials (C_{ij}) is given by the geometric mean of the constants (C_{ii} , C_{jj}) for each of the two solids, i. e.

$$C_{ij} = (C_{ii} C_{jj})^{1/2} \quad (2.42)$$

According to Böhme et al. (1969), this rule works well for the values of $\bar{\omega}$, i. e.

$$\bar{\omega}_{ij} = (\bar{\omega}_{ii} \bar{\omega}_{jj})^{1/2} \quad (2.43)$$

Thus, the adhesion energy, from Eq. (2.39) may be written as

$$W = \frac{(A_{ii} A_{jj})^{1/2}}{12\pi z_o^2} \quad (2.44)$$

$$\text{where } h \bar{\omega} = \frac{4\pi}{3} A$$

In Table 2-7 the available values of $\bar{\omega}$ are shown for the materials of interest. There are no values for ionic solids (apart from KBr), so that the interaction constant has to be found by a more approximate method. By using the single frequency approximation (as in London's theory), Gregory (1969) has derived an expression for the Hamaker constant (A_{ii}) in terms of the optical dielectric

Table 2-7

Adhesion of Metals from Macroscopic Theory

<u>Data</u>	$h\bar{\omega}$ (eV)	rel. permty. ϵ	Hamaker constant A (10^{19} J)
Au	11.86 ¹		4.5
Ag	9.0 ²		3.4
Cu	8.5 ²		3.25
KBr	2.0 ¹		0.76
		2.43	0.84*
NaCl		2.32	0.76*
mica		2.56	0.94*
glass		2.34	0.78*

Adhesion parameters

		<u>NaCl</u>	<u>mica</u>	<u>glass</u>
<u>Au</u>	z_o (10^{10} m)	2.7	2.7	2.74
	W (mJ m ⁻²)	70.0	74.8	66.1
<u>Ag</u>	z_o (10^{10} m)	2.8	2.7	2.75
	W (mJ m ⁻²)	54.5	67.2	57.2
<u>Cu</u>	z_o (10^{10} m)	2.55	2.6	2.58
	W (mJ m ⁻²)	64.0	61.5	62.5

References: 1 Krupp (1967); 2 Böhme et al. (1969)

* assuming characteristic frequency of 15 eV

constant (ϵ_i) and the characteristic frequency ω_i

$$A_{ii} = 0.230 \hbar \omega_i \frac{(\epsilon_i - 1)^2}{(\epsilon_i + 1)^{3/2} (\epsilon_i + 2)^{1/2}} \quad (2.45)$$

The values of A_{ij} for NaCl, mica and glass have been calculated from this equation (see Table 2-7) assuming a characteristic frequency corresponding to 15 eV. The adhesion between mica plates has been measured by Tabor and Winterton (1969), who found the Hamaker constant to be $1.07 \times 10^{-19} \text{ J}$ - some 10% higher than the theoretical value (Table 2-7).

The adhesion energies of Au, Ag and Cu can now be calculated from Eq. (2.44), with the adsorption distance (z_o) as used in the continuum approximation (see Table 2-6). The results shown in Table 2-7, indicate adhesion energies around 60 mJ m^{-2} on NaCl, mica and glass. Thus, as for the continuum approximation the macroscopic theory underestimates the adhesion when the interfacial separation (z_o) is of the order of an atomic spacing. This theory does, however, give a good estimate of the adhesion of macroscopic particles (diameter of a few microns), and has been used extensively in colloid science (see Krupp 1967).

2.1.5. Summary

In the above section, the adsorption of single atoms on solid surfaces and the adhesion between solids have been discussed in terms of the van der Waals forces between atoms. The adsorption of metal atoms on the surfaces of ionic crystals, rock-salt and mica, was

calculated by summation over the interactions of the adatom with the nearest ions in the crystal; alternatively, the adsorption can be considered by regarding the solid as a homogenous isotropic medium. A comparison between the two methods shows that the continuum approximation cannot normally account for the adsorption if the adsorption distance is of the order of atomic dimensions. However, if the contribution due to the surface layer of ions in the crystal is added, the two approaches are in reasonable agreement. Because of the uncertainty in the values of the parameters for the dispersion constants, even the summation method will be accurate to only 30%. The continuum approximation (with the surface contribution) is more inaccurate since the value of the adsorption distance (z_0) has to be assumed. For this reason, the adhesion of metals to glass cannot be regarded as more than an order-of-magnitude calculation.

The macroscopic theory is based on assumptions similar to the continuum approximation, and therefore similarly underestimates the adhesion between solids of a few ångströms' separations.

2.2. Electrostatic Adhesion

The origin of electrostatic adhesion can be understood from the properties of electrical double layers. Supposing there exists, at the interface between two materials in contact, a surface charge of density σ_1 , at the surface of material 1, and of density σ_2 on material 2. If the interface as a whole is neutral, then

$$\sigma_1 + \sigma_2 = 0 \quad (2.46)$$

i. e., the two surface charges are equal in magnitude and opposite in polarity. Eq. (2.46) describes the basic idea of the electrical double layer as first proposed by Helmholtz (1853) for thin parallel sheets of charge at the interface between metals. The concept can be generalised to include space charge layers which extend for some distance from the interface.

It is immediately obvious that the two charge layers will attract each other electrostatically, and, therefore, the attraction contributes to the adhesion between the two materials. Without going into the details of the mechanisms by which electrical double layers are established at interfaces (these are described in Chapter 3) the electrostatic adhesion forces between metals, semi-conductors and insulators are considered below (Sect. 2.1.2.1).

Since this work is concerned with the adhesion energy of thin films, the electrostatic contribution to this energy must be examined. In the past, the electrostatic adhesion energy has been equated with the work done in separating two solids against electrostatic forces (Deryagin et al. 1957). However, this procedure does not provide

a unique definition of the electrostatic adhesion energy, since the work done against electrostatic forces depends on the way in which the materials are separated (see Sect. 2.2.2). An alternative definition which is more satisfactory from a theoretical point of view is therefore proposed below.

It is important to distinguish electrostatic adhesion from other contributions to the adhesion between two solids. Electrostatic adhesion results from the electrostatic interaction between the electrical charges at the interface. The interaction of an electric field with the electrical dipole of a particle (neutral or charged), called the induction effect (Sect. 2.1.1.2), is fundamentally different.

2.2.1. Definition of Electrostatic Adhesion

The importance of electrical double layers at metal-electrolyte interfaces was recognised long ago (see Deryagin and Landau 1941, Verwey and Overbeek 1948). From thermodynamic reasoning it was shown that the Helmholtz free energy of the metal-electrolyte system contains a contribution due to the electrical double layer. The origin of this contribution can be shown by considering the formation of the double layer in two steps (Frenkel 1946); supposing the double layer is established spontaneously, resulting in a surface charge density σ . If the potential drop across the double layer is V_0 , the free energy change is $-\sigma V_0$. But, in forming the double layer, the work done against

the electrostatic forces as the charge is built up, is $\int_0^\sigma V_o \, d\sigma$

Thus, the total change in free energy is

$$\begin{aligned} F_{el} &= -\sigma V_o + \int_0^\sigma V_o \, d\sigma \\ &= -\int_0^{V_o} \sigma \, dV_o \end{aligned} \quad (2.47)$$

F_{el} is called the free energy of the double layer; the negative sign before the integral of Eq. (2.47) indicates that the free energy is decreased. A rigorous thermodynamic derivation of this expression has been published by Sparnaay (1967).

In the previous chapter (Sect. 1.1) a thermodynamic definition of the adhesion energy of two materials was given in terms of the free energy. In the same way we can define the electrostatic component of adhesion, using Eq. (2.47). The work done in separating an interface against electrostatic forces under equilibrium conditions is equal to the free energy change, $-F_{el}$, as defined by Eq. (2.47). Hence the (thermodynamic) electrostatic adhesion energy, E_{el} , is given by

$$E_{el} = \int_0^{V_o} \sigma \, dV_o \quad (2.48)$$

The electrostatic adhesion between two solids in thermodynamic equilibrium is therefore uniquely defined by the electrical charge at the interface. In practice, however, the adhesion is usually measured by separating the two solids in contact; if the equilibrium conditions are not maintained during separation, then the work done against electrostatic forces is no longer equal to the electrostatic adhesion energy as defined by Eq. (2.48). The electrostatic work of adhesion therefore depends on the way in which the solids are separated; particular cases are considered in the following sections.

2.2.2. Electrostatic Work of Adhesion

2.2.2.1. Electrostatic force

Let us consider two solids in contact with their surfaces at a constant separation z ; an electrical double layer lies across the interface, with surface charge densities σ_1 and σ_2 , on the two solids, such that

$$\sigma_1 + \sigma_2 = 0 \quad (2.46)$$

If the potential drop across the double layer is V_g , the electric field energy of this capacitor is

$$E_v = \frac{1}{2} C V_g^2 \quad \text{per unit volume} \quad (2.49)$$

$$\text{and } C = \frac{\epsilon_g \epsilon_o}{z}$$

where ϵ_g is the relative permittivity of the gap.

The force (P) between the two solids can be found by differentiation of Eq. (2.49) with respect to separation, i. e.

$$P = - \frac{1}{2} \epsilon_g \epsilon_o \frac{V_g^2}{z} \quad \text{per unit area} \quad (2.50)$$

$$\text{or, since } \sigma_1 = \epsilon_g \epsilon_o \frac{V_g}{z} \quad (2.51)$$

$$P = - \frac{\sigma_1^2}{2 \epsilon_g \epsilon_o} \quad (2.52)$$

If the electric charge in one or both solids is spread out over a volume below the surface, then, for a one-dimensional space charge distribution, $\rho(x)$, where x is the distance from the surface; the charge in each solid is given by:

$$\sigma = \int \rho(x) dx \quad \text{per unit area} \quad (2.53)$$

where the integral is taken over the whole space charge region in the solid. The electrostatic force between the solids is still given by Eq. (2.52) with σ given by Eq. (2.53). The force therefore depends on the distribution of charge in each solid.

A part of the potential drop across the interfacial region now lies across the space charge regions; the parameter V_g in the above equations is therefore the potential difference across the gap (of width z) only. It follows immediately, that for a given p.d. across the interfacial region (including space charge layers), the more the space charge is spread out into the solids in contact, the smaller is the electrostatic attraction between them; this is just what one would expect.

At this stage, an estimate can be made of the magnitude of the electrostatic force of attraction between two solids in contact. It will be shown in Chapter 3 that the surface charge densities can have values up to about $10^{13} \text{ e cm}^{-2}$; from Eq. (2.52) the corresponding electrostatic force will exert up to 10^7 N m^{-2} ($10^8 \text{ dynes cm}^{-2}$) across the interface. For comparison, the van der Waals' forces between parallel surfaces at a separation of about 0.3 nm are in the range of 10^7 to 10^8 N m^{-2} (see Sect. 2.1.3). Thus, the adhesive force of a thin film to its substrate will have an electrostatic component which is normally small compared with the van der Waals' contribution.

In our experiments on thin film adhesion, the adhesion energy is determined by separating the film from its substrate.

The work done, W_{el} , in separating the interface between two solids against the electrostatic forces of attraction will depend on the conditions of the process. Let us assume that the surfaces remain parallel as their separation is increased from the initial value $z = z_0$. If the electrostatic force at a separation z is $P(z)$, the total electrostatic work done in separating the surfaces to infinite separation, is

$$W_{el} = \int_{z_0}^{\infty} P(z) dz \quad (2.54)$$

In the following sections, the electrostatic work of adhesion, as defined by Eq. (2.54), is assessed for various specific cases.

2.2.2.2 Separation under equilibrium conditions

The equilibrium conditions are maintained during the separation of an interface, if the charge neutrality is conserved throughout, i. e., if the charges, $\sigma_1(z)$ and $\sigma_2(z)$, in the two solids are related by

$$\sigma_1(z) + \sigma_2(z) = 0 \quad (2.55)$$

Since the charges at the interface must decrease during the separation, (thus keeping the potential drop (V_0) across the interfacial region constant) the equilibrium conditions can only be satisfied, if the solids are conductors. We shall consider the general case of two semi-conductors with space charge layers of density $\rho(x_1)$ and $\rho(x_2)$, where x_1 and x_2 are the distances from the interface (see Fig. 2-5). The potential differences across the two space charge regions, V_{s1} and V_{s2} , vary with the separation z , as given by the equation,

$$V_0 = V_{s1} + V_g + V_{s2} \quad (2.56)$$

where V_g is the potential across the gap between the solids
(see Fig. 2-5). The charge density is related to these potentials
at a separation z , by

$$\sigma_1(z) = \frac{\epsilon_g \epsilon_o}{z} V_g \quad (2.57)$$

$$= \frac{\epsilon_g \epsilon_o}{z} (V_o - V_{s1} - V_{s2}) \quad (2.58)$$

where ϵ_g is the dielectric constant in the gap.

The potential drop across a space charge region depends on the
charge distribution in that region; let us assume a simple
distribution, with Debye length L ,

$$\rho(x) = \rho \exp - \frac{x}{L} \quad (2.59)$$

From the Poisson equation,

$$\frac{d^2V}{dx^2} = - \frac{\rho(x)}{\epsilon_s \epsilon_o} \quad (2.60)$$

(ϵ_s is the relative permittivity of the solid);

we can find the potential drop V_{s1} by integration,

$$\begin{aligned} V_{s1} &= \frac{1}{\epsilon_{s1} \epsilon_o} \int_0^\infty dx_1 \int \rho_1 \exp - \frac{x_1}{L} dx_1 \\ \epsilon_{s1} \epsilon_o V_{s1} &= \rho_1 L_1^2 = \sigma_1 L_1 \end{aligned} \quad (2.61)$$

and similarly for V_{s2} .

Hence, from Eq. (2.58) and (2.61), the charge density is given

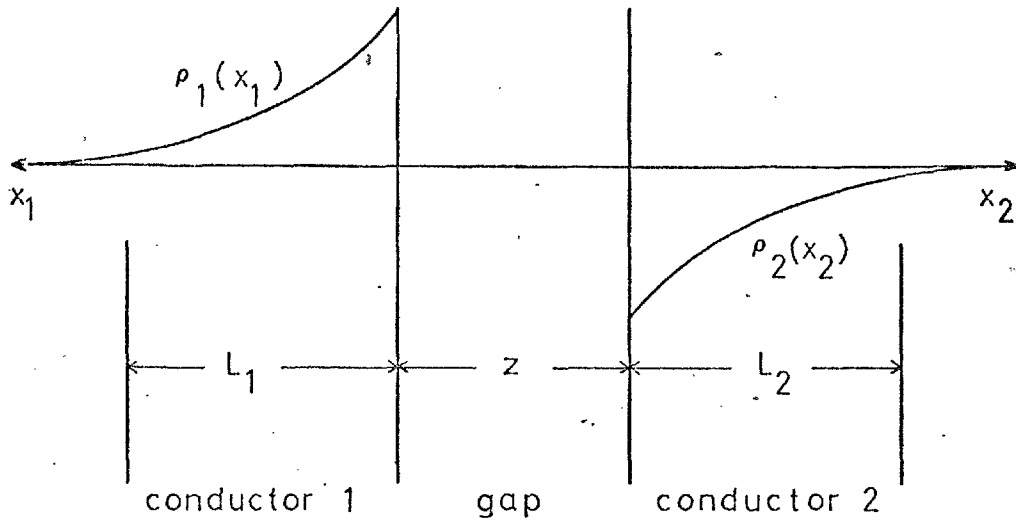
$$\begin{aligned} \text{by} \quad \sigma_1(z) &= \frac{\epsilon_g \epsilon_o}{z} \left[V_o - \frac{\sigma_1(z) L_1}{\epsilon_{s1} \epsilon_o} + \frac{\sigma_2(z) L_2}{\epsilon_{s2} \epsilon_o} \right] \\ &= \frac{\epsilon_g \epsilon_o V_o}{z + L_1/\epsilon_{s1} + L_2/\epsilon_{s2}} \end{aligned} \quad (2.62)$$

If, at the initial separation $z = z_o$,

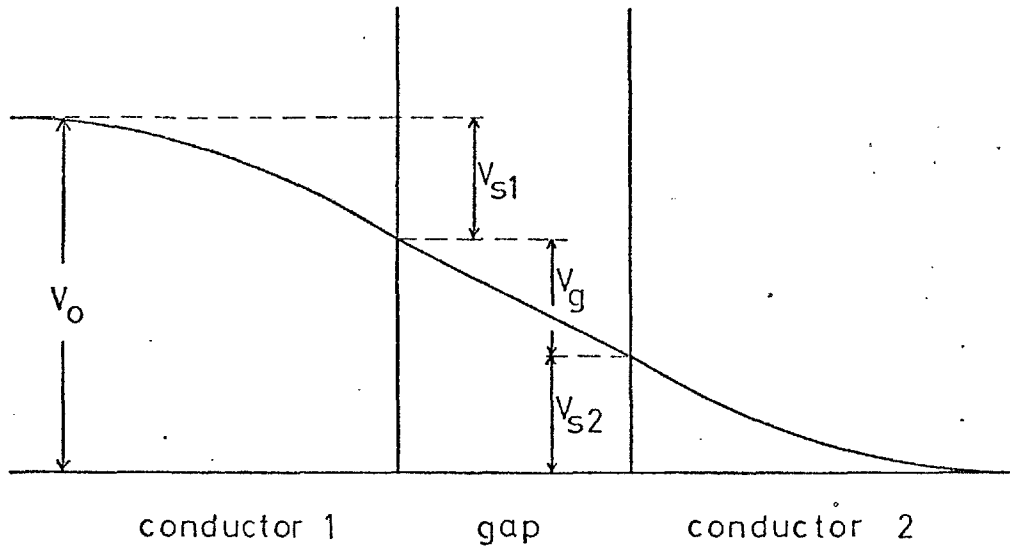
$$\sigma_1(z_o) = - \sigma_2(z_o) = \sigma$$

then, Eq. (2.54) may be written as

$$\sigma_1(z) = \sigma \left[\frac{z_o + L_1/\epsilon_{s1} + L_2/\epsilon_{s2}}{z + L_1/\epsilon_{s1} + L_2/\epsilon_{s2}} \right]^2 \quad (2.63)$$



a) Space charges at interface



b) p.d. across interface

Fig. 2-5 Space charge and potential difference across the interface between two conductors.

The electrostatic force between these solids at a separation z

$$\begin{aligned}
 \text{is } P(z) &= \frac{\sigma_1(z)^2}{2 \epsilon_g \epsilon_o} \\
 &= \frac{\sigma^2}{2 \epsilon_g \epsilon_o} \left[\frac{z_o + L_1/\epsilon_{s1} + L_2/\epsilon_{s2}}{z + L_1/\epsilon_{s1} + L_2/\epsilon_{s2}} \right]^2 \quad (2.64)
 \end{aligned}$$

From Eq. (2.54) the electrostatic work of adhesion is therefore

$$W_{el} = \int_{z_o}^{\infty} P(z) dz = \frac{\sigma^2}{2 \epsilon_g \epsilon_o} \left(z_o + L_1/\epsilon_{s1} + L_2/\epsilon_{s2} \right) \quad (2.65)$$

This expression gives the electrostatic adhesion between two semiconductors with space charge layers of depth L_1 and L_2 at the interface. Eq. (2.65) is easily applied to the case of two metals in contact; since the charge inside a metal must be zero, the charge is concentrated in a thin surface layer (L_1 and $L_2 \ll z_o$), then Eq. (2.65) becomes

$$W_{el} = \frac{\sigma^2 z_o}{2 \epsilon_g \epsilon_o} = \frac{\epsilon_g \epsilon_o V_o^2}{2 z_o} \quad (2.66)$$

Since the separation of the solids was considered to take place under equilibrium conditions, the electrostatic work of adhesion should be equal to the electrostatic adhesion energy as defined by Eq. (2.48) above:

$$E_{el} = \int_0^{V_o} \sigma dV_o \quad (2.48)$$

From Eq. (2.63) at $z = z_o$,

$$\sigma = \frac{V_o}{z_o + L_1/\epsilon_{s1} + L_2/\epsilon_{s2}} \quad (2.67)$$

and therefore

$$E_{el} = \frac{V_o^2}{2 \epsilon_g \epsilon_o \left\{ z_o + L_1/\epsilon_{s1} + L_2/\epsilon_{s2} \right\}} \quad (2.68)$$

hence, E_{el} is equal to W_{el} (Eq. (2.66)).

An estimate of the magnitude of the electrostatic adhesion can be made from the above expressions. The contact p.d. V_o is normally less than 1 eV (see Sect. 3.2); the adhesion between metals, assuming $z_o = 0.4$ nm, will therefore be less than 1 J m^{-2} (10^3 erg cm^{-2}). For two semi-conductors with space charge depths $L = 0.1 \text{ } \mu\text{m}$ (this is a typical value), it can be seen from Eq. (2.65) that the electrostatic adhesion for $V_o = 1 \text{ eV}$ (and $\frac{\epsilon_s}{\epsilon_g} = 10$) is only about 50 mJ m^{-2} .

2.2.2.3. Separation at constant surface charge

The solids are initially in contact with equal charge densities of opposite sign on the two surfaces (Eq.(2.46)), the electrostatic attraction is given by Eq. (2.52) above. Since the surface charge is assumed to remain constant during the separation, the electric field in the gap remains constant and the potential difference V rises linearly with z . The electrostatic work of adhesion is given by

$$W_{el} = \int_{z_o}^{\infty} \frac{\sigma^2}{2 \epsilon_g \epsilon_o} dz = \int_{V_o}^{\infty} \frac{1}{2} \sigma dV \quad (2.70)$$

Theoretically, the adhesion is therefore infinite, but in practice the assumption of constant gap field (and constant surface charge) holds only when the separation is small compared with the dimensions of the charged surfaces. A second practical limitation is given by the potential difference across the gap: at some critical value $V = V_c$ the surface charge may be reduced by charge emission or gas breakdown (see Sect. 3.2.2). Supposing the surface charge is

reduced to a negligible value at a separation z_c ; on a further separation no work is therefore done against electrostatic forces.

For this case the electrostatic work W_{el} is

$$W_{el} = \int_{z_0}^{z_c} \frac{\sigma^2}{2 \epsilon_g \epsilon_o} dz = \frac{\sigma^2}{2 \epsilon_g \epsilon_o} (z_c - z_0) \quad (2.71)$$

This expression was used by Deryagin et al. (1957) to calculate the electrostatic adhesion between insulators, with the assumption that the gap p. d. was limited by Paschen discharge (see Sect. 3.2.2.2).

2.2.2.4. Separation of a metal-insulator contact

In this case, the charge in the insulator remains constant during separation so that an equilibrium condition is not maintained. In the arrangement shown in Fig. 2-6, the insulator is sandwiched between two metals which are electrically inter-connected. The insulator has both a space charge, of density $\rho(x)$, and surface charges σ_1 and σ_2 at the two interfaces with the metals. The charge neutrality condition requires that

$$\sigma_{m1} + \sigma_1 + \int_0^d \rho(x) dx + \sigma_2 + \sigma_{m2} = 0 \quad (2.72)$$

where σ_{m1} and σ_{m2} are the charge densities on the two metals and d is the insulator thickness. Summing the potential differences between the metals, with metal 1 at separation z (see Fig. 2-6)

$$\frac{\sigma_{m1} z}{\epsilon_g \epsilon_o} + \frac{(\sigma_{m1} + \sigma_1) d}{\epsilon_i \epsilon_o} + \frac{1}{\epsilon_i \epsilon_o} \int_0^d dx \int \rho(x) dx - \frac{\sigma_{m2} z_o}{\epsilon_g \epsilon_o} = 0 \quad (2.73)$$

Thus, the charge on metal 1 at a separation z from the insulator

surface is

$$\sigma_{m1} = - \frac{\sigma_1(\epsilon_g d + \epsilon_i z_o) + \epsilon_g \int_0^d dx \int \rho(x) dx + \epsilon_i z_o (\sigma_2 + \int_0^d \rho(x) dx)}{\epsilon_i (z + z_o) + \epsilon_g d} \quad (2.74)$$

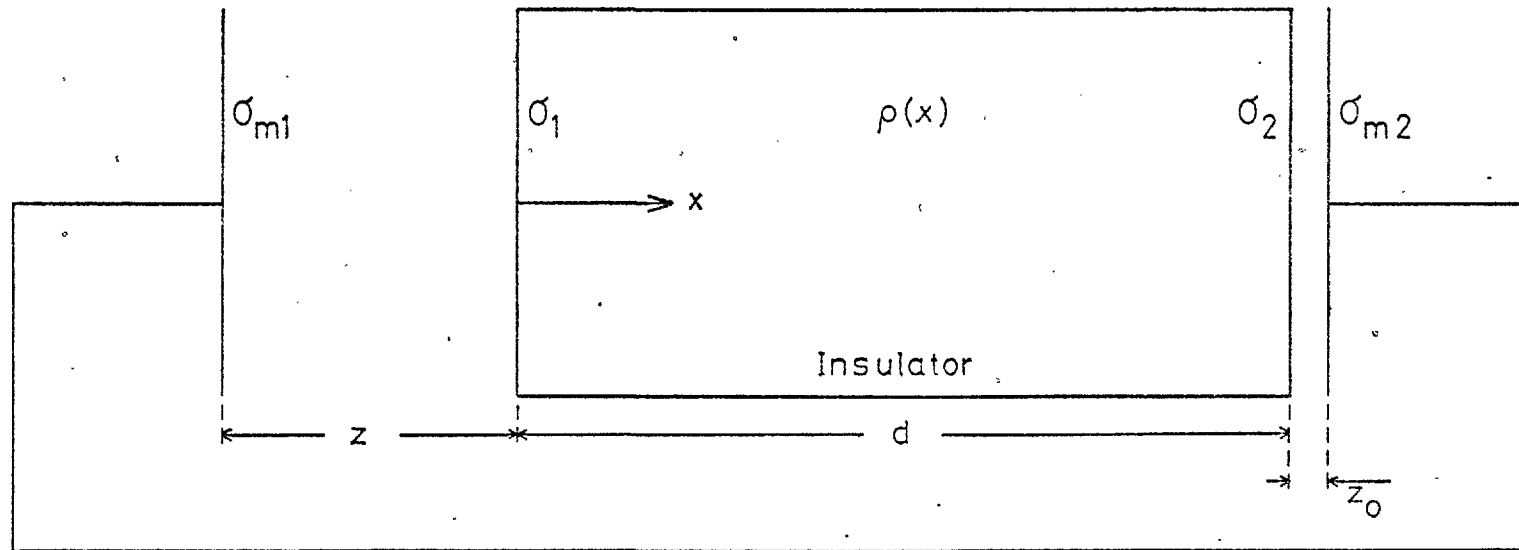


Fig. 2-6 Metal-insulator-metal sandwich (electrodes shorted during separation)

where d and ϵ_2 are the insulator thickness and relative permittivity respectively.

Let us assume that the charge densities at the two insulator surfaces are equal, i. e. ,

$$\sigma_1 = \sigma_2 = \sigma_s$$

It follows from Eq. (2.74) that

$$\sigma_{m1} = - \frac{Q_1 \epsilon_g d / \epsilon_i + Q_t z_o}{z + z_o + d / \epsilon_i} \quad (2.75)$$

where Q_1 is the effective charge on insulator surface 1, given by

$$Q_1 = \sigma_s + \int_0^d \rho(x) dx - \frac{1}{d} \int_0^d x \rho(x) dx \quad (2.76)$$

and Q_t is the net charge in the insulator,

$$Q_t = 2 \sigma_s + \int_0^d \rho(x) dx \quad (2.77)$$

The electrostatic force at separation z is therefore

$$P(z) = \frac{\sigma_s^2}{2 \epsilon_g \epsilon_o} = \frac{1}{2 \epsilon_g \epsilon_o} \left[\frac{Q_1 \epsilon_g d + Q_t \epsilon_i z_o}{\epsilon_i (z + z_o) + \epsilon_g d} \right]^2 \quad (2.78)$$

If the insulator has only surface charges, i. e. , $\rho(x) = 0$,

Eq. (2.78) reduces to

$$P(z) = \frac{\sigma_s^2}{2 \epsilon_g \epsilon_o} \left(\frac{2 \epsilon_i z_o + \epsilon_g d}{\epsilon_i (z + z_o) + \epsilon_g d} \right)^2 \quad (2.79)$$

and the electrostatic work of adhesion

$$\begin{aligned} W_{el} &= \int_{z_o}^{\infty} \frac{\sigma_{m1}^2}{2 \epsilon_g \epsilon_o} dz \\ &= \frac{(Q_1 \epsilon_g d / \epsilon_i + Q_t z_o)^2}{2 \epsilon_g \epsilon_o [2z_o + \epsilon_g d / \epsilon_i]} \end{aligned} \quad (2.80)$$

For the case of zero space charge, this simplifies to

$$W_{el} = \frac{\sigma_s^2}{2 \epsilon_o} \left(\frac{2z_o}{\epsilon_g} + \frac{d}{\epsilon_i} \right) \quad (2.81)$$

If $d / \epsilon_i \gg 2z_o / \epsilon_g$, then, for an insulator with a surface charge, σ_s ,

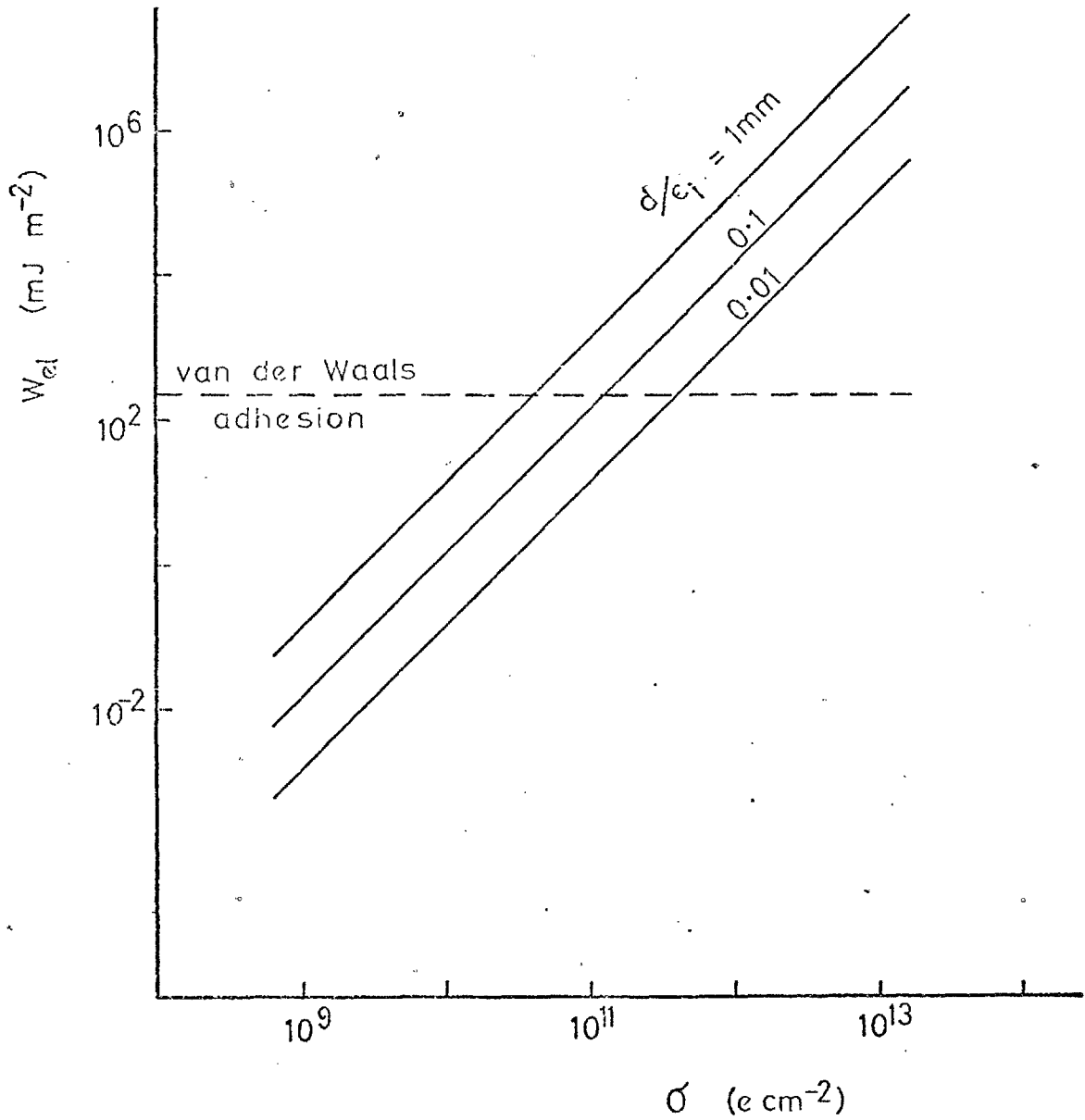


Fig. 2-7 Electrostatic work of adhesion, W_{el} , against charge density, σ , for various values of d/ϵ_i ; typical value of van der Waals adhesion energy indicated for comparison.

the electrostatic work of adhesion is

$$W_{el} = \frac{\sigma_s^2 d}{2 \epsilon_i \epsilon_o} \quad (2.82)$$

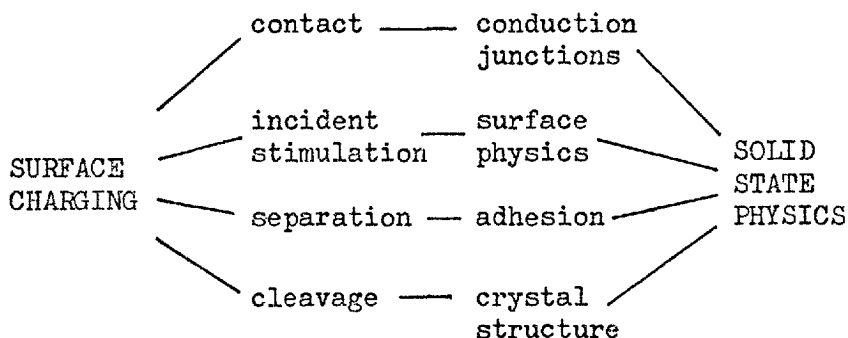
The electrostatic work of adhesion W_{el} given by Eq. (2.82) has been plotted in Fig. 2-7 as a function of the surface charge on the insulator. This plot shows that W_{el} reaches values of about 100 mJ m^{-2} , which are comparable with the van der Waals adhesion at charge densities around $10^{11} \text{ e cm}^{-2}$, for $\frac{d}{\epsilon_i} = 0.1 \text{ mm}$.

CHAPTER III

ELECTRICAL CHARGES AT INTERFACES

The presence of electrical charge at surfaces and interfaces is a well-known phenomenon, which has been studied for a long time. The field of static electrification, which is concerned with the mechanisms of charge generation, has, however, remained a separate and underdeveloped branch of solid state physics. Whereas the electrical properties of conductors have been described in detail, insulators are only now receiving more attention. It is therefore becoming possible to apply the concepts of solid state physics to the problems of the static electrification of both conducting and insulating solids (Krupp 1971). The relation between these two fields of study is summarised diagrammatically in Table 3-1.

Table 3-1



In the previous chapter the electrostatic theory of adhesion was discussed (Sect. 2.2) from a phenomenological point of view. We must now look at the mechanisms of charge generation. Three separate stages are considered: the charges on solid surfaces, the charges generated by contact between solids and the charge movements occurring during separation of interfaces. The theories of charge transfer by electrons and ions across the interfaces between conductors and non-conductors are developed. Particular emphasis is placed on the description of metal-insulator interfaces, which is used below (Ch. 6) for the interpretation of the experimental results obtained in this work. The experimental evidence for the mechanisms of charge transfer is reviewed.

3.1. Charges on Solid Surfaces

The properties of solid surfaces have become of great interest in thin film physics. With the development of ultra-high vacuum techniques it has become possible to characterise solid surfaces chemically (e. g. by Auger spectroscopy) and structurally (e. g. by low-energy electron diffraction). Information about the electrical properties of surfaces can be obtained from work function measurements on conductors. Although net charges cannot exist at the surface of conducting solids in the absence of external electric fields, electrical double layers are often formed by the adsorption of gases. The resulting "surface potential" (i. e. the p. d. across the double layer) contributes to

the work function of the solid; the work function is consequently very sensitive to surface contamination (e. g. see Gundry and Tompkins 1968).

The situation is more complicated with insulating solids since non-equilibrium charges can be stored on their surfaces. Such charges are easily generated by the incidence of neutral and charged particles and by radiation. Even in the absence of these external effects, an insulator may have a net surface charge. For example, when an ionic crystal is cleaved in vacuum the surface may be strongly charged. This has been observed in the case of mica (Deryagin and Metsik 1960); patches of charged areas of both polarities ($\sim 10^{11} \text{ e cm}^{-2}$) were found after vacuum cleavage. This was thought to arise from the irregular distribution of potassium ions on the (001) surface. On the other hand, the surface charges on silicate crystals cleaved in ultra-high vacuum (Ryan et al. 1968, Grossman 1968) were attributed to the charged regions surrounding dislocations (Fröhlich and Suisky 1964).

A different mechanism for the generation of surface charge on ionic crystals was proposed by Frenkel (1946). In ionic crystals, a common defect is the Schottky defect (Schottky 1935), that is, a lattice vacancy formed by an ion moving from a lattice site to the surface. If the free energy of formation of a defect differs for the positive and negative ions in the crystal, then an

unequal number of positive and negative ion vacancies is formed and a net charge is established on the surface, with a compensating space charge layer extending into the crystal. The model has been extended to take into account other types of point defects (e. g. interstitials, divalent ions) and its characteristics have been calculated in detail (Kliever and Köhler 1965, Poeppel and Blakley 1969). The existence of Frenkel double layers has been confirmed experimentally: for AgBr crystals at room temperature (Trautweiler 1968) a surface charge density of more than $10^{11} \text{ e cm}^{-2}$ was deduced. e /

The presence of electrical charges on the surface of any solid alters the potential barrier which a charge carrier has to overcome in order to be emitted from the solid into vacuum or into another solid. The process of charge transfer between two solids may therefore be affected by the surface charges which existed before the solids were brought into contact. The details of the charge transfer process are discussed in the following sections.

3.2. Contact Charging

In this section the electrical processes occurring during the formation and separation of a contact between two solid surfaces are discussed. The concepts of the band theory of solids are used to describe the electron transfer processes at the interface between conductors. For the metal-insulator contact, various models of electron transfer based on the electronic properties of insulators are proposed; the effect of ions is also considered. A comparison is made between these models and recent experimental results on contact charging.

It is important to define clearly what is meant by "contact" between two surfaces. Harper (1967b) proposed a complicated scheme of classification, but for our purposes it is sufficient to define the term "direct" contact. Two surfaces are regarded as being in direct contact if the separation of the surface atoms (ions) of the two solids is sufficiently small for electrons to cross the interfacial potential barrier. As will be seen below, the interfacial separation must be less than about 1 nm for the solids to be in direct contact.

In an ideal case, the width of the interface would be of the order of a lattice spacing. In practice, solid surfaces are not atomically smooth (and are covered with contaminants). Thus, when the surfaces of two bulk solids are placed in contact, a direct contact will exist only at the microscopic regions of surface asperities; the charge transfer process across such interfaces is therefore restricted to a small fraction of the interfacial area.

A solid-solid contact that approaches the ideal case can, however, be achieved by deposition of thin films. A thin film can follow the contours of the substrate surface and can be in direct contact at virtually all points of the interfaces. Except under very clean conditions, the interfacial separation will be increased by the presence of contaminating layers. Considerable precautions have been taken in this investigation of contact charging to minimise the contamination at the interface.

A large part of the literature on surface charging deals with triboelectrification, that is, contact charging by sliding or rolling two surface across each other. In these experiments the charging process is further complicated by uncontrollable factors, such as deformation, material transfer and temperature gradients at the interface. The interpretation of these methods is therefore often ambiguous and we shall confine most of this discussion to cases of static contact.

3.2.1. Mechanisms of Contact Charging

In this section, the ways in which electrical charges may be generated at the interface between two materials as a result of forming a contact, are discussed. The term contact charging is used here to describe the processes of charge movement caused by the formation of an interface in the absence of any external sources of charge.

Contact charging can occur, in principle, by transfer of charged particles across the interface, or by accumulation (depletion)

of electrical charge at the interface. A transfer of charge across an interface will take place if the following conditions are satisfied:

- (i) there is a driving force causing charge carriers to cross the interface;
- (ii) the charge carriers are mobile in both materials in contact.

The driving force may be a concentration gradient and/or an electric field across the interface. If the concentration of mobile carriers differs in the two materials, a diffusion across the interface can occur. As soon as the transfer of charge has commenced, however, there will be an electric field across the interface, opposing the diffusion process. A situation of dynamic equilibrium is eventually reached when the two opposing forces are equal.

The electrical characteristics of a material determine the type of charge carrier which can take part in the transfer process. In the case of metals and semiconductors, electrons (holes) are obviously the most mobile charge carriers; in insulators both electrons and ions may be sufficiently mobile to cause a significant transfer of charge. Theoretical models for charge transfer will be developed below for contact between metals (Sect. 3.2.3), semiconductors (Sect. 3.2.4) and insulators (Sect. 3.2.5).

The second mechanism of contact charging does not involve a transfer of charge across the interface. Charge carriers may be preferentially adsorbed at the interface, or neutral particles may be ionised after adsorption. A common example of this mechanism occurs at the metal-electrolyte interface. Electrolytic ions of a given type may accumulate at the interface, thus forming a space charge layer below the interface and inducing an equal and opposite charge layer on the metal surface (Overbeek 1952). The resultant electrical double layer has thus been established without a net transfer of charge across the interface. A similar process may occur at contact between solids where the transfer of charge is impeded in some way.

3.2.1.1 Transfer of electrons across interfaces

A theoretical description of the process of electron transfer across the interface between two materials can be approached from a thermodynamical point of view, without reference to the electrical properties of the materials concerned. At thermodynamic equilibrium, an assembly of n electrons in a material is characterised by its electro-chemical potential energy $\bar{\mu}$, defined by the relation (Herring and Nicols 1949)

$$\bar{\mu} = \left(\frac{\partial F}{\partial n} \right)_{P,T} \quad (3.1)$$

where F is the Helmholtz free energy of the system. (This can be shown as follows: the work done in taking δn electrons up to the surface of the material from infinity and dissolving them

in the material, $\bar{\mu} \delta n$, is equal to the change in free energy, δF , at constant temperature and pressure; hence Eq. (3.1) follows).

This is analogous to the statistical description, in which the electrons are distributed in the available energy states according to Fermi-Dirac statistics; the probability of occupancy of a given state E is

$$f(E) = \frac{1}{1 + \exp^{(E-E_F)/kT}}$$

where E_F is the Fermi energy, which is identical with the electrochemical potential energy, $\bar{\mu}$ (Fowler and Guggenheim 1939).

These quantities can be related to the macroscopic electrical potential, ϕ , referred to the potential of an electron at infinity (normally equated to zero). The work done in raising an electron from the Fermi energy ($\bar{\mu}$) inside the material to the macroscopic potential, ϕ_o , outside the material is called the work function, ϕ . It follows from the above descriptions that, since, by convention, the electrostatic potential energy outside the solid is $-e \phi_o$, the work function is given by

$$\phi = -\bar{\mu} - e\phi_o \quad (3.2)$$

where e is the electronic charge. The parameters in equation (3.2) can be seen from the representation by an energy level diagram of the solid-vacuum interface (Fig. 3-1). The electrical potential outside (ϕ_o) a material is represented by the vacuum level; the electron energy corresponding to the electrochemical potential is represented by the Fermi level. A further parameter, the chemical potential energy, μ , is defined as the energy

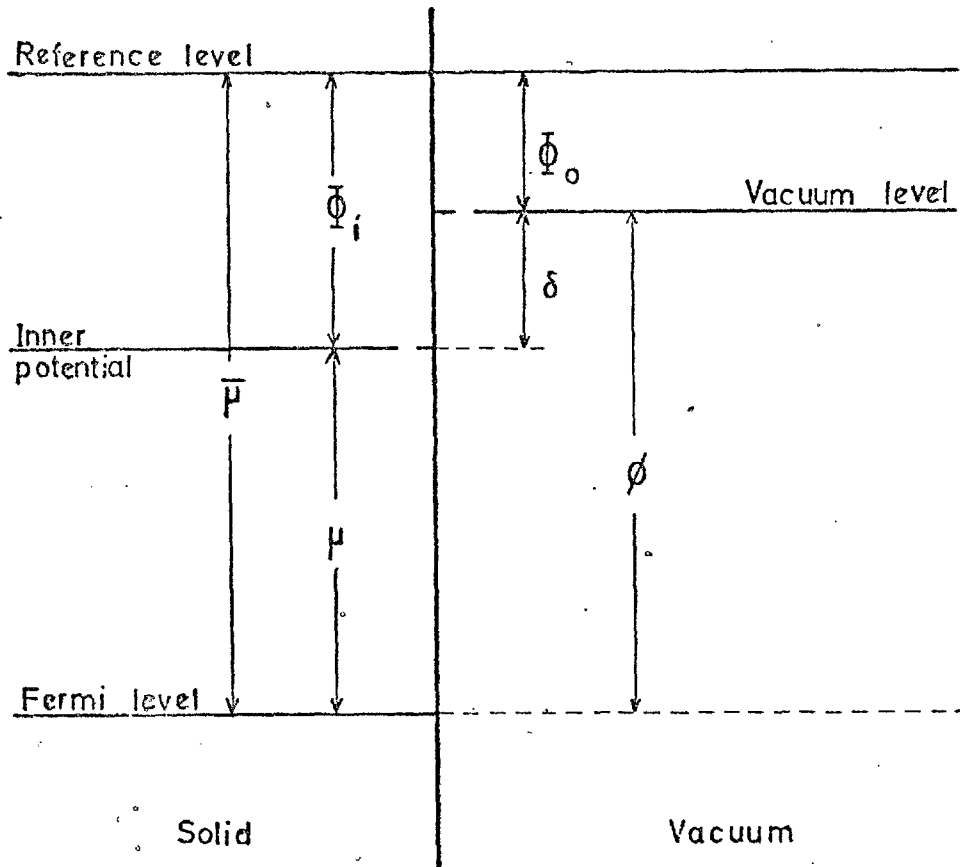


Fig 3-1 Energy level diagram
for solid-vacuum interface

required to raise an electron from the Fermi level to the inner potential ϕ_i ; it follows that

$$\mu = \bar{\mu} + e\phi_i \quad (3.3)$$

The work function can therefore be expressed from Eqs. (3.2) and (3.3), as

$$\phi = -\mu - e\delta \quad (3.4)$$

$$\delta = \phi_o - \phi_i \quad (3.5)$$

Thus, the work function consists of a bulk component (μ) and a surface component (δ).

Consider now two isolated materials of work functions ϕ_1 and ϕ_2 respectively; this situation is represented in Fig. 3-2a for two metals and in Fig. 3-3a for a metal and a semiconductor. The outer potentials of the two solids are equal at this stage. If the two solids are now placed in direct contact, such that electrons can cross the interface, then an equilibrium situation will be reached, in which the electro-chemical potentials are equal, i. e.

$$\bar{\mu}_1 = \bar{\mu}_2 \quad (3.6)$$

Hence, there now exists a contact potential difference (c. p. d.), V_{12} , between points just outside the two solids (see Figs. 3-2b, 3-3b), defined by

$$V_{12} = \phi_{o1} - \phi_{o2} \quad (3.7)$$

It follows from Eqs. (3.4) to (3.7) that the contact p. d. is equal to the work function difference:

$$V_{12} = \phi_2 - \phi_1 \quad (3.8)$$

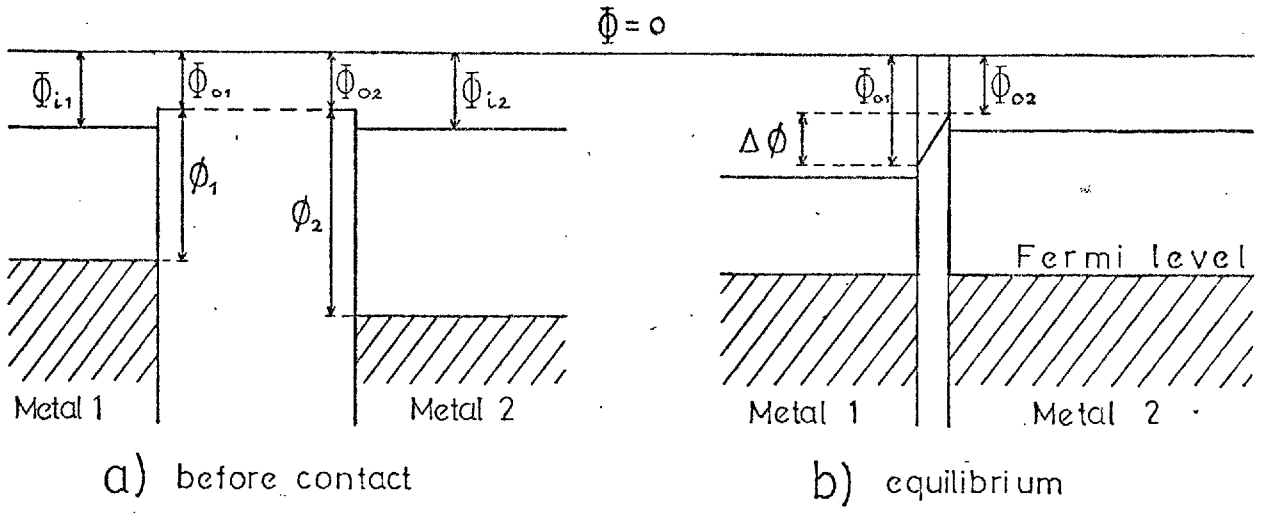


Fig 3-2 Metal - metal contact

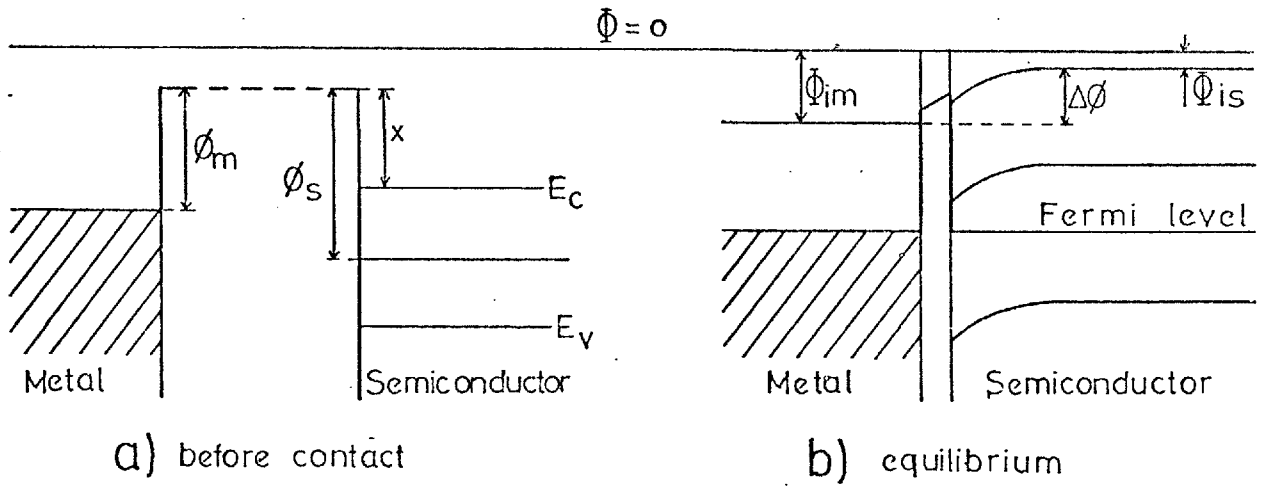


Fig 3-3 Metal - semiconductor contact

It should be noted that for the metal-semiconductor contact (Fig. 3-3), V_{12} is the potential drop across both the gap and the space charge region; the c. p. d. is equal to the change of inner potential only if the surface potentials (δ_1 and δ_2) are equal before contact (see Fig. 3-3b).

We have now a framework for the electron transfer process which can be applied to particular materials. The electrical charge at the interface can be determined by integration of the Poisson equation,

$$\text{div } \underline{D} = \rho \quad (3.9)$$

for a given space charge distribution, ρ , in the two materials

The boundary condition required for this equation is given by

Gauss' law: for a surface with charge density σ , the electrical flux density is discontinuous across the surface, i. e.

$$D_2 - D_1 = \sigma \quad (3.10)$$

3.2.2. Separation of Interfaces

In many experiments of contact charging (discussed below) the electrical charge remaining on one of the solids is measured after separation of the interface. The magnitude of the charge is likely to be smaller than that originally present at the interface, since some of the surface charge may be lost by emission into or across the gap between the surfaces. In the following section the mechanisms of charge redistribution during separation of the interface are outlined.

3.2.2.1. Thermionic emission and tunneling

An electron has to overcome the potential barrier at the surface of a solid in order to be emitted into vacuum. Thermionic emission can occur if an electron is thermally excited from the Fermi level (in the case of a metal) to the vacuum level; the thermionic current depends strongly on the barrier height V_b and on the temperature T of the emitting surface, as given by the Richardson equation:

$$j_{th} = A T^2 \exp - \frac{V_b}{kT} \quad (3.11)$$

If an external electric field is applied, the barrier height is lowered by an energy of $e(eF)^{\frac{1}{2}}$; the resultant enhancement of electron emission is known as the Schottky effect (Schottky 1914). For barrier heights of several electron volts, as encountered in practice, the thermionic current is very small at room temperature and moderate applied fields.

The tunneling of electrons through a potential barrier is a quantum-mechanical effect, arising from the finite probability of transmission of an electron through a barrier, of which the maximum height is greater than the electron energy. In general the tunnel current is a product of the transmission probability, $D(E_x)$, and the number of electrons available for tunneling, $N(E_x)$, where E_x is the electron energy component normal to the barrier,

$$j_t = e \int_0^{\infty} D(E_x) N(E_x) dE_x \quad (3.12)$$

The tunnel current depends on the barrier height (relative to E_x) and on the barrier width; the evaluation of the integral in Eq. (3.12) is extremely complex, except for very simple barrier shapes (Duke 1969). For a potential barrier at the interface between two solids, the tunnel current depends on the number of available states into which electrons can tunnel; thus, the supply function, $N(E_x)$, must be multiplied by a factor, $(1 - f_2(E_x))$, where $f_2(E_x)$ describes the distribution of electrons in the solid into which the electrons are transferred.

For very strong electric fields at the surface, the effective thickness of the potential barrier may be reduced sufficiently for the emission of electrons by tunneling. A quantum-mechanical description of the tunnel process leads to the following expression for the "field emission" current (Fowler and Nordheim 1928):

$$j_{fe} = a \frac{E^2}{\phi} \exp - \frac{0.69 \phi^{3/2}}{E} \quad (3.13)$$

The field emission process becomes important for electric fields of $\geq 10^7 \text{ V cm}^{-1}$.

The electron transfer between two solids is determined by the two processes discussed above. If two solids of different work functions are placed into contact, both thermionic and tunnel currents may flow, such that electrons are transferred to the solid of higher work function (see Fig. 3-2 for contact between metals). The transfer of charge reduces the difference in barrier heights (initially the work function difference), thus

decreasing the thermionic current; the tunnel current is also reduced since the number of states from which electrons can tunnel ($N(E_x)$ in Eq. (3.12)), is now smaller. When the Fermi levels of the two solids have been equalised (see Fig. 3-2b, 3-3b), the contact p.d. has been established and the net current across the interface is zero.

Let us now consider the processes occurring during separation of an interface between two solids in equilibrium. Supposing the separation between the solids is increased instantaneously by a small amount. Before any charge rearrangement occurs, we can see from Fig. 3-4 that, since the gap capacitance has been decreased, the potential drop across the gap has been increased (by an amount v in Fig. 3-4). The relative probability of tunneling has therefore been increased in the direction tending to reduce the surface charge (by transfer from metal 2 to metal 1 in Fig. 3-4); also, since the barrier heights now differ, the thermionic emission is greater (by a factor $\exp \frac{v}{kT}$) in one direction. The tunnel and thermionic currents will therefore flow, thereby reducing the surface charge until a new equilibrium situation is reached, when the contact p.d. lies across the interfacial region.

The tunneling process can operate only up to separations of about 1 nm; the equilibrium between the solids cannot therefore be maintained at larger separations. If the initial separation between the solids is 0.4 nm, the surface charge will be reduced

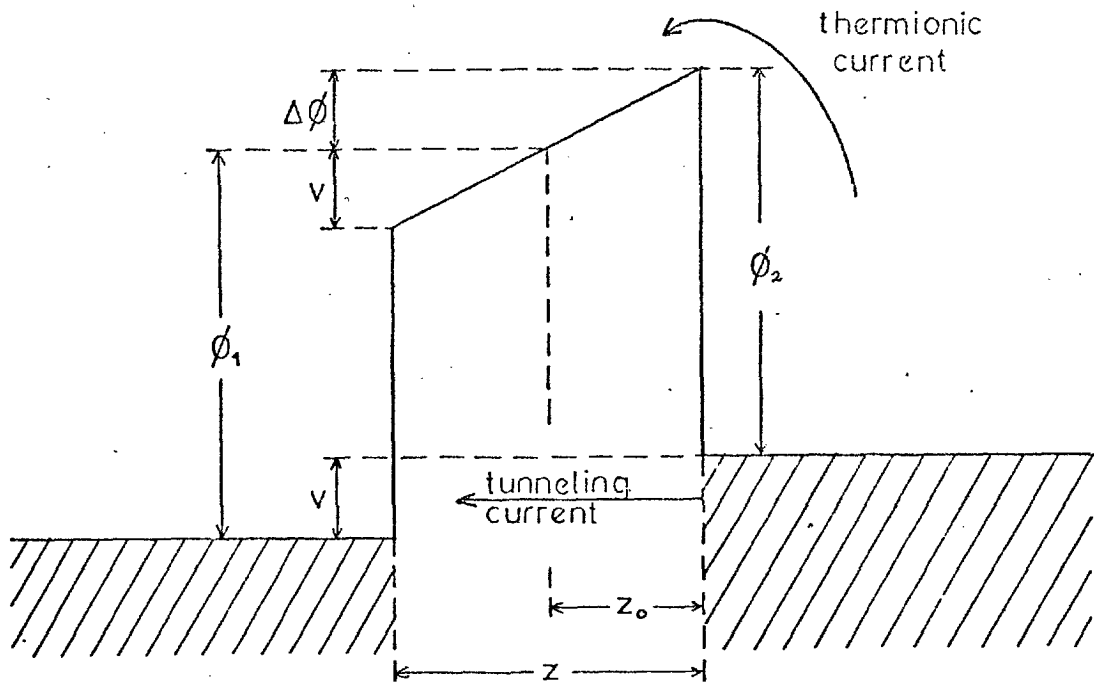


Fig 3-4 Separation of metals —
non-equilibrium situation

to about 40% of its original value by these processes. However, for solids of high surface resistivity the charge transfer process is slowed down, so that the loss in surface charge may not be as large as for separation under equilibrium conditions (see below).

So far the surfaces in contact have been regarded as being ideally smooth. In practice, solid surfaces are never smooth on an atomic scale; the electrical field across a small gap between two surfaces may therefore rise locally to values exceeding the average by one or two orders of magnitude. According to Llewellyn-Jones (1967) field emission from metal surfaces in vacuum can be observed at average applied fields of 10^5 V cm^{-1} . If the electric field between two surfaces were limited to this value during the separation of the interface, the remaining surface charge would be less than $10^{11} \text{ e cm}^{-2}$.

3.2.2.2 Discharge

An electron which is emitted into the gap between two surfaces may create further charged particles, either by incidence on the opposite surface or by collision with gas molecules in the gap. If a sufficient number of charges are created, the emission current is amplified rapidly and, in the case of an externally applied electric field, a breakdown of the gap p. d. results.

The ionisation of gas molecules by collision with the electrons leads to the so-called Paschen discharge. The potential

difference which has to be applied between the electrodes in order to achieve a Paschen discharge is determined by the gap width, d , and the gas pressure, p , between the electrodes.

According to Paschen's law (see von Engel 1964) the breakdown potential, V_c , is given by

$$V_c = \frac{B (pd)}{C + \ln (pd)} \quad (3.14)$$

where B and C are constants for a given gas. In Fig. 3- 5 the breakdown potential has been plotted as a function of (pd) for air ($B = 365$, $C = 1.18$). The product (pd) is directly proportional to the number of gas molecules in the gap. Thus, at high values of (pd) the electron mean free path in the gap is very short; the energy gained by acceleration in the electric field is therefore insufficient for ionisation, unless a high potential is applied across the gap. On reducing (pd) the ionisation process becomes more efficient and, consequently, the breakdown potential is lowered; according to Eq. (3.14) V_c decreases almost linearly as (pd) is reduced. However, the number of gas molecules becomes smaller and hence the ionisation process becomes less efficient as (pd) is lowered. Thus, the breakdown potential reaches a minimum and rises more rapidly at small values of (pd) , as shown in Fig. 3- 5. For air, the Paschen curve has a minimum at $(pd)_m = 0.4 \text{ mm Hg cm}$, $V_{cm} = 360 \text{ V}$.

At atmospheric pressure the Paschen minimum for air occurs at an electric field of about $2 \times 10^6 \text{ V cm}^{-1}$; a field of this magnitude is almost sufficient to cause field emission of

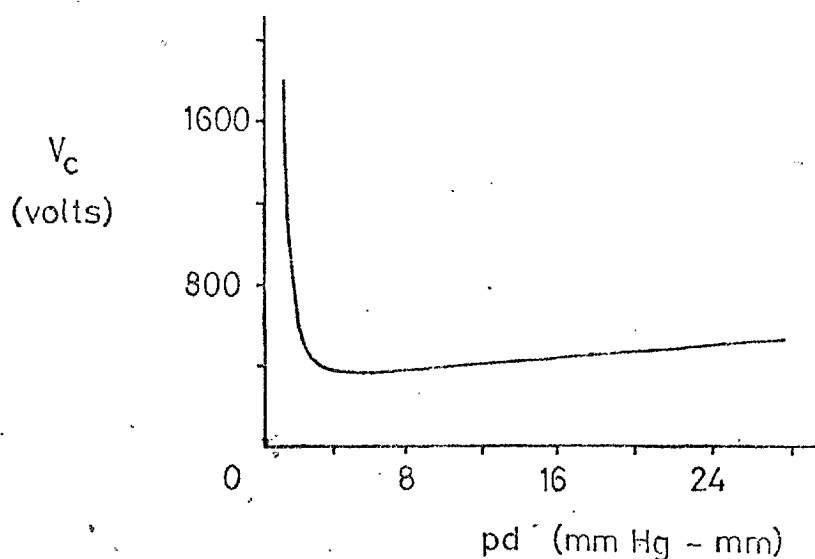


Fig. 3-5 Paschen curve - plot of breakdown potential V_c against (pd) for air.

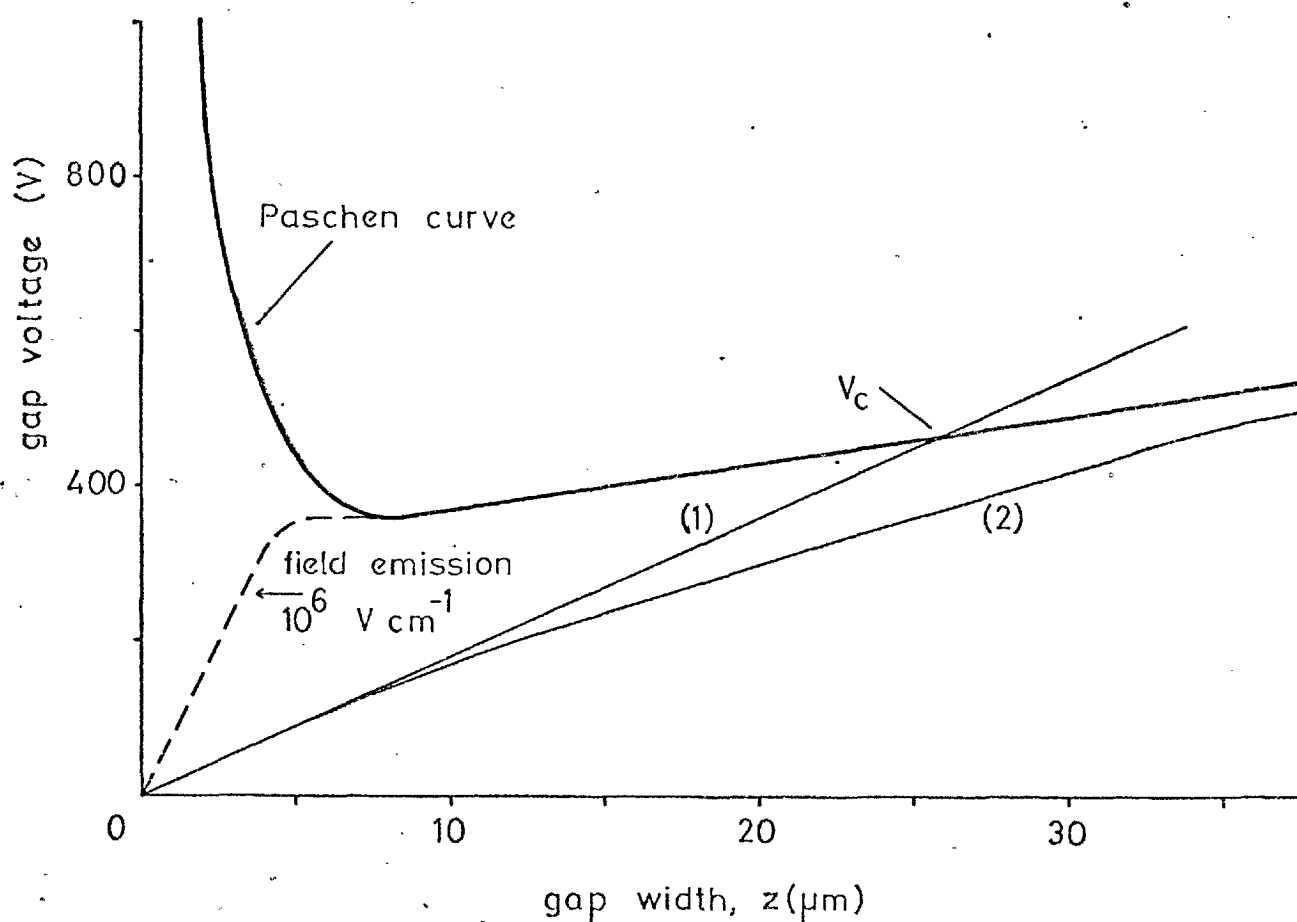


Fig. 3-6 Variation of gap voltage with gap width

- (1) for conductors with constant surface charge ($10^{11} \text{ e cm}^{-2}$)
- (2) for conductor and insulator with constant surface charge ($10^{11} \text{ e cm}^{-2}$)

Paschen curve for air at atmospheric pressure

electrons from the electrodes. It has therefore been suggested that for gaps of less than about 5 μm the gap potential is limited by field emission at atmospheric pressure (Schaffert 1962); the breakdown potential at small values of (pd) therefore falls linearly to zero, rather than following the Paschen curve (see Fig. 3-6).

At the opposite extreme, that is, at low gas pressure, the Paschen law also becomes invalid. The electron mean free path in vacuum is limited by the dimensions of the gap, so that electrons and ions may be produced by collision with the electrode surfaces. The mechanisms of breakdown in vacuo (below 10^{-3} torr) have been described by Llewellyn-Jones (1967). The processes leading to breakdown are very sensitive to the surface conditions and often occurs at applied fields of 10^5 V cm^{-1} . It is therefore difficult to obtain more than a qualitative picture of the breakdown process (see review by Hawley and Zaky 1967). For the special case of small gaps, the collisions at the surfaces may result in the release of atoms (molecules) adsorbed on the surface; the resultant rise in pressure in the gap may be sufficient to allow Paschen discharge to occur (Llewellyn-Jones 1967).

We can now consider the conditions arising during the separation of solids; supposing the surface charge (σ) remains constant as the gap (z) between the surfaces is widened. The potential drop (V) across the gap will therefore rise linearly (for a planar geometry) until the breakdown potential is reached. In Fig. 3-6 the variation of V with increasing gap width is shown

(curve 1) for a constant surface charge of $10^{11} \text{ e cm}^{-2}$; the intersection with the Paschen curve at atmospheric pressure shows the potential and gap width at which breakdown occur. There is no intersection, i. e. no breakdown, if the surface charge is less than about $5 \cdot 10^{10} \text{ e cm}^{-2}$; charges of this magnitude are often found on surfaces which have been charged in the atmosphere.

The variation of the gap p. d. with the separation between an earthed conductor and a charged insulator (see Sect. 2.2.2.4) is shown by curve 2 (Fig. 3-6); curve 2 was calculated from Eq. (2.75) for a surface charge of $10^{11} \text{ e cm}^{-2}$ (and $d/\epsilon_i = 0.1 \text{ mm}$). The gap p. d. increases less rapidly than in curve 1 and does not intersect the Paschen curve.

3.2.3. Contact between Metals

The theory of electron transfer developed in Sect. 3.2.1.1 can be applied to the contact between two metals. Since the electric field inside a conductor must be zero, an electric charge can exist only in a thin surface layer. For two metals of work functions ϕ_1 and ϕ_2 in contact at an equilibrium separation z_o , surface charge densities of equal magnitude, σ , and opposite polarity are formed at the interface. As shown above (Sect. 3.2.1.1) the contact p. d. is equal to the difference in work functions, $\Delta\phi$. Thus, the surface charge density is given by

$$\sigma = \epsilon_g \epsilon_o \frac{\Delta\phi}{z_o} \quad (3.15)$$

where ϵ_g is the dielectric constant in the gap. The work functions of metals are in the region of 3 to 5 eV, so that the work function differences are typically less than 1 eV. For $z_o = 0.4$ nm the maximum surface charge is therefore less than $10^{13} \text{ e cm}^{-2}$.

Extensive work on the contact charging of metal spheres in air has been carried out by Harper (1951). The charge measured after separation of the spheres was found to depend linearly on the contact p. d., as predicted by Eq. (3.15). However, the magnitudes of the measured charges were somewhat smaller than predicted, even after allowing for the charge leakage by tunneling at separations up to 1.2 nm. The discrepancy is attributed (Harper 1967a) to surface irregularities which enable the tunneling process to continue after the average separation has reached the critical value, at which tunneling ceases.

Similar results were obtained by Bredov and Kshemianskaia (1957) for the contact charging of metal plates. These comrades observed a strong dependence of the measured charge on the speed of separation. It is difficult to see how this effect could result from tunneling, unless the metal surfaces were covered with thick oxide layers.

3.2.4. Metal-Semiconductor Contact

As a result of technological interest, the electrical properties of semiconductor surfaces have been investigated thoroughly over the past decade. The theoretical description of metal-semiconductor interfaces is well established and can be found in textbooks (e. g. Henish 1957, Many et al. 1965). In this section, expressions will be derived for the charge transferred across metal-semiconductor interfaces in terms of the electrical properties of the solids in contact.

3.2.4.1. Theoretical description of charge transfer

In Fig. 3-7 the energy level diagram is shown for a metal-semiconductor interface at equilibrium. The charge (here positive) transferred to the semiconductor is spread over a surface region of typically $.1 \mu\text{m}$ thickness; in addition, some charge, of density σ_{ss} per unit area, may be trapped in surface states. At equilibrium, the charge density at the metal surface σ_m , is equal to that in the semiconductor, i. e. ,

$$\sigma_m + \sigma_{sc} + \sigma_{ss} = 0 \quad (3.16)$$

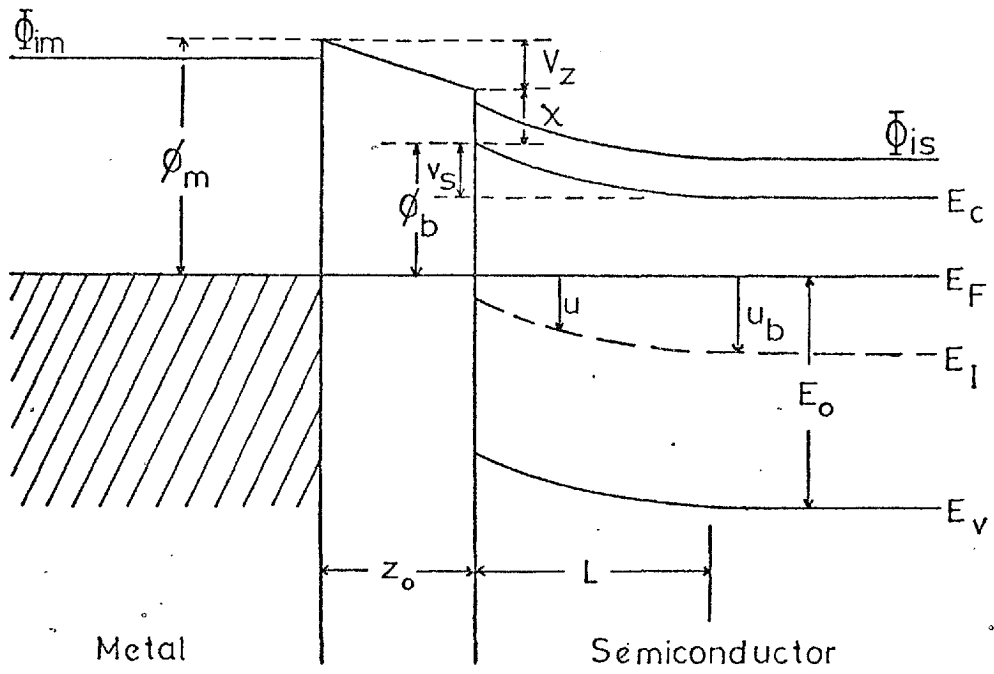


Fig 3-7 Metal-semiconductor interface

where σ_{sc} is the contribution due to the space charge in the semiconductor. To find the value of σ_{sc} the one-dimensional Poisson equation must be integrated. Following the notation and definitions of Many et al. (1965), the space charge density $\rho(x)$ as a function of the distance x from the surface is

$$\rho(x) = e(p - p_b - n + n_b) \quad (3.17)$$

where n and p are the electron and hole densities at x , n_b and p_b are the corresponding bulk values.

Defining the dimensionless potential,

$$u = \frac{e}{kT} (E_F - E_I) \quad (3.18)$$

where E_I is the intrinsic Fermi level ($E_I = \frac{1}{2}(E_C - E_V)$); if the potential in the bulk is u_b , we can define the potential barrier $v = u - u_b$ (see Fig. 3-7).

From these definitions it can be shown that for a non-degenerate semiconductor,

$$n = n_b e^v, \quad p = p_b e^{-v} \quad (3.19)$$

The Poisson equation can now be written as

$$\frac{d^2 v}{dx^2} = - \frac{e^2}{\epsilon_s \epsilon_0 kT} \left[p_b (e^{-v} - 1) - n_b (e^v - 1) \right] \quad (3.20)$$

Integration w. r. t. v , using $2 \frac{d^2 v}{dx^2} = \frac{d}{dv} \left[\frac{dv}{dx} \right]^2$,

with the boundary condition as $x \rightarrow \infty$, v and $\frac{dv}{dx}$ tend to zero, gives:

$$\left(\frac{dv}{dx} \right)^2 = \frac{2e^2 n_b}{\epsilon_s \epsilon_0 kT} \left[(e^v - v - 1) + \frac{p_b}{n_b} (e^{-v} + v - 1) \right] \quad (3.21)$$

If the electric field at the semiconductor surface is E_s (directed normally outward from the surface), the surface charge

$$\sigma_{sc} = \epsilon_s \epsilon_0 E_s = \frac{kT}{e} \epsilon_s \epsilon_0 \frac{dv_s}{dx} \quad (3.22)$$

where v_s is the band bending (dimensionless potential barrier) at the surface. Hence,

$$\sigma_{sc} = \mp (2 \epsilon_s \epsilon_o kT n_b) f(v_s) \quad (3.23)$$

$$f(v_s) = \left[(e^{v_s} - 1) + \frac{p_b}{n_b} (e^{-v_s} - 1) \right]^{\frac{1}{2}} \quad (3.24)$$

where the -ve sign is appropriate for $v_s > 0$, the +ve sign for $v_s < 0$; note that the function $f(v_s)$ (Eq. (3.24)) is positive for any v_s .

The charge induced on the metal surface is determined by the potential drop across the gap (of width z_o), i. e.,

$$\sigma_m = - \epsilon_g \epsilon_o \frac{V_z}{z_o} \quad (3.25)$$

where ϵ_g is the effective dielectric constant of the gap. If we define the flat-band work function, ϕ_s^{fb} , for the uncharged surface of the semiconductor (i. e. at $v_s = 0$), the gap p. d. is

$$V_z = \frac{1}{e} (\phi_m - \phi_s^{fb}) + v_s \frac{kT}{e} \quad (3.26)$$

where ϕ_m is the metal work function.

The condition of charge neutrality (Eq. (3.16)) uniquely determines the value of the band bending, v_s . An exact solution for v_s can be found numerically, and the charge at the metal surface σ_m can be deduced subsequently for Eqs. (3.26) and (3.25) (see case (c) below). More physical insight can, however, be gained from approximate analytical solutions for special cases. We shall consider two limiting cases:

(a) Approximation for small band bending $v_s \ll 1$ (either sign)

For this approximation, the Eq. (3.23) reduces to

$$Q_s = [\epsilon_s \epsilon_0 kT (n_b + p_b)]^{1/2} \quad (3.27)$$

where

$$\sigma_{sc} = -Q_s v_s \quad (3.28)$$

We can assume a uniform distribution of surface states, $N_s \text{ cm}^{-2} \text{ eV}^{-1}$ which are filled in the band gap below the Fermi level; defining E_0 as the energy difference between the Fermi level and the valence band edge in the bulk of the semiconductor (see Fig. 3-7), the surface states charge is

$$\sigma_{ss} = -N_s (kT v_s + E_0) \quad (3.29)$$

For the above approximation ($v_s \ll 1$) it follows that

$$\sigma_m = - \frac{Q_z (Q_s + N_s kT)}{Q_z + Q_s + N_s kT} \frac{\Delta\phi}{kT} \quad (3.30)$$

where $\Delta\phi = \phi_m - \phi_s$ is the work function difference (ϕ_s is the true semiconductor work function). Thus, in the case considered for this approximation the charge induced on the metal varies linearly with the work function difference.

The range of validity of this approximation is, however, somewhat restricted: for $\sigma_{ss} = 0$, the band bending is given by

$$v_s = - \frac{\phi_m - \phi_s^{fb}}{kT \left[1 + Q_s/Q_z \right]} \quad (3.31)$$

Since the work function difference is typically of the order of $10kT$, the condition for $v_s \ll 1$, is fulfilled if

$$Q_s/Q_z = \frac{z_0}{\epsilon_s} \frac{\epsilon_s}{L} \gg 1 \quad (3.32)$$

where L is the effective depth of the space charge layer, given by

$$L = \left[\frac{\epsilon_s \epsilon_0 kT}{e^2 (n_b + p_b)} \right]^{\frac{1}{2}} \quad (3.33)$$

For a typical semiconductor, L is about $0.1 \mu\text{m}$, while $z_0 < 1 \text{ nm}$, thus, the condition of Eq. (3.32) is not normally fulfilled.

(b) Approximation for large band bending, $v_s < 0$, $|v_s| \gg 1$

An approximate solution for the potential barrier at the surface of a depleted n-type semiconductor has been derived by Cowley and Sze (1965). Defining the potential barrier, ϕ_b , as the energy difference between the conduction band edge and the Fermi level at the semiconductor surface, (see Fig. 3-7) an approximate expression is derived for ϕ_b :

$$\phi_b = \gamma (\phi_m - \chi) + (1 - \gamma) (\phi_s - \chi) \quad (3.34)$$

$$\gamma \equiv \frac{1}{1 + kT N_s / Q_z} \quad (3.35)$$

and χ is the electron affinity.

Using Eq. (3.25), the charge induced on the metal is given by

$$\sigma_m = - \left(\frac{N_s}{1 + kT N_s / Q_z} \right) \Delta\phi \quad (3.36)$$

Thus, again the charge induced on the metal varies linearly as the work function difference. It should be noted, however, that in deriving Eq. (3.34) Cowley and Sze (1965) have ignored the effect of the space charge on the barrier height ϕ_b . This assumption is valid only if the surface states charge is large compared with the space charge contribution, σ_{sc} , i. e. if

$$N_s \gg \frac{Q_s}{kT} = \frac{\epsilon_s \epsilon_0}{e L} . \text{ For } \frac{L}{\epsilon_s} \simeq 10 \text{ nm, this condition}$$

is fulfilled if $N_s \gg 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$.

A number of semiconductors, especially those of Group IV of the Periodic Table, have surface states densities of $> 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$ when in contact with metals (see Sect. 3.2.4.2). In these cases it is found that the potential barrier is almost independent of the metal work function (i. e. $\gamma \ll 1$) so that the Fermi level at the surface is "pinned", normally at an energy of $\frac{2}{3}E_g$ above the valence band edge (Mead 1966).

The charge induced on the metal, for very large values of N_s ($\gg 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$), is approximately

$$\sigma_m = - \epsilon_g \epsilon_0 \frac{\Delta\phi}{z_0} \quad (3.37)$$

i. e. the surface charge is the same as that between two metals of work function difference $\Delta\phi$ at separation z_0 . This is justification for regarding the effect of surface states as "metallising" the semiconductor surface.

(c) Numerical solution

An exact solution for the charge transferred across a metal-semi-conductor interface has been calculated numerically; in Fig. 3-8 the computed values of σ_m have been plotted against the work function difference $\Delta\phi$ for various values of the uniform surface states distribution, N_s . For positive values of $\Delta\phi$ (i. e. $\phi_m > \phi_s$, $v_s < 0$), the plot is linear and agrees closely with the Cowley and Sze approximation for $N_s > 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. In the region of negative $\Delta\phi$, σ_m rises more rapidly with $\Delta\phi$, but is reduced on increasing the surface states density (at small values of $N_s \lesssim 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$). This occurs because, at a given value of

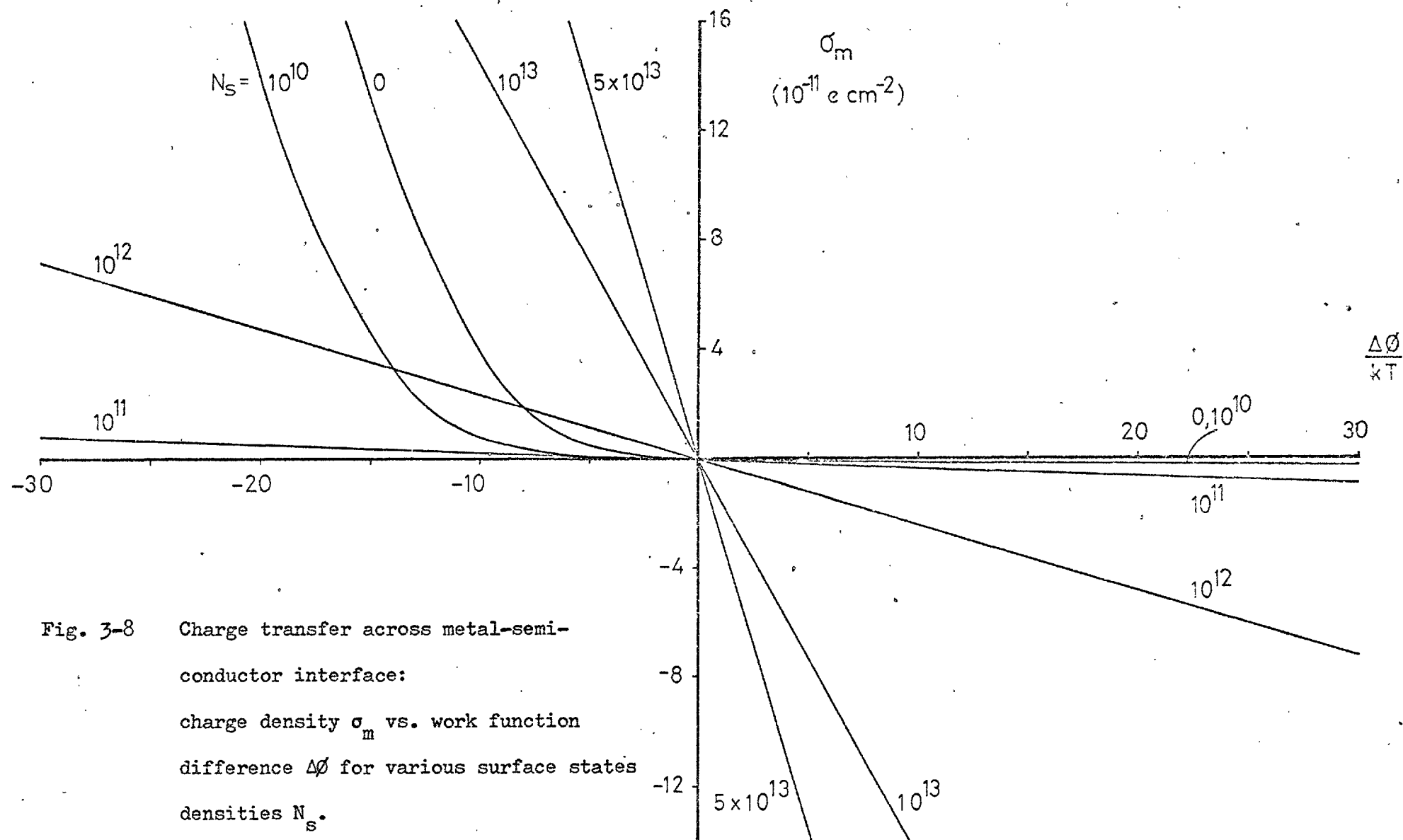


Fig. 3-8 Charge transfer across metal-semiconductor interface:
charge density σ_m vs. work function difference $\Delta\phi$ for various surface state densities N_s .

$\Delta\phi$, v_s (+ve) is reduced on increasing N_s ; σ_{sc} increases roughly exponentially with v_s (see Eq. (3.2.4)) and is greater than σ_{ss} in magnitude - hence the total charge is reduced in magnitude. For larger values of N_s , σ_{ss} becomes the dominant contribution, so that the gradient of the plot, which is linear again because $v_s < 0$, increases with N_s .

We have thus a detailed theoretical description of the charge transfer across metal-semiconductor interfaces. In the next section the experimental evidence for the charge transfer will be discussed.

3.2.4.2. Experimental evidence of charge transfer

In spite of the interest in semiconductor surfaces very few direct measurements of the contact charging of semiconductors appear to have been reported in the literature. Bredov and Kshemianskaia (1957) measured the charge transferred to semiconductors by contact with metals after separation of the interface. They observed a linear variation of the contact charge with the contact p.d., and in the case of Ge and Te, the variation was independent of the bulk carrier concentration. These results suggest the presence of a large density of surface states, but since no absolute values of charge density were published in this paper, a comparison with the above theories (Sect. 3.2.4.1) is not possible.

Indirect information about contact charging can be obtained from measurements of the potential barrier (ϕ_b) at the metal-

semiconductor interface. These measurements (e. g. Mead 1966 , Rhoderick 1970) have been used to determine the surface states density at the interface. For many semiconductors of Group IV and III-V compounds, the potential barrier does not depend strongly on the metal work function, although a linear correlation is usually found. The variation in ϕ_b agrees well with the expression of Cowley and Sze (1965) (see Eq.(3. 34) above) from which the surface states density N_s (assumed uniform in space and energy) is found to be greater than $10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$. Assuming a maximum work function difference of about 1 eV, the surface charge induced on the metal (see Eq. (3. 36)) therefore can be up to about $10^{13} \text{ e cm}^{-2}$. It should be noted that the surface states density is very sensitive to contamination at the interface (Turner and Rhoderick 1968).

The interpretation of potential barrier measurements is complicated by the fact that the metal work function cannot be measured simultaneously. In view of the strong dependence of the work function on the surface conditions, it is unreliable to assume that ϕ_m has the same value whether the surface is in vacuum or in contact with a solid. In fact, as pointed out in Section 3. 2. 1. 1, the work function consists of a bulk and a surface component (Eq. (3. 4)); the surface potential is due to the dipole arising from the extension of the electron wave function beyond the geometrical surface. Obviously, the surface dipole is much smaller when the metal is in contact with a solid, so that the chemical potential is a more appropriate parameter than the vacuum work function. According to Mead (1966) the chemical potential

is directly related to the electronegativity (Pauling 1967); a plot of the potential barrier Φ_b against the electronegativity of the metal is linear, with a gradient which is related to the surface states density in a way similar to the parameter γ in the Cowley and Sze expression (Eq. (3.35)).

3.2.5. Metal-Insulator Contact

An electrical charge generated on an insulator can remain at the surface for a long period of time. This phenomenon was discovered long ago (for a historical review see Benjamin (1968)) and is investigated today in the field of static electrification. The main interest in this field has arisen from the industrial hazards caused by "static", the charge on insulators resulting from contact with other materials. Far less scientific work has been published in this subject - possibly because of its reputation for giving irreproducible results. Since the electrification is usually carried out in an uncontrolled environment and with contaminated surfaces, it is not surprising that the surface charge, especially when produced by frictional electrification, is often found to be determined by haphazard surface contamination rather than by the materials in contact.

While the charge transfer between conductors is explained adequately by electronic properties, there remains considerable controversy over the mechanisms of contact charging of insulators. The importance of electrons in the charge transfer process was recognised by Vick (1953), but no detailed models have been proposed

until recently (Krupp 1971). On the other hand, Harper (1967b) concluded that only ions are sufficiently mobile in insulators to cause a charge transfer of the magnitude observed experimentally. In the last five years, however, a number of controlled experiments have been performed which can be explained only in terms of electron transfer.

The difficulty in proposing detailed electronic models of static electrification of insulators arises from the insufficient knowledge of their electronic properties. In solid state physics no basic distinction is made between semiconductors and insulators. The basic ideas used in the previous section (Sect.3.2.4.1) to describe the metal-semiconductor contact can therefore be applied to the contact charging of insulators. Obviously, there are essential differences since insulators are (a priori) poor conductors of electricity. Recent interest in the conduction properties of insulators, especially of amorphous thin films (Jonscher 1971), has led to a better understand of the behaviour of charge carriers in insulators. In the following section, this background information is used to propose models of contact charging of insulators, based on electronic properties.

3.2.5.1. Electron transfer models

Intrinsic insulators

A simple model of a crystalline insulator regards the solid as a wide band gap ($E_g > 2 \text{ eV}$) semiconductor; the conductivity of this "intrinsic" insulator, being proportional to $\exp - \frac{E_g}{2kT}$,

would therefore be very low. As suggested by Mott and Gurney (1948), a charge transfer can take place at a metal-insulator interface by thermionic emission of electrons from the metal into the insulator conduction band. This process results in the formation of a space charge layer (accumulation layer) below the interface if the insulator work function, ϕ_i , is greater than the metal work function, ϕ_m . Using the same notation as in the previous section, the space charge is given by

$$\rho(x) = -e(n_b e^v - n_b) \quad (3.38)$$

Integration of the Poisson equation for the space charge region gives the following expression for the surface charge at the interface (see Eq. (3.2.3) above) :

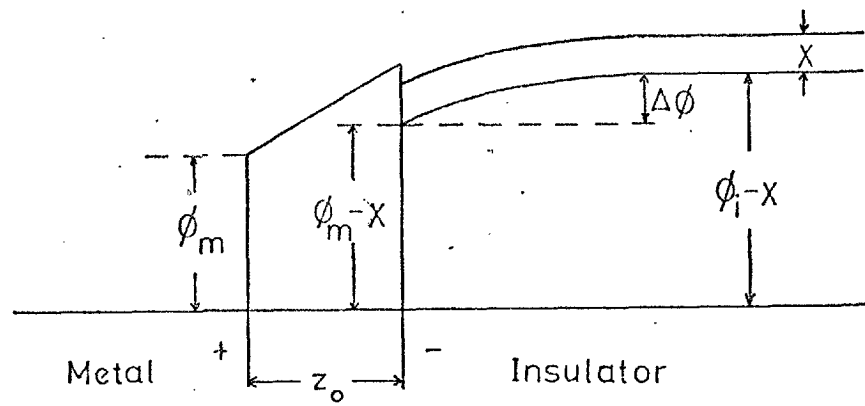
$$\sigma_{sc} = -(2\epsilon_i \epsilon_o kT n_b)^{\frac{1}{2}} (e^{v_s} - v_s - 1)^{\frac{1}{2}} \quad (3.39)$$

The charge on the metal surface is

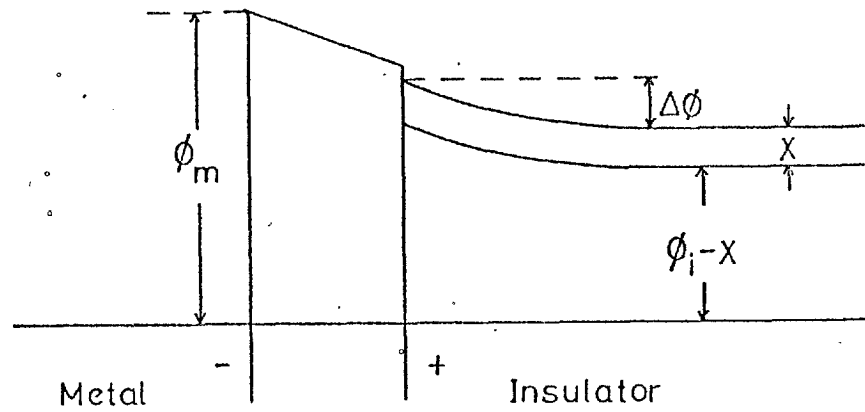
$$\sigma_m = -\frac{\epsilon_i \epsilon_o}{e z_o} (\Delta\phi + v_s kT) \quad (3.40)$$

where $\Delta\phi = \phi_m - \phi_i$; it has been assumed that the equilibrium situation has been reached by the charge transfer, such that the Fermi levels of the materials are aligned (see Fig. 3.9).

It is normally assumed (Simmons 1970) that the band bending at the surface corresponds to the work function difference i.e. $v_s kT = -\Delta\phi$; however, it is obvious from Eq. (3.40) that for this condition, the charge on the metal would be zero, thus violating the charge neutrality condition. In practice, the charge injected into the insulator is relatively small since the potential barrier is usually greater than 1 eV. Assuming, therefore, that



a) $\phi_m < \phi_i$



b) $\phi_m > \phi_i$

Fig 3-9 Metal - insulator contact

$$v_s \approx \frac{\phi_i - \phi_m}{kT} \gg 1, \text{ then}$$

$$\sigma_{sc} \approx - (2 \epsilon_i \epsilon_o kT N_c)^{\frac{1}{2}} \exp - \frac{\phi_m - \chi}{2kT} \quad (3.41)$$

where N_c is the effective density of states in the conduction band, related to n_b by

$$n_b = N_c \exp - \frac{\phi_i - \chi}{2kT} \quad (3.42)$$

For a potential barrier of 0.5 eV, the surface charge on the insulator, from Eq. (3.41), is less than 10^8 e cm^{-2} . Contact charging experiments usually result in far higher surface charges, typically more than $10^{10} \text{ e cm}^{-2}$, so that this model can account for only a small fraction of the total charge transfer. A similar conclusion can be reached from the conduction properties of insulators; the conductivity predicted by the intrinsic model is far lower than is actually observed (Simmons 1970).

Extrinsic Insulator

A real crystal contains imperfections and impurities in its lattice structure. These defects give rise to localised energy states. Two types of localised states may be distinguished (Jonscher 1971), depending on whether they are electrically neutral when occupied by an electron (donors and acceptors), or when electron deficient (traps). The first type is important in semiconductors; donor states arise from substitution of atoms of higher valency in a lattice of lower valency atoms (e.g. P atoms

in Si lattice). The donor state lies in the band gap at an energy just below the conduction band. Thus a small activation energy is required for the donor to be ionised by excitation of its electron into the conduction band. Similarly, an acceptor level lies just above the valence band, and is ionised by accepting a hole from the valence band. Trap levels on the other hand, are usually considered to lie at a much greater energy separation from the band edges. Electron traps can therefore be filled by electrons from the conduction band or from a donor level. Similarly, a hole trap can be filled by a hole transferred from the valence band or from an acceptor. The effect of traps in a semiconductor is generally to reduce the conductivity of the material (Simmons 1968).

In addition to the localised states in the bulk of a material, the states at the surface need to be considered. The conditions at the metal-semiconductor interface were seen in the previous section (Sect. 3.2.4) to be dominated by the presence of a large density of surface states ($N_s > 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$). Experimental evidence (Kurtin et al. 1969) suggests that the surface states density at metal-insulator interfaces is less than 10^{11} cm^{-2} . This is in agreement with the Shockley theory of surface states (Shockley 1939): by considering the splitting of atomic energy levels as the lattice constant of a crystal is decreased, Shockley concluded that there exist two distinct regions of surface states. When the overlap between atomic wave functions is small (i. e. in ionic crystals) the surface states are not very different from

those in the bulk, and therefore have high densities near the edges of the conduction and valence bands. On the other hand, for covalent crystals (large overlap of wave functions) the surface states have high densities near the middle of the band gap. Thus, in ionic crystals (insulators) the Fermi level at the surface can move through most of the band gap without a large change in the occupancy of surface states: the more covalent a crystal is, the more its Fermi level is stabilised (or "pinned"). A measure of the degree of Fermi level stabilisation is given by the dependence of the potential barrier Φ_b on the metal work function, or on the electronegativity X_m ; thus, for a value of $\frac{d\Phi_b}{dX_m}$ close to unity, the Fermi level is not stabilised (small surface states density), while for $\frac{d\Phi_b}{dX_m} \ll 1$, the Fermi level is pinned. Using the electronegativity difference, ΔX , of the ions in a crystal as a rough indication of the degree of "ionicity" in the bonding of the crystal, Kurtin et al. (1969) plotted the experimental value of $\frac{d\Phi_b}{dX_m}$ against ΔX for various semiconductors and insulators, as shown in Fig. 3-10. The plot shows a remarkably abrupt transition from strong to weak Fermi level stabilisation with increasing ionicity. Thus, ionic crystals, which are electrically insulating, have small surface states densities ($\leq 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$) when in contact with metals.

On the basis of the above discussion of the electron states in insulating solids, we can now consider the processes by which an electron can be transferred across the metal-insulator interface. Various processes which are statistically possible

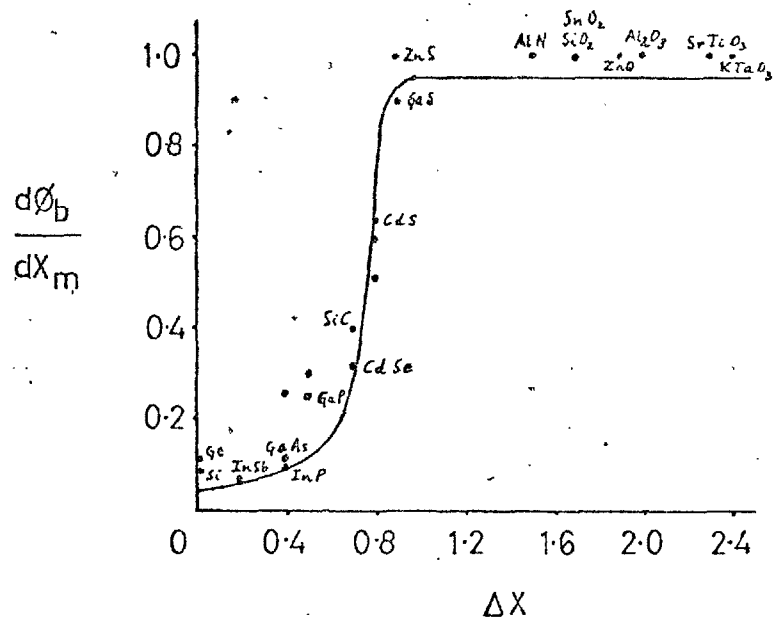


Fig. 3-10 Fermi level stabilisation:

plot of $\frac{d\phi_b}{dX_m}$ against electronegativity difference ΔX

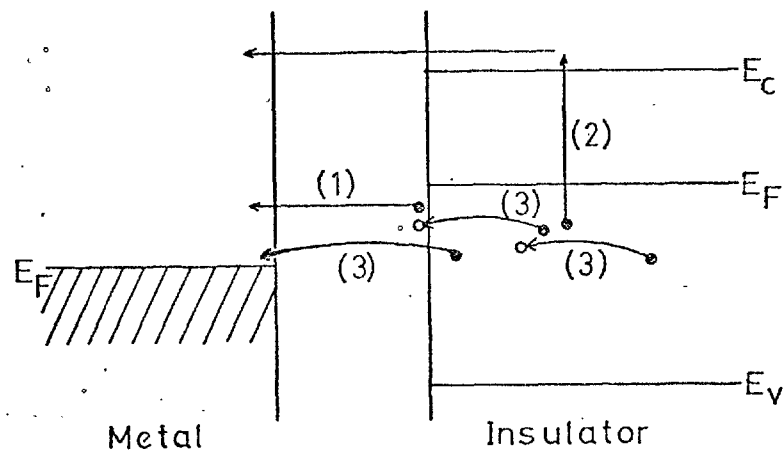


Fig. 3-11 Charge transfer across metal-insulator interface

process (1): tunneling
 (2): Schottky emission
 (3): hopping

are shown schematically in Fig. 3-11.

Surface states can be filled or emptied by tunneling of electrons across the interface (process (1) in Fig. 3-11); as seen earlier (Sect. 3.2.2.1) this process is practically instantaneous for interfacial separations up to 1 nm. An equilibrium situation can therefore be reached within a very short time; for a uniform and continuous distribution, N_s , the charge in the surface states is given by

$$\sigma_{ss} = - N_s (v_s kT + E_o) \quad (3.43)$$

where v_s is the surface band bending, as defined in Sect. 3.2.4. If there are no other contributions to the charge at the insulator surface, the charge induced on the metal is

$$\sigma_m = - \frac{N_s}{1 + e N_s z_o / \epsilon_o \epsilon_g} \Delta\phi \quad (3.44)$$

i. e. the charge transferred is directly proportional to the work function difference. (Eq. (3.44) is identical to the expression of Cowley and Sze (1965), Eq. (3.36) above). From the above discussion, the surface states density is likely to be small ($N_s \ll 10^{13} \text{ cm}^{-2} \text{ ev}^{-1}$): for this case, Eq. (3.44) becomes

$$\sigma_m \simeq - N_s \Delta\phi \quad (3.45)$$

A similar expression has been derived by Krupp (1971) for the charge at metal polymer interfaces.

Localised states below the interface can be filled or emptied by two types of processes (see Fig. 3-11): an electron can be emitted over the potential barrier at the interface by thermal excitation

(Schottky emission; process (2) in Fig. 3-11) or by tunneling out of localised states near the insulator Fermi level (process (3)).

At room temperature the Schottky current (given by Eq. (3.11)) becomes very small for barrier heights (V_b) greater than about 1 eV; in order to transfer a charge of 10^{10} e cm⁻², the Schottky process takes about 1 minute at $V_b = 1.0$ eV, 10^7 min. for $V_b = 1.5$ eV. Since an electron is most likely to be emitted from a localised state near the Fermi level the potential barrier is of the order of $(\Phi_i - \chi)$. If the Fermi level lies near the centre of the insulator band gap ($E_g > 2$ eV) the potential barrier will be greater than 1 eV. Previous authors have therefore concluded (Bauser et al. 1970, Krupp 1971), that only surface states can be filled by the charge transfer process at metal-insulator interfaces.

There is, however, a second process by which localised states below the insulator surface can be filled. If the density of localised states at the Fermi level is sufficiently high (e. g. in amorphous insulators) a charge transport can take place by hopping between these states (Mott 1969). Thus, an electron could be injected from the metal Fermi level and hop into localised states below the interface (Hill 1972). This process, called thermally activated hopping, is known to be the main conduction mechanism in amorphous semiconductors at low temperatures (see Mott and Davis 1971). The probability of hopping between two localised states at a separation R is given by

$$\exp - \frac{2\alpha R}{kT} - \frac{\Delta E}{kT} \quad (3.46)$$

where ΔE is the energy difference between the two states (this energy is gained by collision with a phonon) and α is dependent on the degree of localisation of the state (wave function decays as $\exp -\alpha r$).

Thus, the hopping probability depends on the density (in space and energy) of localised states. This process can operate for hopping distances up to about 10 nm and activation energies up to 0.5 eV (Hill 1972). The minimum density of localised states must therefore be about $2 \cdot 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$, near the insulator Fermi level; densities of this magnitude have been observed for amorphous semiconductors (Cohen 1969), and may also exist in amorphous insulators.

For a density of localised states $N(E)$, the activation energy, E , for hopping has been given (Mott 1969) as

$$\Delta E = \frac{3}{4\pi} \left[R^3 N(E) \right]^{-1} \quad (3.47)$$

For hopping across the metal-insulator interface, the geometrical factor should probably be reduced to $(3/2\pi)$. The hopping current across the interface is roughly

$$e [N(E)]^{2/3} \nu_p \exp \left[-2\alpha R - \frac{\Delta E}{kT} \right] \quad (3.48)$$

where ν_p is of the order of 10^{13} sec^{-1} . For $R = 10 \text{ nm}$, $E = 0.5 \text{ eV}$ and $N(E) = 2 \cdot 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ the hopping current is roughly $10^{-11} \text{ A cm}^{-2}$; the time required to transfer $10^{10} \text{ e cm}^{-2}$ is therefore about 100 secs. For densities of localised states greater than $10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ one can thus expect the hopping process to provide a reasonably quick transfer across the metal-insulator interface.

As a first approximation, consider an insulator with a uniform and continuous distribution of traps, $N_t \text{ cm}^{-3} \text{ eV}^{-1}$; the solution of the Poisson equation, using the notation of Sect. 3.2.4. gives

$$\sigma_{sc} = - (\epsilon_i \epsilon_o e N_t) v_s \frac{kT}{e} \quad (3.49)$$

In the presence of surface states (Eq. (3.43)) the charge induced on the metal is

$$\sigma_m = - \frac{\frac{Q_t}{kT} + \frac{N_s}{Q_z}}{1 + \frac{Q_t}{Q_z} + \frac{kT}{Q_z} \frac{N_s}{Q_z}} \quad (3.50)$$

$$\text{where } Q_t = (\epsilon_i \epsilon_o e N_t)^{\frac{1}{2}} \frac{kT}{e} \quad (3.51)$$

$$Q_z = \epsilon_g \epsilon_o \frac{kT}{e} z_o \quad (3.52)$$

Eq. (3.50) has been used in Fig. 3-12 to plot the surface charge transferred across the interface (σ_m) as a function of the surface states density for various values of the trap density N_t (at $\Delta\phi = 10kT$). There are two regions of practical interest :

- (1) for $N_s \lesssim 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, $N_t = 0$; this region is applicable to insulating crystals, where only surface states are likely to be filled. The charge transfer for such small surface states densities is described by Eq. (3.45) and the maximum surface charge will be about $10^{11} \text{ e cm}^{-2}$ per eV of work function difference.
- (2) for $N_t > 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$, $N_s < 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$; this region may apply to amorphous insulators with high trap densities, as discussed above. Trap levels in a layer of 100 nm or less will be filled within a short time, so that an equilibrium situation can be reached. Assuming the surface states densities are less than $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, as for insulating crystals. Fig. 3-12 shows that the charge transfer is hardly affected by surface states. The charge densities transferred for these parameters are typically $10^{12} \text{ e cm}^{-2}$ per eV of work function difference.

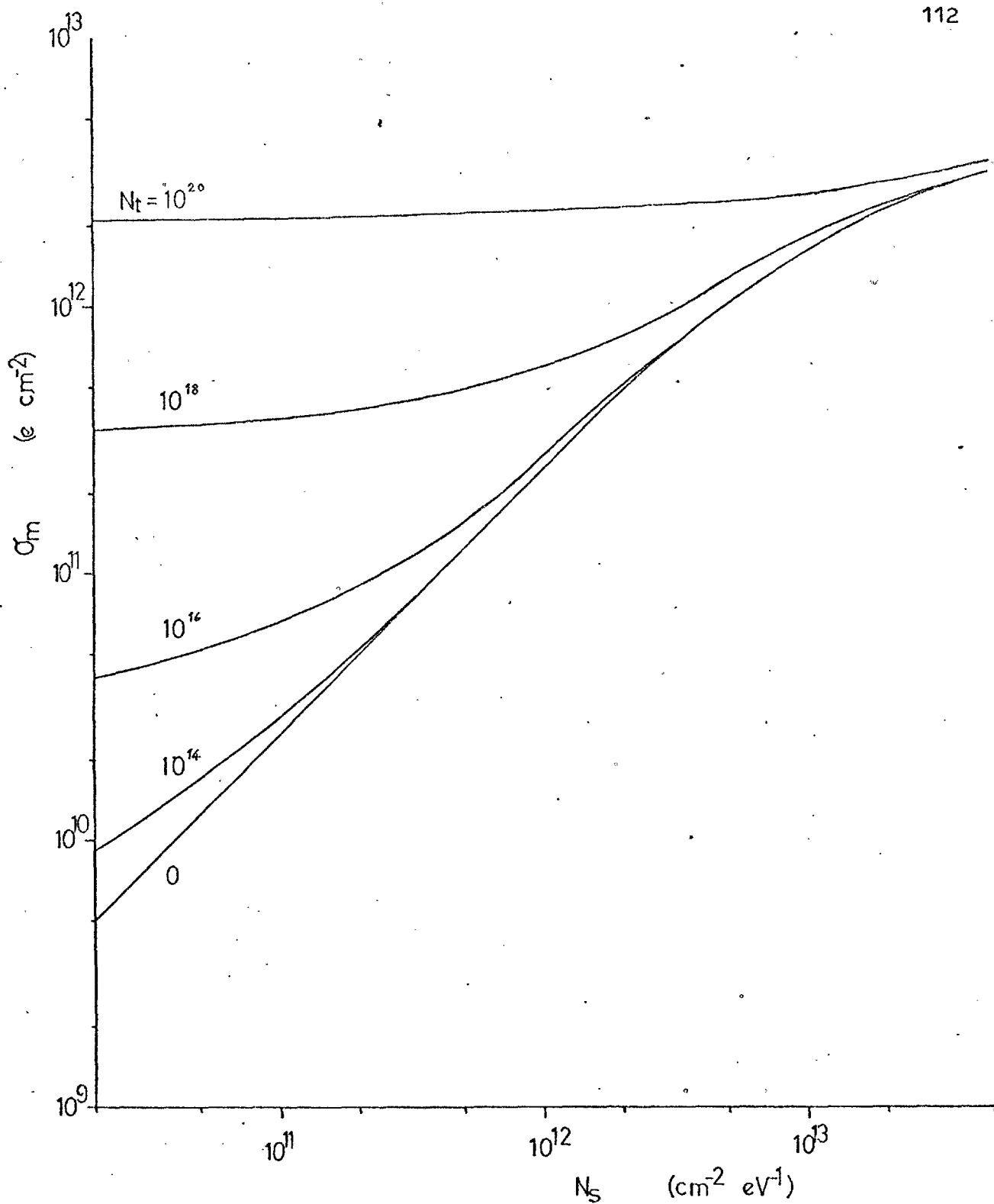


Fig. 3-12 Charge transfer across metal-insulator interface
plot of charge density σ_m against surface states
density N_s for various values of trap density N_t

3.2.5.2. Ionic effects

The presence of ions at the interface between two solids can lead to contact charging. A simple model for the process of redistribution of ions at the interface has been described by Henry (1957). It is supposed that the ions of a given type in each solid are preferentially adsorbed at the interface at the surface. If the ground state energy of the ions differs at the two surfaces in contact (see Fig. 3-13), then a transfer of ions between two energy states will occur, just as in the case of electrons. Given sufficient mobility, an equilibrium situation is reached, where the occupancy of the two energy states (n_1 and n_2) is described by the Boltzmann distribution,

$$\frac{n_1}{n_2} = \exp - \frac{\Delta W}{kT} \quad (3.53)$$

where ΔW is the energy difference between the two ground states at equilibrium.

The surface charge remaining after separation of the interface, can be determined by assuming that the equilibrium distribution of ions is maintained up to a separation z_c . At this separation, the potential drop across the electrical double layer is (assuming the ionic states are distance z_c apart)

$$V_c = \sigma \frac{z_c}{\epsilon_0} \quad (3.54)$$

If the energy difference before transfer is ΔW_0 , then

$$\Delta W = \Delta W_0 - qV_c \quad (3.55)$$

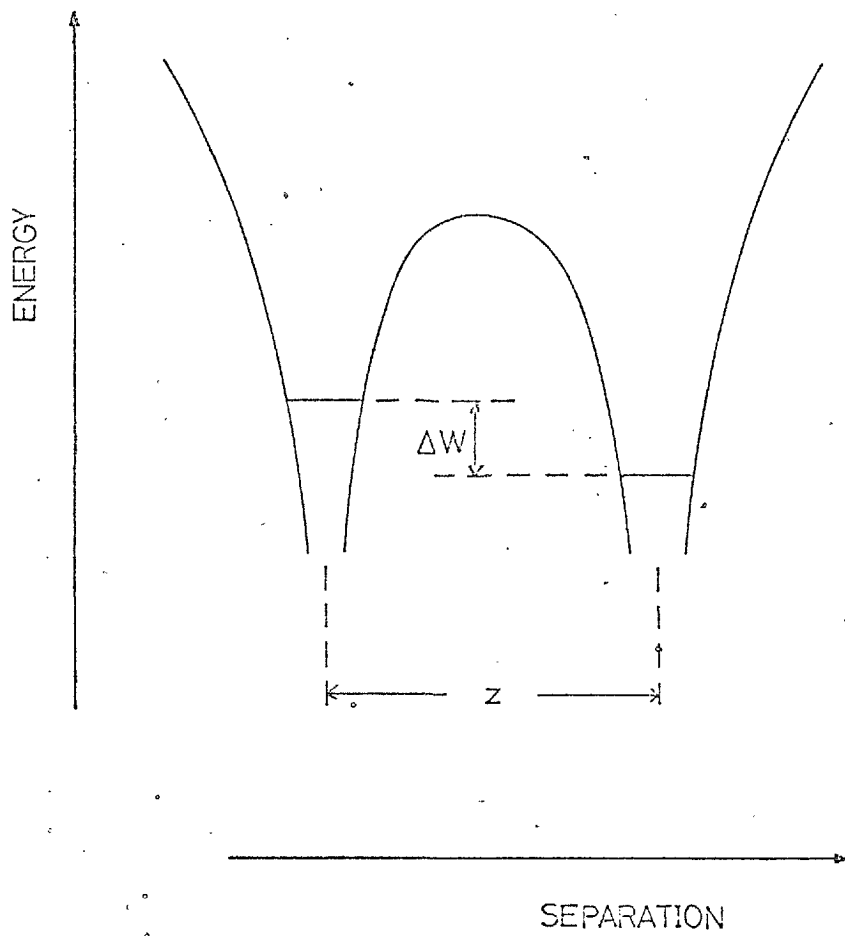


Fig. 3-13 Potential Energy Variation for Ions at
an Interface
(ground state energy difference ΔW)

where q is the charge on the ion; hence, the surface charge is given by

$$\sigma = \frac{\epsilon_i \epsilon_o}{q z_c} \Delta W_o + kT \ln \frac{n_1}{n_2} \quad (3.56)$$

If $\Delta W_o \gg kT$, the second term in Eq(3.56) is negligible; for $\Delta W_o = 1$ eV, the surface charge may be greater than 10^{13} e cm⁻².

A similar model has been proposed by Deryagin and Smilga (1967) to describe the charge transfer (electrons or protons) between organic materials. The energy states at the two surfaces in contact are regarded as a donor-acceptor pair; however, as pointed out by Krupp (1967), this description is analogous to the case of electron transfer between materials of different work functions in the presence of high densities of surface states.

The above model indicates that the presence of mobile ions at the interface can have a strong effect on the surface charge. The effect of surface contamination on contact charging is therefore largely due to mobile charges (e. g. sodium and hydrogen ions); the simplest way of controlling the effect of these ions is to remove them as far as possible by experimentation in vacuum.

3.2.5.3. Experiments of contact charging of insulators

A large volume of experimental data on the static electrification of insulators has been published over the last century, although few scientists have investigated this subject for more than a few years. Much of the work carried out in this field up to

1965 has been reviewed by Harper (1967a) (see also Montgomery 1959, Loeb 1958). At that time, very little work had been carried out in controlled environments and industrial interest was concerned mainly with frictional charging. As a result, these experiments were quite irreproducible and quantitative results gave little indication of the mechanisms of contact charging.

There are two main factors which complicate experiments carried out at atmospheric pressure in air: surface contamination and gas discharge. Whatever method is used for cleaning the surface, there always remains an adsorbed layer of gases, especially water vapour. Mobile ions are therefore likely to abound on the surface and, as discussed in Sect. 3.2.5.2, even a small coverage (e. g. 1%) of these ions could dominate the charge transfer process. The effect of humidity on contact charging has been noted frequently (e. g. Herish and Montgomery 1955) and by deliberate contamination of the surface the importance of ionic effects has been confirmed (Shaw and Jex 1928).

The effect of gas discharge becomes apparent at high magnitudes of surface charge. At atmospheric pressure, the breakdown strength of air is about 30 kV cm^{-1} , so that the surface charge is usually limited to densities below a few $10^{10} \text{ e cm}^{-2}$ (e. g. Macky 1928). Larger charges ($> 10^{12} \text{ e cm}^{-2}$) have been observed (Medley 1953) on polymer foils by contact with mercury; since Paschen breakdown cannot occur below about 300 V, (see Sect. 3.2.2.2) a higher charge is retained on thinner foils.

In spite of these difficulties the sign of the contact charge is usually consistent for a given pair of materials, even for frictional charging. Consequently, various "tribo-electric series" have been published (e. g. Henry 1953, Rose and Ward 1957), in which solids are ordered according to the sign of the contact charge. However, it has not been possible to correlate this series with any intrinsic property of the solids concerned.

During the last five years a number of experiments of metal-insulator contact have been carried out, in which the surface charge and the metal work function were measured. In all these experiments, performed both in vacuum (Davies 1967a, 1969, 1970, Inculet and Wituschek 1967, Challande 1970) and in air (Arridge 1967, Cunningham and Hood 1970), it was found possible to correlate the surface charge with the metal work function. This correlation suggests, as shown in Sect. 3.2.5.1, that the charge transfer is due to electrons.

Davies (1967a) measured the charge densities on glass and polymers after contact with various metal electrodes in vacuum ($10 \mu\text{torr}$ of pressure); he found that the charge saturated after a few minutes of contact ($\sim 10^{10} \text{ e cm}^{-2}$) and varied linearly with the metal work function as measured in situ. In a later series of experiments, (Davies 1969) polymer foils were charged by repeated rolling contact with metals and much higher charge densities ($\geq 10^{12} \text{ e cm}^{-2}$) were obtained. This difference may be due to a much smaller area of direct contact achieved in the earlier method.

Davies (1967a) proposed a simple model of electron transfer to explain his results. As in the models discussed above, the transfer process was assumed to reach an equilibrium state, in which the Fermi levels of the two materials are aligned, without stating how the charge was accommodated in the insulator, Davies assumed that a uniform space charge layer is formed in a surface layer of thickness λ ; solution of the Poisson equation gives the following expression for the surface charge:

$$\sigma = \frac{2 \epsilon_i \epsilon_0}{e \lambda} \Delta \phi \quad (3.57)$$

From Eq. (3.57) the space charge depth λ for various polymers, lies in the range of 10 to 50 nm (Davies 1970); the effective polymer work functions are between 4 and 5 eV.

In this model it is assumed that the charge transferred to the insulator is accommodated in a space (of a depth λ) below the surface. The discussion in the previous section (Sect. 3.2.5.1) suggests that localised states below the surface can be filled by a hopping process if their density is greater than about $10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$; indeed, such high values might be expected for polymers which are largely amorphous.

This explanation is contrary to that of Krupp (1971) who argued that only surface states could be filled by the contact of metals with polymers. However, if interpreted by surface states, Davies' results suggest (from Eq. (3.45)) a density of $10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$. It is doubtful whether such a high density can arise at a polymer surface, except as a result of contamination. For comparison, the charge density at the polymer - germanium interface has been shown to be only about $10^{10} \text{ e cm}^{-2}$ (Krotova et al. 1967).

In the contact charging of ionic crystals, the surface charge is often found to increase on repeating the contact (e. g. see Harper 1967a). Experiments performed in vacuo (Weingärtner et al. 1968) have shown that the contact charge on potassium chloride crystals saturates after repetition of contact at regular intervals; the saturation value was found to depend on the bulk conductivity of the crystal. Weingärtner et al. explained these results in terms of electron transfer, although little dependence on the contact metal was observed. On the other hand, a correlation of the surface charge with the metal work function has been reported (Challande 1970) for the frictional charging of sapphire; in this work the charging of alkali halide crystals was also found to depend on the contact pressure.

3.3. Summary

In this chapter a detailed discussion has been given of the mechanisms by which electrical charges are generated at the surfaces of solids. The contact charging was explained in terms of the electronic properties of solids; theoretical descriptions of the charge transfer process assume that the electron populations in the two solids reach an equilibrium distribution at the interface, such that the Fermi levels are equalised. For the contact between metals the charge transfer is determined by the work function difference, for semiconductors it depends largely on the surface states density. These predictions are confirmed by experimental evidence.

The electronic description of the charge transfer process was applied to insulators (Sect. 3.2.5). For a metal-insulator contact, the most important question is, whether a given mechanism of charge transfer is fast enough to contribute significantly to charging process within a reasonable length of time. It was concluded that electrons may be sufficiently mobile to be transferred across the interface between a metal and an insulator containing a high density of localised states, e. g. an amorphous insulator. This conclusion appears to be supported by experimental evidence.

However, in the case of crystalline insulators, no electronic process can account for the magnitudes of charge transfer observed in practice. The presence of ions at the interface may have a significant effect; since these ions are usually a result of contamination, it is difficult to put forward a theoretical description.

CHAPTER IV

THE MEASUREMENT OF ADHESION

The aim of this work is to obtain information about the mechanisms by which a thin film adheres to its substrate, in particular to assess the significance of electrostatic forces. An essential part of this work is therefore the measurement of thin film adhesion. The definition of adhesion - the work required to separate unit area of interface reversibly - immediately suggests a method of measurement by separating a thin film from its substrate. Indeed, numerous variations of this method are used (Campbell 1970) and some of these are described below (Sect. 4.1). Since, in practice, two materials cannot be separated at zero rate, the separation process is not reversible; unless care is taken to minimise the energy dissipated in irreversible processes, it is not possible to obtain a quantitative measure of adhesion.

As described in Sect. 2.2, the electrostatic component of adhesion can be deduced from measurements of the charge at the film-substrate interface. In this chapter, we review the available evidence for electrostatic adhesion, as deduced from measurements of the interfacial charge and the adhesion of the film.

Adhesion is fundamentally a property of the interface and is therefore strongly influenced by the structure of the interface. Contamination of the substrate surface and surface roughness affect the adhesive performance of a thin film, complicating the interpretation of adhesion measurements. Furthermore, it is not

always possible to determine whether a film is separated from its substrate by adhesive or cohesive failure.

An indirect estimate of thin film adhesion can be made from nucleation experiments. The growth processes of thin films have been described by various theories based on the adsorption properties of clusters of atoms. A comparison can be made between the adsorption energies deduced from nucleation experiments and those calculated in Sect. 2.1.2.

4.1. Methods involving Separation of the Interface

As a result of technological interest in adhesives and surface coatings, a large number of adhesion tests have been developed. A measure of the adhesive performance of a material is obtained in these tests by applying a mechanical force to the adherands until a break of the bond occurs. A quantitative analysis of these tests is usually complicated since the materials are subjected to a mixture of tensile and shear stresses; the measured bond strength is determined in part by the adhesion across the interface - if the fracture occurs at the interface - and in part by the mechanism of fracture.

A direct measure of the adhesion of a material can be obtained only if the following criteria are satisfied :

- 1) failure occurs at the interface;
- 2) the forces applied to unit area of interface can be calculated;
- 3) the applied forces cause only elastic deformation of system right up to the moment of failure.

4.1.1. Mechanical Methods

Pull Test

Various types of pull tests have been used in the past to determine the strength of adhesive joints (Eley 1961). In the measurement of thin film adhesion by this method (Belser and Hicklin 1956, Butler et al. 1971, Lin 1971, Sundahl 1972) an external force is applied at some angle to the plane of the interface: as a result the materials are deformed until fracture is initiated at the weakest area in one of the adherands or at the interface. Once a crack has been formed, the materials will separate effectively by a peeling process.

The breaking force determined by this method will depend on a large number of factors other than the properties of the adherands. The adhesion of the film is weakened by the attachment of a device by which a force can be applied (e. g. a wire soldered to the film); a further weakening may result from the roughness of the substrate surface and from flaws (imperfections) at the interface, with associated stress concentrations. It is therefore not surprising that no agreement with theoretical predictions based on van der Waals' forces can be found – generally the measured values are an order of magnitude too small (Good 1967).

Evidence of electrostatic effects was obtained by Skinner et al. (1953) on pulling apart a metal-polymer-metal sandwich; gas discharge was observed at the instant of fracture (Skinner et al. 1956), indicating a surface charge greater than $10^{10} \text{ e cm}^{-2}$.

Skinner et al.(1953) used the Mott and Gurney model (see Sect. 3.2.5.1) to explain the origin of the surface charge; this model, which, unfortunately is not applicable to the metal-polymer contact, led to the conclusion that the electrostatic adhesion was insignificant.

Scratch test

The scratch test has been used extensively in the past (Heavens 1950, Benjamin and Weaver 1960) to obtain a measure of thin film adhesion. The test is carried out by drawing a stylus with a rounded tip across the film; a vertical load is applied to the stylus, up to a critical value at which the stylus scratches through to the interface. Benjamin and Weaver (1960) took the critical load as a measure of the adhesion of the film. Microscopic observation of the scratch track (Butler et al. 1970, Chapman 1969) showed that the failure does not always occur at the interface and that, consequently, this test cannot give more than a qualitative comparison of thin film adhesion.

Benjamin and Weaver (1960) analysed this method by assuming that the stylus causes plastic deformation of the substrate. For thin metal films on alkali halide crystals they found (Benjamin and Weaver 1963) that the critical shear stress acting on the film is roughly proportional to the calculated van der Waals' forces of adhesion. The scratch adhesion of thin metal films on glass substrates showed an aging effect (Benjamin and Weaver 1960a,1961) which was attributed to formation of an oxide layer at the interface. These results will be compared below with our measurements.

Stripping Method

This method is essentially a modification of the peel test which is commonly used to measure the adhesion of polymer films (Kaelble 1967). Whereas in the peel test the film is normally backed by an adhesive tape, in the stripping method as devised by Chapman (1969), the film is peeled from its substrate without a backing. This procedure avoids stressing the film even before application of a force; unlike the methods described above, the force which causes the film to peel off, is applied over a well-defined area of the film. A detailed analysis of this method, which has been used in our experiments, is given in Sect. 5.1.

A direct measure of the adhesion may be obtained if the stripping process is at least approximately reversible, e. g. at very slow rates of stripping. Chapman (1969, 1971) measured the work done in stripping (the stripping energy) gold films from soda glass substrates; at very slow speeds of stripping (down to $10 \text{ } \mu\text{m sec}^{-1}$) the stripping energy was found to be about 500 mJm^{-2} . Chapman concluded that the adhesion could be accounted for either by van der Waals' or electrostatic forces.

The stripping method has been used by Deryagin and co-workers (see Deryagin and Smiliga 1967) in an extensive study of polymer adhesion. The adhesion energy of polymer films is usually found to exceed the values typical for van der Waals adhesion by a factor of 10^3 to 10^5 (Gardon 1967); this difference is usually attributed to the irreversibility of the stripping process. However, Deryagin et al. (1957, 1960) analysed their results in terms of the electrostatic

theory of adhesion (see Sect. 2.2). When a polymer film is peeled from its substrates, the potential difference across the gap is assumed to rise until a discharge occurs. From the known characteristics of Paschen discharges in air (see Sect. 3.2.2.2), the breakdown potential (V_c) and the separation (d) of the surfaces at the point of breakdown were deduced (see Fig. 3-6). The work done against electrostatic forces (W_{el}) was calculated by assuming that the electric field in the gap was constant up to the breakdown separation d (about $2 \mu\text{m}$); thus,

$$W_{el} = \frac{1}{2} \epsilon_g \epsilon_o \frac{V_c^2}{d} \quad (4.1)$$

where ($\epsilon_g \epsilon_o$) is the permittivity of the medium in the gap. The resulting values of W_{el} ($10^2 - 10^3 \text{ J m}^{-2}$) were found to be in good agreement with the experimental stripping energies. The emission of electrons of high energy ($> 10 \text{ keV}$) was observed during the stripping process in vacuo (see Deryagin 1955), and the electron energy was correlated with the stripping energy (Krotova et al. 1967).

All these results indicate the existence of a very high charge density ($\sim 5 \cdot 10^{13} \text{ e cm}^{-2}$) at the interface. However, the corresponding electric field in the gap should be about 10^{10} V m^{-1} - a value which lies well within the region for field emission, rather than Paschen discharge. Unfortunately, the surface charge does not appear to have been measured directly by these workers, except for polymer-germanium interfaces (Krotova et al. 1967), where charge densities of only about $10^{10} \text{ e cm}^{-2}$ were found.

4.1.2. Acceleration Methods

A simple way of applying a force directly to the interface between two solids is achieved by subjecting the adherands to an acceleration or deceleration. For an acceleration, a , in a direction normal to the interface, the force (P) acting on a solid of uniform thickness t and density ρ is equal to $(a \rho t)$ per unit area of interface. If the adhesive force between the solids is P_o , the minimum acceleration required to separate the interface is given by

$$a_{\min} = P_o / \rho t \quad (4.2)$$

For van der Waals adhesion, P_o is about 10^7 N m^{-2} , so that, assuming $\rho = 10^3 \text{ kg m}^{-3}$, the minimum acceleration is

$$a_{\min} = 10^6 / t \quad (4.3)$$

In practice, accelerations of about 10^7 m sec^{-2} can be achieved, so that the adherand must have a thickness of more than 0.1 mm in order to be detached by this method. These methods are therefore not suitable for measuring the adhesion of continuous thin films. However, for discontinuous films and for small particles, the ratio of mass to adhesive area can be much greater than in the case considered above, so that sufficiently large forces may be achieved.

The following acceleration methods have been used in the past:

Vibration Method

The adherands are subjected to an ultrasonic vibration, thus periodically increasing and decreasing the adhesive force; the vibration frequency is increased until the adherands separate. This method has been used for surface coatings (Moses and Witt 1949)

and for powders (Deryagin and Zimon 1961). Fauré et al. (1972) have recently measured the adhesion of dis-continuous metal films up to a mean thickness of 25 nm; these workers observed a re-ordering of the islands of the film before detachment; an interpretation of their results is possible only if it is assumed that the island are not set into resonance by the applied vibration.

Centrifugal Method

A centrifugal force can be applied to an adherand deposited onto a cylindrical substrate which is rotated about its axis. By experimentation in vacuo, accelerations up to 10^6 g have been achieved (Beams et al. 1955, Böhme 1964), the limitation being the strength of the rotor. This method does not appear to have been used for thin film adhesion, although direct quantitative analysis is possible.

Extensive work on the adhesion of small particles has been carried out by Krupp (1967). The electrostatic component of adhesion has been deduced from measurements of the adhesion of gold particles on cadmium sulphide crystals (Schnabel 1969, 1970). The contact p.d. ($\Delta \Phi$) between the adherands was varied by illumination of the substrate (the work function of CdS can be changed by exposing the material to light); the adhesion force determined by the centrifugal method, was found to depend parabolically on the contact p.d., as expected for electrostatic adhesion forces (see Sect. 2.2) if the surface charge is proportional to the contact p.d.. The adhesion force was found to reach a minimum value (at $\Delta \Phi = 0$) which represents the van der Waals component of adhesion. The electrostatic component

could therefore be deduced; the two components had the same magnitude at a charge density of about $10^{12} \text{ e cm}^{-2}$.

Impact Method

The adhesion of surface coatings (May et al. 1957) and of powders (Deryagin 1968) has been measured by firing the substrate like a bullet into a target; Deryagin (1968) confirmed the importance of the electrostatic adhesion of powder particles by combining this method with the measurement of the charges on the powder particles before and after contact with the substrate.

4.2. Nucleation Methods

The adsorption energy of a single atom on the surfaces of ionic crystals has been calculated above (Sect. 2.1.2.1). This quantity can be derived from theoretical interpretations of thin film nucleation experiments. In nucleation experiments the growth processes of islands (clusters) of deposited material are studied. Observable quantities, such as the density of islands and the rate of nucleation of islands can be related to the adsorption energy of an adatom by various theoretical approaches.

The theories of nucleation have been developed in great detail but cannot, in general, give an explanation of the experimental results. For our purposes, it is sufficient to outline the basis of these theories from which the adsorption energies of metal atoms on insulating substrates (especially on rock-salt, mica and glass) have been derived (see Campbell 1970). The available values derived from these theories are summarised in Table 4-1.

(1) Critical Condensation

The formation of a stable nucleus of atoms on a surface depends on the adsorption energy (E_a) of the adatom, and the temperature of the surface. Frenkel (1924) introduced the concept of a critical rate of arrival of atoms on a surface for the formation of a stable nucleus. Assuming that two atoms can form a stable nucleus (with binding energy E_2 between them), the critical arrival rate was shown to be proportional to

$$\exp - \frac{E_a + E_2}{kT} \quad (4.4)$$

Thus, by measuring the conditions at which a film is just formed (e. g. by observing the change in resistance), the value of $E_a + E_2$ has been derived (Rhodin 1949, Benjamin and Weaver 1959). However, apart from experimental difficulties, the theoretical basis of this method is unsatisfactory (Lewis 1967) since the size of the smallest stable nucleus may be greater than two atoms.

(2) Nucleation Rate

The critical size i^* of a cluster of atoms is defined in such a way that a nucleus containing more than i^* atoms is stable. Rhodin and Walton (1964) developed a model in which the rate of formation of a nucleus of size i^* (i. e. the nucleation rate, j_{i^*}) is related to the adsorption, diffusion and binding energies of the nucleus.

$$j_{i^*} \propto \exp \frac{E_{bi^*} + (i^* + 1) E_a - E_d}{k T} \quad (4.5)$$

A plot of $\ln j_{i^*}$ against the reciprocal temperature for various values of i^* , shows that at certain temperatures the nucleation rate changes discontinuously as a result of a change in the value of i^* . One such

Table 4-1Summary of Nucleation Parameters for MetalAtoms on Ionic Solids

(Adsorption energy E_a , diffusion energy E_d , binding energy E_2 ,
in units of electron volts)

		<u>Au</u>	<u>Ag</u>	<u>Cu</u>	<u>Al</u>
<u>NaCl</u> (100)	E_a	0.6 ³ 0.36*	0.4 ⁵ 0.27*	0.15*	0.6 ⁴
	E_d	0.2 ³ 0.11*	0.2 ⁵ 0.09*	0.08*	
	$E_a + E_2$		0.14 ¹ 1.2 ⁵		1.35 ² 0.24 ¹
<u>Mica</u> (001)	E_a	0.80*	0.75*	0.55*	
	E_d	0.3*	0.3*	0.16*	
	$E_a + E_2$				1.22 ¹ 1.83 ²
<u>Glass</u>	E_a	0.35*	0.28*	0.14 ⁵ 0.12*	
	$E_a + E_2$		0.15 ¹		0.19 ¹ 0.65 ²

References: 1 Benjamin and Weaver (1959), 2 Rhodin (1949),
3 Lewis and Campbell (1967), 4 Wexler (1958),
5 Walton et al. (1963)

* calculated in Sect. 2.1.2.1

transition was observed by Walton et al. (1963) in the nucleation of silver on rock-salt; the energy parameters in Eq. (4.5) could therefore be deduced (see Table 4-1).

(3) Saturation Density

An atom which is incident on the surface of a substrate, has a finite probability of being re-evaporated; however, as more atoms are deposited on the surface, an incident atom is more likely to be captured by adsorbed atoms or clusters. Thus, the density of clusters on the surface quickly reaches a constant, saturation value. This idea was developed by Lewis and Campbell (1967) who deduced that the saturation density was proportional to

$$\exp - \frac{E_a - E_d}{k T} \quad (4.6)$$

However, a high rate of incidence or low substrate temperatures no atoms are re-evaporated - the saturation density is reached immediately and will depend on

$$\exp \frac{E_d}{kT}$$

In this way the values of the adsorption and diffusion energies were derived (see Table 4-1).

In Table 4-1 the adsorption energies deduced from the nucleation methods are compared (where values are available) with the energies calculated in Sect. 2.1.2.1. A direct comparison is possible only for Au and Ag on rock-salt; in these cases the calculated values of E_a and E_d are about half of the experimental values. In view of the over-simplified approach of the nucleation theories discussed above, the discrepancy is not surprising.

CHAPTER V

EXPERIMENTAL DETAILS

The above discussions of thin film adhesion and of the charge transfer processes at interfaces form the background to the experimental part of this work. The measurement of adhesion must be performed in such a way that the experimental results can be compared with the theories of adhesion (Chapter 2). It appears from the considerations of Chapter 4, that only the stripping method has any hope of yielding results which can be interpreted quantitatively. An analysis of this method is given in this chapter.

Secondly, we want to assess the importance of the electrostatic component of adhesion. As discussed in Chapter 2, the electrostatic adhesion can be deduced from measurements of the charge at the interface. Unfortunately, for a metal-insulator contact, it is not normally possible to measure the interfacial charge while the solids are still in contact; however, we can measure the charge remaining on the insulator surface after separation of the interface. Various techniques of charge measurement are discussed below; the charge probe method used in our experiments is analysed in detail.

The measurement of adhesion and surface charge have been performed in vacuo for various film-substrate combinations. The procedure used for the preparation of the samples and the subsequent measurements are outlined below. A number of additional experiments are described in Chapter 6.

5.1. Film Stripping

In this investigation the stripping method (see Sect. 4.1.1) has been used to remove thin films from their substrates. Suppose a film of width a is removed by applying a force F to the film at an angle α to the substrate (see Fig. 5-1). We can define the work done in stripping unit area of film as the stripping energy S , given by

$$S = \frac{F}{a} (1 - \cos \alpha) \quad (5.1)$$

If a length x of the film is peeled off, the total work done in the process is

$$U_T = -a x (W - S) + A_{el} + A_p \quad (5.2)$$

where W is the adhesion energy of the film; the energy of elastic deformation is A_{el} and for inelastic deformation A_p . The elastic energy stored in the film will consist of a component (E_b) due to bending the film through an angle α and a tensile component E_t . For a given applied force, the radius of curvature of the film is constant and hence, the bending energy is constant. The work done in stretching the film (E_t) is given by:

$$E_t = \frac{F^2}{2 Y a t} x \quad (5.3)$$

If the stripping process is assumed to be reversible, then

$$\frac{d U_T}{dx} = 0 \quad (5.4)$$

Thus, it follows from Eq. (5.2) (with $A_p = 0$) that

$$\frac{d U_T}{dx} = -a (W - S) + \frac{F^2}{2 Y a t} \quad (5.5)$$

for a film of thickness t and Young's modulus Y .

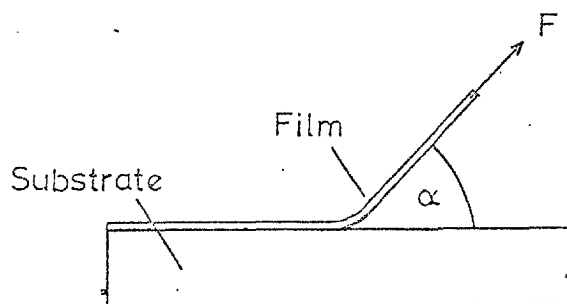


Fig. 5-1 The Film Stripping Method

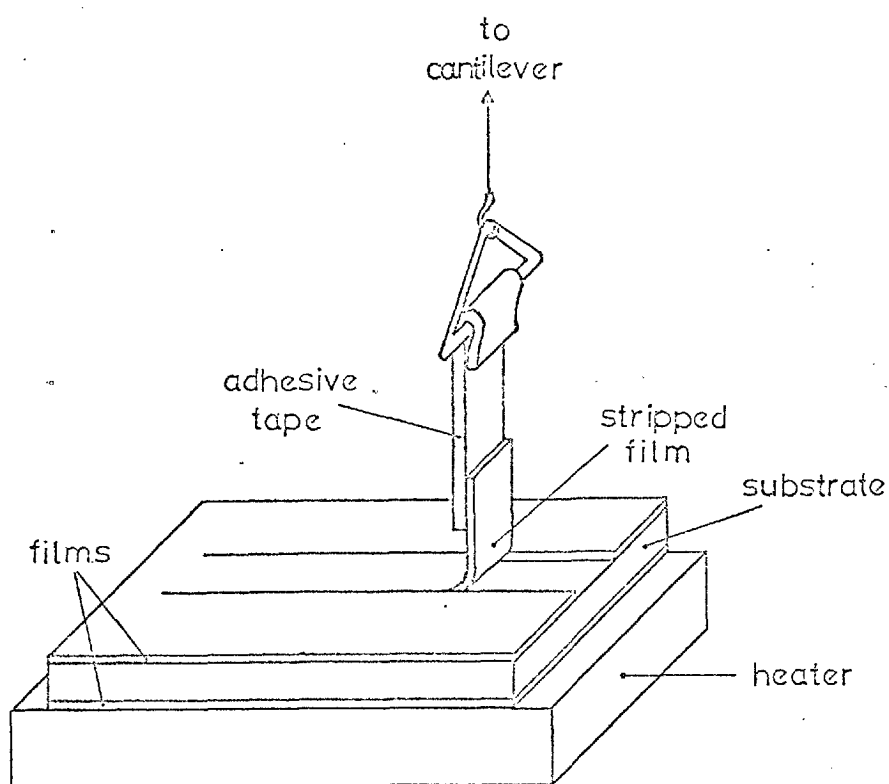


Fig. 5-2 Film Stripping Apparatus

With the assumption of reversibility, the stripping energy is therefore

$$S = W - \frac{F^2}{2 Y a^2 t} \quad (5.6)$$

The work done in stretching a film of $0.5 \mu\text{m}$ thickness (10mm width) assuming a typical value of $F = 10^{-2} \text{ N}$, is only about 1 mJ m^{-2} . Since the adhesion energy is expected to be several hundred mJ m^{-2} (see Sect. 2.1.3), the elastic energy is negligible. This conclusion is a contrast with the situation in cleavage experiments, where a large part of the total energy is stored in the crystal (e. g. cleavage of mica sheets, Bowden and Tabor 1964). The stripping energy is therefore practically equal to the adhesion energy, if the film is stripped reversibly.

The above discussion shows the importance of estimating the extent to which the stripping process is reversible. Irreversible processes are likely to occur at the interface due to the inelastic deformations of the film and substrate, which eventually lead to the rupture of the adhesive bonds between the two materials.

Apparatus

A diagram of the film stripping apparatus is shown in Fig. 5-2. The substrate is placed on a carriage with facilities for heating. The width of the film to be removed is defined by two parallel scribed lines. A short strip of adhesive tape is attached at one end of the film; the tape is connected to a load cell by a thin wire. The load cell is mounted on a vertical shaft which can be displaced at a constant speed by a motor mounted outside the vacuum chamber. By the

vertical displacement of the load cell the portion of the film which is backed by the tape, is first pulled upwards and thus peeled from its substrate. If the film is sufficiently strong, the unsupported part is also stripped off, and it is over this area that the adhesion is measured.

The minimum film thickness for stripping an unsupported film obviously depends on the adhesion to the substrate. If $P_{\max}$ is the breaking strength of a metal film, then a film of thickness t and width a can be stripped off, if the stripping energy S fulfills the condition,

$$\begin{aligned} S &< P_{\max} t \\ \text{or} \quad t &> S/P_{\max} \end{aligned} \quad (5.7)$$

The breaking strength of single-crystal gold films is about $3 \cdot 10^7 \text{ N m}^{-2}$ (Neugebauer 1960). If the stripping energy is 1 J m^{-2} , the minimum film thickness (from Eq. (5.7)) is about 40 nm.

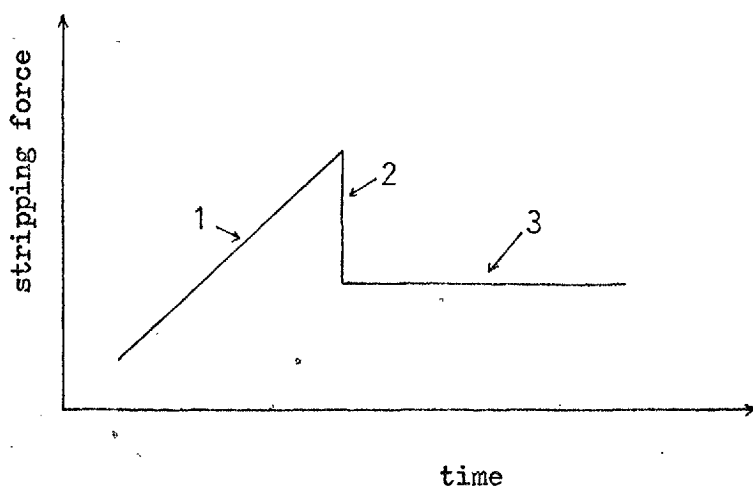
In practice, it was found very difficult to strip unsupported films thinner than about 100 nm. This is in part due to the dynamics of the stripping process, in part due to the stress concentrations arising from the adhesive tape. The stripping force for a tape-backed film was found to be several times that for the unsupported film; thus at the end of the tape-backed region a large part of the energy stored in the stripping system is suddenly released and the resulting impulse can rupture the film.

The force applied to the film is measured by a strain gauge bridge. Four silicon strain gauges are attached to a cantilever to

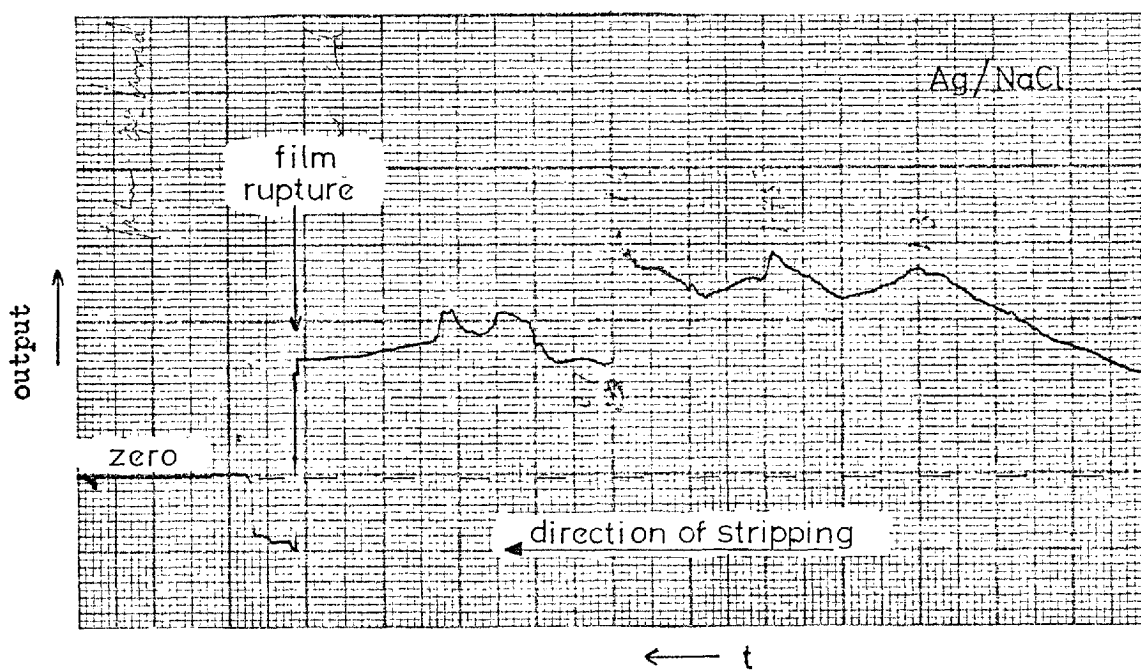
which connection is made with the adhesive tape (see Fig. 5-2).

The out-of-balance signal from the bridge is amplified and monitored by a X-t recorder. The sensitivity of the system is 17.5 mV N^{-1} (5% linearity up to 20g-wt). The accuracy of the force measurement is limited by thermal drift (about $10 \text{ } \mu\text{V}$ per hour) to $\pm 5 \cdot 10^{-4} \text{ N}$ (50 dynes).

The recorded signal is used to calculate the stripping energy, using the definition of Eq. (5.1). The analysis of the recorded signal is carried out as follows: three basic regions must be distinguished, as shown in Fig. 5-3a. In region (1) the stripping force increases before any peeling occurs; the energy is stored in the system, but this does not contribute to the stripping energy. In region (2), the stored energy is suddenly released as a short length of the film is peeled off. If the peeling proceeds at a constant rate, the stripping force will be constant as in region (3). In practice combinations of these three regions occur and care must be taken in the analysis. Fig. 5-3b is an actual recorded trace which we shall use to illustrate the possible methods of analysis. The first step is to decide on the zero level for the output. This was taken to be the output level after a film had been detached completely and was suspended from the cantilever (the weight of the film is negligible). It was sometimes necessary to correct for the zero drift by taking the average zero level over the length of the time of the stripping experiment. Thus, the stripping force F at any time during the stripping experiment can be calculated, however, both the width of stripped film (a) and the angle of stripping (α) may vary during a run. In order to



a) Regions of film stripping



b) Trace of recorded output (Ag film on NaCl)

Fig. 5-3 Analysis of Film Stripping Measurements

deduce the stripping energy (using Eq. (5.1)) at any point of the run, these three variables (F , a , α) must be known. With the geometry chosen the variation in α is small over stripping distances of several millimetres; a significant error may result if the width varies rapidly.

An alternative procedure is to calculate the stripping energy from the area under the recorded trace. The average stripping energy over an area A of removed film is

$$\bar{S} = \frac{1}{A} \int_0^l F(x) dx \quad (5.8)$$

where x is the distance moved by the applied force $F(x)$; however, the force is recorded as a function of time; if the speed of stripping is $\dot{x}$, then

$$\bar{S} = \frac{1}{A} \int_0^{t_l} F(t) \dot{x} dt \quad (5.9)$$

If the speed of stripping is assumed to be constant, the area under the recorder trace (proportional to

$$\int F(t) dt), \text{ is}$$

proportional to the average stripping energy.

5.2. Charge Measurement

A net electrical charge on the surface of a solid can be detected by the effect of the electric field due to this charge, on another body. Thus, a surface charge may be observed by the attraction of powder particles (resulting in the so-called Lichtenberg figures). For quantitative measurement a charge is often detected by the induction of charge or by the force of attraction on a conductor.

The principle of induction is frequently applied to the measurement of surface charges: when a conductor is brought up to a charged surface, a charge of opposite polarity is induced on the conductor. If the conductor is connected to an electrometer the induced charge is transferred to the measuring capacitor of the electrometer. Various types of instruments have been designed to carry out this process continuously (see reviews by Gubkin et al 1959, van Turnhout 1970).

5.2.1. Theory of the Charge Probe

The method of measuring the charge at the surface of insulators in this work is based on the induction principle. Consider the arrangement shown in Fig. 5-4 ; an insulator of constant thickness and relative permittivity ϵ_1 is placed on an earthed electrode; second electrode, the probe of area A , is placed at a distance h above the insulator surface. The probe is screened by an earthed conductor so that the system approximates to a parallel-plate capacitor. If the insulator has a surface charge of density σ and a volume charge density $\rho(x)$, where x is the distance below the insulator surface, then the electric field E_g due to these charges induces a charge Q_p on the probe such that

$$Q_p = \epsilon_g \epsilon_o A E_g \quad (5.10)$$

The resulting potential difference (V) across the whole capacitor is given by

$$V = E_g h + \int_0^d E(x) dx \quad (5.11)$$

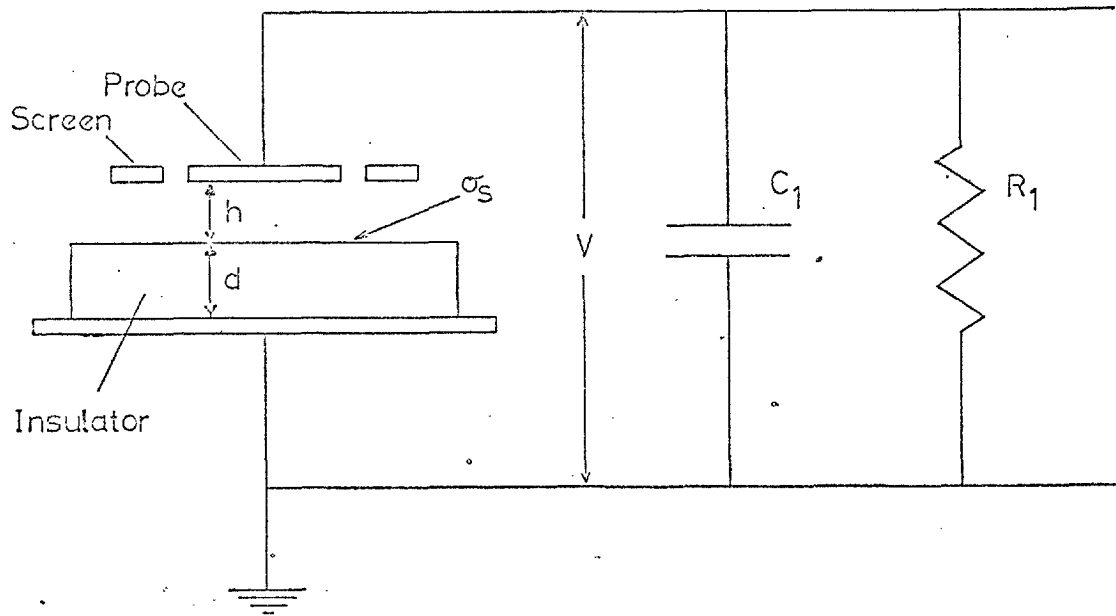


Fig. 5-4 Probe Input Parameters

where $E(x)$ is the electric field in the insulator, such that
(from Gauss' law)

$$\epsilon_i \epsilon_o E(x) = \epsilon_g \epsilon_o E_g + \int_0^x \rho(x) dx \quad (5.12)$$

Eqs. (5.11) and (5.12) assume that the electric fields are uniform, i. e. the probe height h is small compared with the probe diameter.

The electric field, E_g , in the gap between the probe and insulator is therefore,

$$E_g = \frac{V - \sigma_s d / \epsilon_i \epsilon_o}{h + \epsilon_g d / \epsilon_i} \quad (5.13)$$

where σ_s is the effective surface charge given by

$$\sigma_s = \sigma + \frac{1}{d} \int_0^d dx \int \rho(x) dx \quad (5.14)$$

The probe is connected to an electrometer of input capacitance C_1 , the charge induced on the probe is taken from this capacitor. If the electrometer has a negligible input conductance (i. e. $R_1 \rightarrow \infty$) then the charge Q_p on the probe is conserved, i. e.

$$Q_p + C_1 V = 0 \quad (5.15)$$

It follows from Eqs. (5.10) to (5.15)

$$V \left(1 + \frac{C_1}{C_{21}} \right) = \frac{\sigma_s d}{\epsilon_i \epsilon_o} \quad (5.16)$$

$$\text{where } C_{21} = \frac{\epsilon_g \epsilon_o A}{h + \epsilon_g d / \epsilon_i} \quad (5.17)$$

If $C_1 \gg C_{21}$, $\epsilon_g = 1$

$$V = \frac{\sigma_s A}{C_1 (1 + \epsilon_i h / d)} \quad (5.18)$$

Thus, the probe potential V is proportional to the surface charge

if the measuring capacitor (C_1) is large compared with the "sample"

capacitance C_{21} . A similar expression has been derived previously

(Davies 1967b, Wintle 1970). The charge σ_s on the insulator can therefore be deduced from the probe potential and the geometry of the apparatus. Alternatively, σ_s can be found by applying a bias potential V_b to the electrode in contact with the insulator, in such a way that there is no charge induced on the probe. This condition is achieved when the gap field is zero, i. e. from Eq. (5.13) when

$$V = V_B = \frac{\sigma_s d}{\epsilon_i \epsilon_o} \quad (5.19)$$

This null method is normally used in the Kelvin method (Kelvin 1898) for measuring the contact p. d. between conductors.

In practice, the probe potential is measured by an electrometer of finite input resistance (R_1): the charge induced on the probe will therefore leak away at a rate determined by the electrometer input time constant ($R_1 C_1$). The probe potential therefore has to be measured within a time which is short compared with ($C_1 R_1$). This is achieved, either by using an electrometer with a long input time constant (~ 100 sec) [see Hughes and Secker 1971, Sessler and West 1971, Foord 1969], or by modulating the probe signal (Davies 1969, Reedyk and Perlman 1968, Boksenberg et al. 1968).

5.2.2. Apparatus

The charge measurement apparatus (Fig. 5-5) used in this work is based on the method of Davies (1969). An earthed, metallic shutter is rotated between the probe and the insulator surface such that a probe signal of about 1 msec pulse width is generated. The probe consists of a thin electrode, along the axis of an earthed

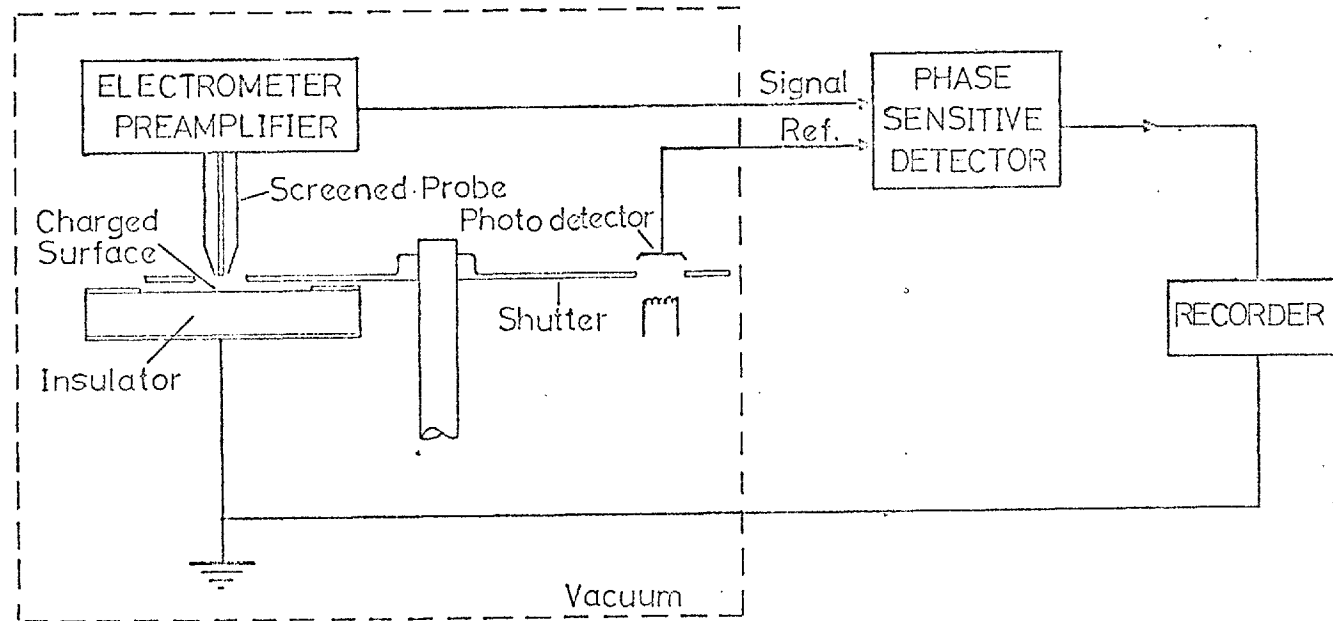


Fig. 5-5 The Charge Measurement System

cylindrical screen. The impedance of the probe is stabilised by a $10^{10} \Omega$ resistor (to earth) at the input of a high-impedance preamplifier; the input capacitance C_1 is minimised by using the shortest possible leads to the preamplifier (which is, in fact, placed into the vacuum chamber). The input time constant is about 0.1 secs.

As shown in Fig. 5-5, the signal is fed into a phase sensitive detector which is synchronised with the shutter frequency by a reference pulse from a photo detector. The rectified output has a much improved signal-to-noise ratio and is practically free of mains interference; it can be monitored continuously to record the variation of the surface charge as a function of time or displacement across the insulator surface. The system is linear and reproducible to 2% for probe heights up to 1.7 mm. From Eq. (5.18), the sensitivity s , defined as the output per unit surface charge density, is given by

$$s = \frac{G V}{\sigma_s} = \frac{G A}{C_1 (1 + \epsilon_i h/d)} \quad (5.20)$$

where G is the system gain; for the apparatus described

$$\frac{G A}{C_1} = 0.4 \text{ V nC}^{-1} \text{ cm}^2 \text{ (or } 2.5 \text{ V per } 10^{11} \text{ e cm}^{-2} \text{)}$$

The smallest detectable charge density is about 10^7 e cm^{-2} at

$$d/\epsilon_i = 0.1 \text{ mm.}$$

By displacing the insulator beneath the probe, the spatial distribution of the surface charge can be recorded. The spatial resolution of the probe has been determined by measuring the dependence of the output on the size of a charge area. In Fig. 5-6 the output has been plotted as a function of the width w of a charged region (e. g.

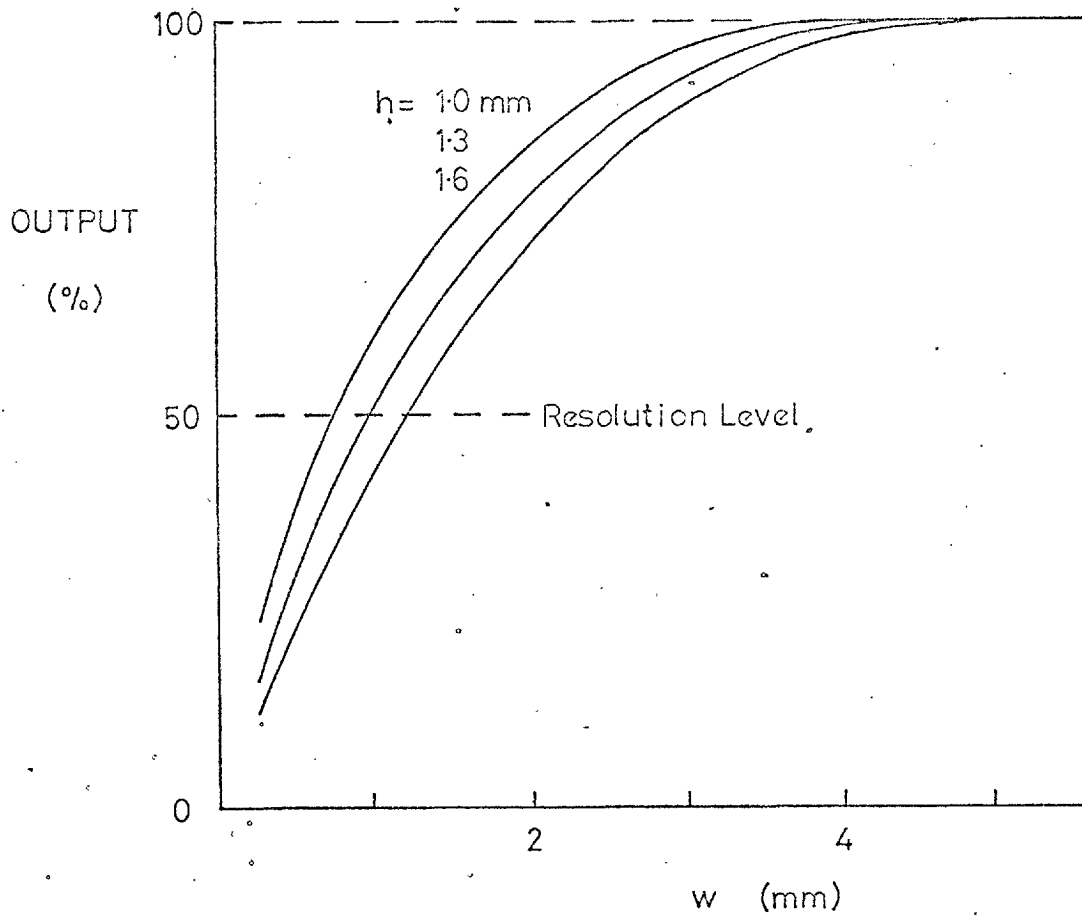


Fig. 5-6 Spatial Resolution of the Charge Probe
at probe heights $h = 1.0, 1.3, 1.6$ mm

a strip of conductor biased w. r. t. earth) at various probe heights h . The resolution, given by the half-height level, is of the same order as h , i. e. about 1 mm.

5.3. Procedure

The experiments on thin film adhesion were carried out in a conventional vacuum chamber, pumped to a pressure of about 1 μ torr by an oil diffusion pump (with liquid nitrogen trap) and backed by a rotary pump. The experimental chamber is shown in Fig. 5-7. The metal films are evaporated on to the substrate which is mounted on a carriage. The carriage is moved to the centre of the vacuum chamber for the film stripping. Finally the charge on the substrate is measured by moving the carriage to a position such that the substrate surface can be scanned by the probe. It should be noted that the sample does not need to be exposed to the atmosphere at any stage after the film has been deposited.

5.3.1. Substrate Preparation

Glass substrates (2" x 1" slides) were initially washed in detergent to remove surface grease; they were then immersed in isopropyl alcohol and cleaned by ultrasonic vibration. At this stage drying marks were still visible on the surfaces. The substrates were therefore placed in a reflux condenser and degreased in isopropanol vapour for about an hour; they were left to dry in this vapour. This procedure resulted in surfaces which were free of drying marks. The surfaces were examined in a scanning electron microscope (after coating with carbon). On substrates of borosilicate glass (Corning 7059) no surface features were observed, apart from a very few contaminant particles. The surfaces of borosilicate glass are in fact highly polished to a smoothness of about 50 $\text{\AA}$, as



Fig. 5-7 Experimental Chamber

1 evaporator, 2 cantilever, 3 probe,
4 substrate carriage

measured by a 'tally surf' scan.

The simple cleaning procedure described above was chosen because chemical treatments (e. g. etching in hydroflouric acid) tend to roughen the surface - as was observed by Chapman (1969). The interpretation of both adhesion and charge measurements is complicated by this additional roughness (see below), and in any case the chemical etchants leave contamination on the glass surface.

The crystalline samples (mica and rock-salt) were prepared as follows: a film was first evaporated on to the crystal. The sample was then taken out of the vacuum chamber and cleaned in air, immediately before placing it back into the vacuum; the film of which the adhesion was to be measured, was deposited on to the cleaved surface.

The cleavage leaves a large number of steps on the surface of the crystal. With mica it is possible to produce surfaces with few large cleavage steps over an area of some square centimetres. This is not possible in the case of rock-salt, where it is impossible to avoid cleavage steps. Obviously, a film, which is deposited over a cleavage step of a height comparable to the film thickness, will easily break along the cleavage step when an external force is applied; as a result the stripping of films on rock-salt usually failed.

5.3.2. Film Deposition

Metal films of the same material were evaporated on to the two sides of a substrate. After deposition of the back film, the substrate was placed on the carriage and outgassed for several hours at temperatures up to 300°C . The metal films (purity of 3N) were then evaporated from a molybdenum boat (turned upside down) or from a tungsten spiral at 10-15 cm distance from the substrate (see Fig. 5-7). The deposition rates were in the range of 5 to $15 \text{ \AA sec}^{-1}$, and the film thickness was varied between 0.2 and $0.5 \text{ }\mu\text{m}$. A small number of films were deposited by sputtering (see Sect. 6.1).

5.3.3. Film Stripping

The films are stripped by the method described above (Sect. 5.1) in the vacuum chamber at 20°C . Two parallel lines are scribed through the film, at about 5 mm separation. A short strip of adhesive tape is attached to the portion of the film between the scribed lines as shown in Fig. 5-2 . If exposure of the sample to the atmosphere is to be avoided, the tape has to be attached by manipulation from outside the chamber.

The films are stripped at speeds of 0.1 to 100 mm min^{-1} (about 2 to $10^3 \text{ }\mu\text{m sec}^{-1}$); the angle of stripping was normally kept near 90° ($\pm 5^{\circ}$) to the substrate. Over the area to which the tape was attached the stripping force corresponds to several grams ($5 \times 10^{-2} \text{ N}$); this is several times larger than the stripping force

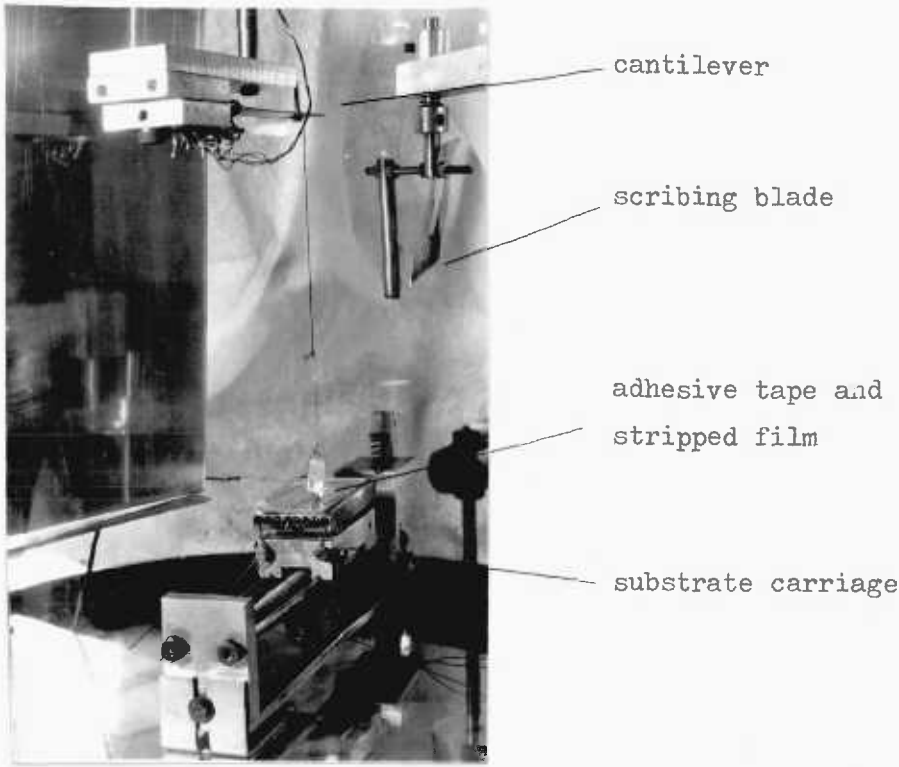


Fig. 5-8 Film Stripping Apparatus

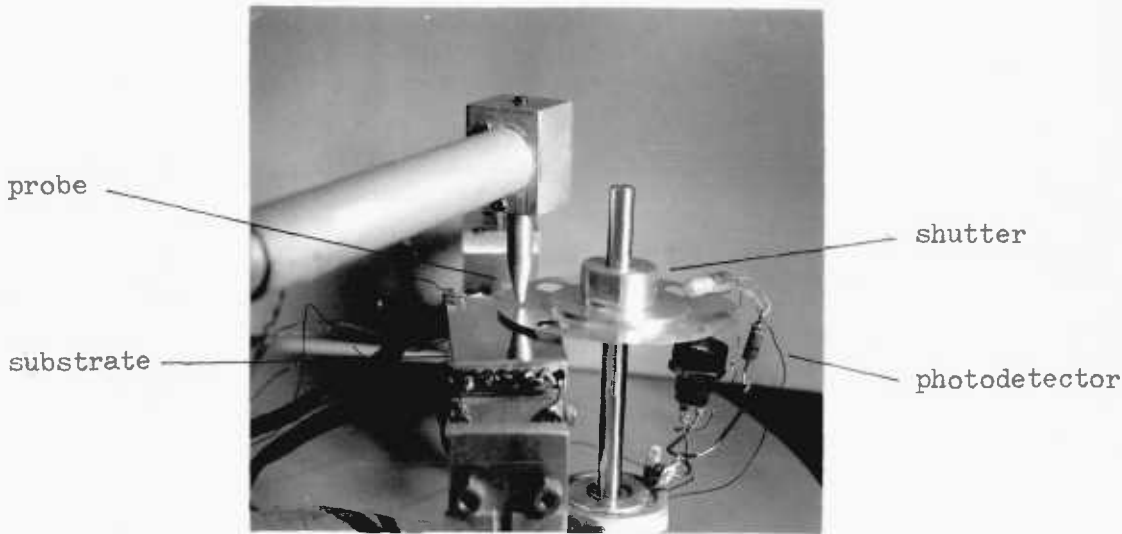


Fig. 5-9 Charge Measurement Apparatus

required for the unsupported films. In order to avoid an abrupt jerk at the end of the tape-backed area, the stripping is slowed down over the transition region. The adhesion of the film is, of course, determined from the measurements over the unsupported area of the film. Figure 5-8 shows a photograph of the apparatus during a film stripping experiment.

5.3.4 Charge Measurement

The details of the charge measurement system have been described above (Sect. 5.2). In order to measure the charge on an insulating substrate, the carriage is moved to a position below the probe, as shown by the photograph of Figure 5-9. The carriage is displaced by a motor, so that the whole substrate area can be scanned. Alternatively, the substrate can be maintained^q in a given fixed position while measuring the charge decay. The zero level for the recorded output is obtained simply by measuring the signal when the probe is placed above the earthed metal film; this is important at small signal amplitudes (i.e. for small surface charges and on thin substrates) so that any voltage offset introduced by the amplifier system can be subtracted from the output.

CHAPTER VI

RESULTS AND DISCUSSION

6.1 Adhesion of Metal Films to Glass Substrates

The adhesion of thin metal films to alumino-borosilicate glass (Corning 7059) has been investigated in this work; glass substrates of this type are commonly used in thin film studies. Thin films of gold, silver and copper adhere relatively weakly to glass and could therefore be removed from the substrate by the stripping method (see Sect. 5.1). Furthermore, Corning 7059 glass contains a very low concentration of alkali ions and, consequently, it has an extremely low electrical conductivity at room temperature. The electrical charge generated on the glass surface could thus be measured conveniently by the probe method described in Sect. 5.2.

By contrast, a surface charge on soda-lime glass decays rapidly at room temperature. In this case, the probe method could be used to measure the charge decay, but the magnitudes of the initial charges had to be deduced by extrapolation. The charge measurements on Corning 7059 glass are therefore more reliable, and for this reason soda-lime glass was not investigated further. The adhesion of metal films to the two types of glass was found to be very similar (see below).

6.1.1 General Results

A large number of metal films (Au, Ag and Cu) were stripped from Corning glass substrates by the procedure described in Sect. 5.3. The film was normally stripped a few hours after deposition, when the substrate had cooled to room temperature. The majority of these experiments were carried out in a vacuum of 1 to 10 μ torr, at stripping speeds between 20 and 50 mm min⁻¹ and angles of 80 to 90° to the substrate. The results for the average stripping energy (S) and the charge density (σ) on the glass surface are shown in Table 6-1. The stripping energy varies by up to 30 % over a given sample, so that the mean values, averaged over five or more samples are accurate to about 20 % . As shown in Table 6-1, the stripping energies for gold and silver films are close to 1 J m⁻², but about 25 % smaller for copper films.

The charge remaining on the glass surface after removing the film depends strongly on the material of the film. The charge resulting from the contact with gold films is positive ($1.5 \cdot 10^{10}$ e cm⁻²) but negative for silver ($- 8 \cdot 10^{10}$ e cm⁻²) and copper. Over a given sample the charge varies by up to 50 % ; a charge reversal was never observed. At room temperature the surface charge was found to remain unchanged over a period of several days, unless the ambient pressure was raised above about 1 mtorr.

Table 6-1Stripping Energy and Charge for Metal Filmson Corning 7059 Glass

Film	Charge density on glass, σ (10^{-10} e cm $^{-2}$)	Stripping Energy (mJ m $^{-2}$)
Au	1.5 $\pm$ 1	1100 $\pm$ 200
Ag	- 8 $\pm$ 2	1000 $\pm$ 200
Cu	- 6 $\pm$ 2	750 $\pm$ 50

6.1.1.1 Dependence on deposition parameters

The structure of a thin film is determined to some extent by the conditions existing during the deposition of the film. In our experiments the substrate temperature was varied from room temperature to about 300°C during the evaporation; the substrate surface is heated by the radiation from the evaporation source and its temperature may rise above 100°C without additional heating. Our results do not show a systematic dependence on the deposition temperature, the deposition rate or the film thickness. However, films which were deposited by sputtering showed very different properties from evaporated films (see Sect. 6.1.7).

6.1.1.2 Dependence on stripping conditions

The nominal speed at which films were stripped was varied in the range of 0.2 to 100 mm min⁻¹. The angle of stripping was kept close to perpendicular to the substrate, varying by about 5° during an experiment; the nominal stripping speed is therefore nearly constant. Figure 6-1 shows a plot of the stripping energy against speed: the stripping energy is roughly constant at higher speeds, but below about 1 mm min⁻¹ both lower and higher values were recorded.

The ambient pressure during the stripping process has no measurable effect on the stripping energy. The surface charge on the substrate, measured at pressures below 1 mtorr, remains constant over several days. If the pressure is raised above 1 torr a discharge may occur. Films which were stripped at atmospheric pressure usually gave rise to negative charges ($\sim 5 \cdot 10^{10}$ e cm⁻²) on the substrate.

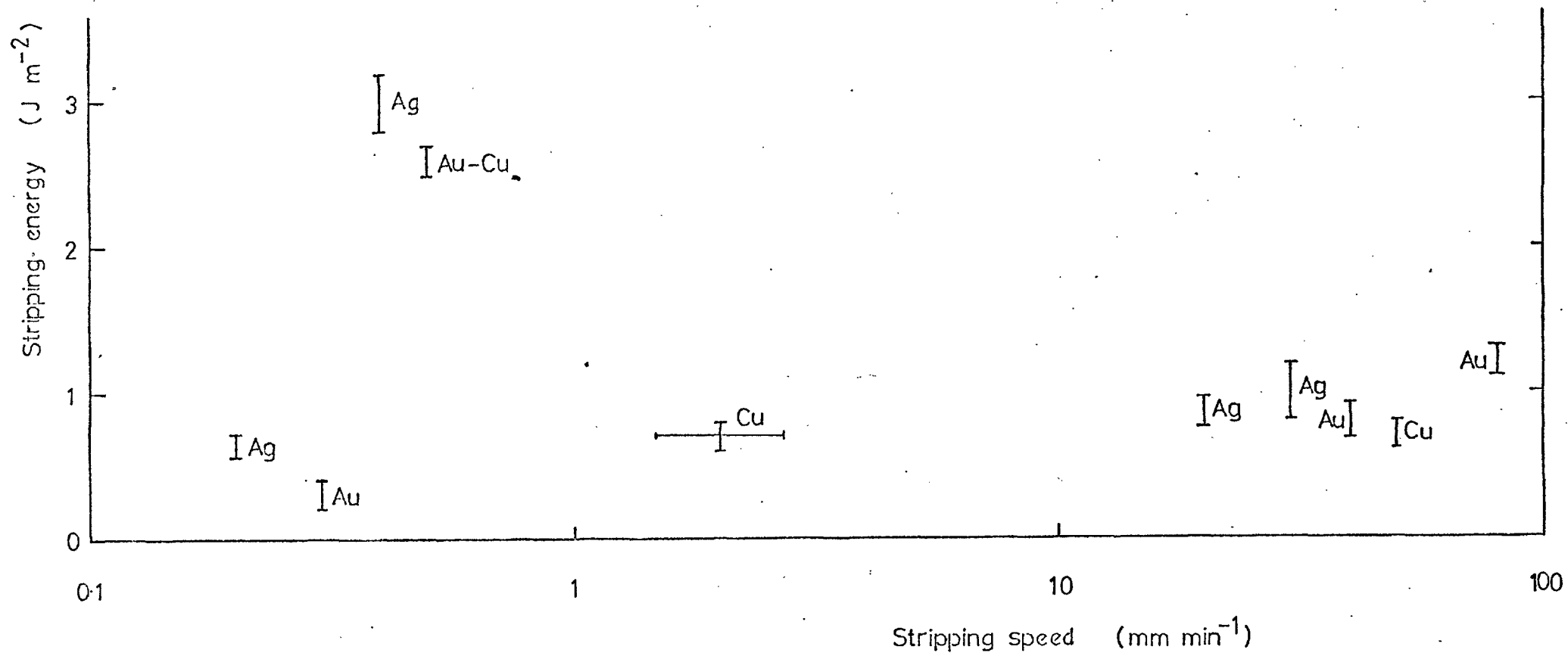


Fig. 6-1 Stripping of Films from Corning 7059 Glass:
plot of stripping energy against stripping speed

6.1.1.3 Aging of films

The stripping experiments were performed on samples up to six months after deposition of the film. No systematic difference was observed between samples which were kept in vacuo throughout and those which were exposed to the atmosphere (for several months, in some cases). The outside surfaces of copper and silver films were oxidised in the atmosphere, but the surfaces in contact with the substrate showed no visible change. In a few cases, the charge remaining on the glass surface after removing copper and silver films was found to be positive ($\sim 10^{10} \text{ e cm}^{-2}$) after exposure to the atmosphere.

An aging effect was observed for a double-layer film of gold on copper (on glass); the initial stripping energy and surface charge corresponded to the values for copper films, i.e. $S = 800 \text{ mJ m}^{-2}$, $\sigma = -5 \cdot 10^{10} \text{ e cm}^{-2}$. Over a period of weeks the colour of the film as seen through the glass substrate changed from pink to brown - thus suggesting an interdiffusion of the two films. Measurements after 200 days showed an increased adhesion ($S \sim 2.5 \text{ J m}^{-2}$) and a small positive charge.

6.1.2 Repeated Stripping

A simple test of the reversibility of the stripping method can be performed as follows: supposing a film is stripped over a certain area of the substrate and is subsequently allowed to re-attach itself over the same area. If some irreversible processes have occurred, then on stripping the film a second time, the stripping energy should be reduced (i.e. in Sect. 5.1, $dU_T/da \neq 0$).

Experiments were carried out, in which a film was re-stripped several times in vacuo. In Fig. 6-2, the stripping energy has been plotted as a function of the time during which the separated surfaces were exposed to the ambient. The stripping energy is seen to decrease remarkably slowly: after one hour's exposure to the ambient (10 μ torr pressure) the stripping energy is around 10% of its initial value; after two hours, the values become comparable with the error in the measurement ($\pm 50 \text{ mJ m}^{-2}$).

6.1.3 Charge Flow during Stripping

If there exists an electrical double layer at the metal-insulator interface, then there will be a net charge on the earthed metal film (equal and opposite to that on the insulator). As the interface is separated, the charge on the metal will flow off to earth until at a large distance from the insulator, it is completely discharged. Therefore, if the current flowing to earth is measured, the total charge which was originally at the interface, can be deduced. Alternatively, the total charge flowing from the film could be measured (in this case the film is not earthed). It was found that the total charge flowing from the film was within 20 % of the charge measured on the insulator by the probe method.

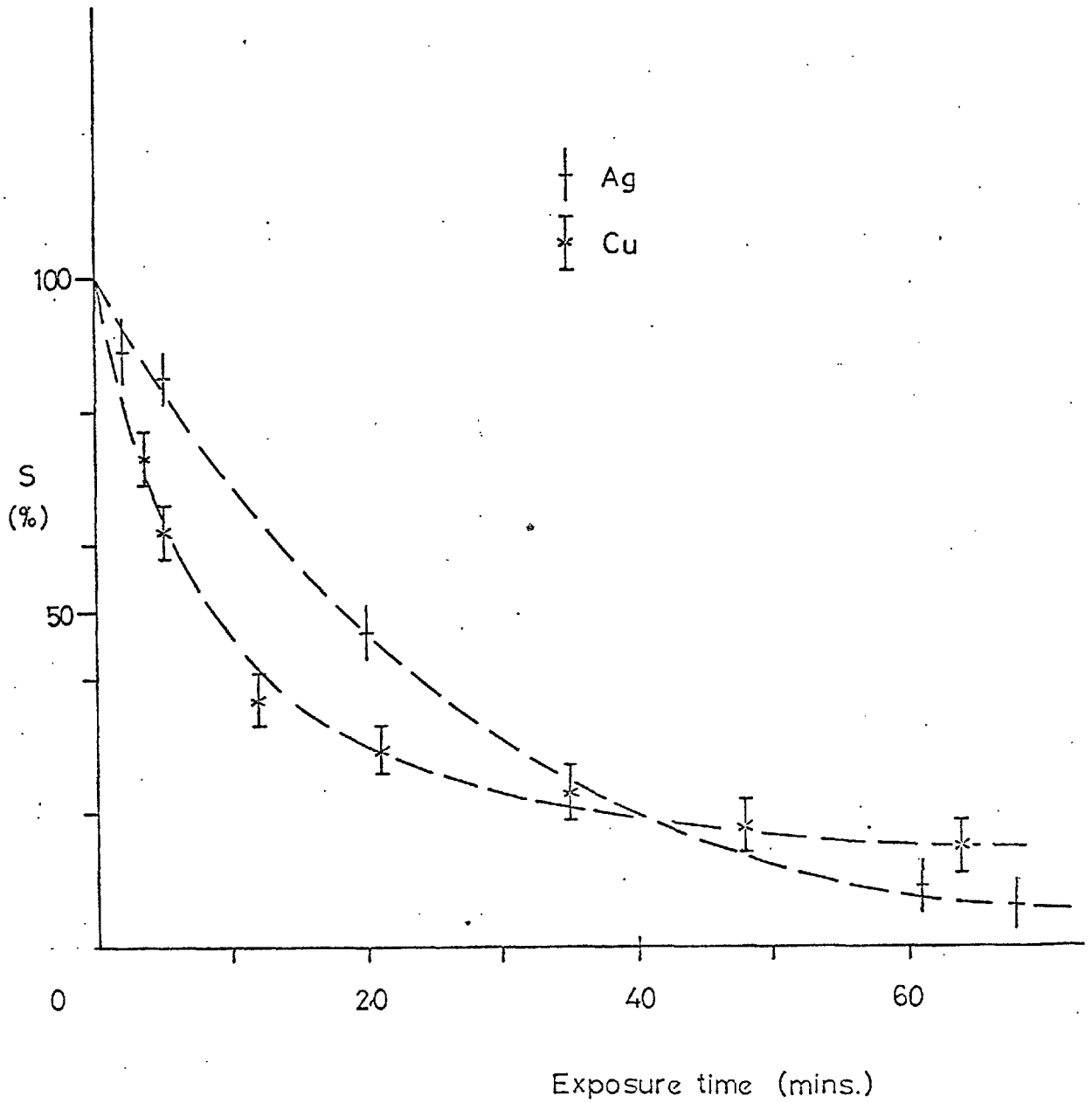


Fig. 6-2 Repeated Stripping Experiments:
plot of stripping energy S against exposure time
for Ag and Cu on Corning 7059 glass

A second application of the current flow method is to monitor the stripping process: the current flowing from the film should be approximately proportional to the speed of stripping. A record of the current flow during the stripping of a gold film is shown in Fig. 6-3. At this stripping rate (35 mm min^{-1}) the current shows numerous sharp pulses which indicate that the stripping speed changes abruptly. A simultaneous record of the stripping force shows that each current spike is accompanied by a sharp drop in the force. The stripping process may therefore progress in a kind of slip-stick fashion. On the other hand, at low stripping speeds (0.5 mm min^{-1}) no current spikes were observed, thus indicating a constant stripping speed.

6.1.4 Charge Decay Measurements

The metal films were deposited on to heated glass substrates ($100^{\circ} - 300^{\circ}\text{C}$); the charge transfer process across the metal-insulator interface takes place at the raised temperature of the substrate. In order to find out more information about the electrical properties of glass above room temperature, the conductivity and the decay of surface charge were measured. The conductivity is extremely low at room temperature and is more conveniently deduced from the charge decay measurement using the potential probe (see Davies 1967a). At temperatures above 150°C the charge decay is very rapid and it is easier to measure the conductivity at constant applied bias.

At temperatures below about 60°C the rate of charge decay was found to be extremely slow (several hours for a 50 % decrease). A more rapid decay occurs at higher temperatures; in Fig. 6-4, the variation in probe potential (proportional to the surface charge) is shown for Corning 7059 glass at $95 \pm 5^{\circ}\text{C}$. After an initial slow decay, li

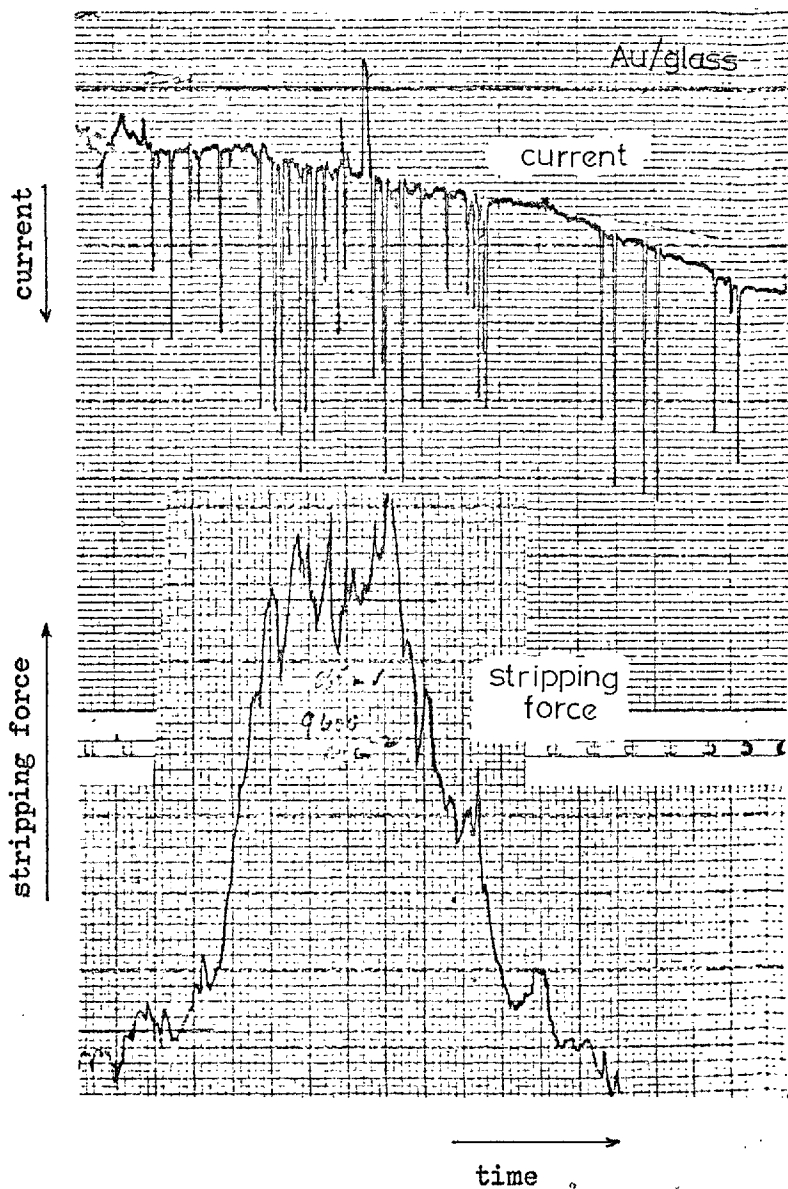


Fig. 6-3 Simultaneous records of current flow and stripping force during a film stripping experiment (stripping speed : 35 mm min^{-1})

the probe potential (V) decreases approximately inversely proportionally with time. An analysis of these results is given below (Sect. 6.2.2).

The temperature dependence of the bulk conductivity of Corning 7059 glass was measured in the range of $150^{\circ} - 300^{\circ}\text{C}$. In Fig. 6-5 the resistivity has been plotted against the inverse temperature; the log-linear plot shows a straight line indicating an activation energy for conduction (assuming a thermally activated process) of about 0.6 eV.

6.1.5 Extraneous Sources of Charge

(1) Electrical charges from the evaporation source

Metal films were deposited by evaporating from a heated source (molybdenum boat or tungsten spiral). It has been observed (Hill 1967) that electrons and ions are emitted from the source; some of these charged particles may reach the substrate and give rise to surface charging. This possibility was investigated by the following arrangement: two grids were placed between source and substrate such as to intersect the vapour beam. The grid nearest the source was maintained at earth potential while the second grid was biased and connected to an electrometer. By appropriate biasing, any charged particles entering the space between the grids could thus be detected.

For neither polarity of bias could a current be detected above the noise level (about 1pA - due to pick-up from source power supply). However, with grids both biased positively the expected thermionic current was detected.

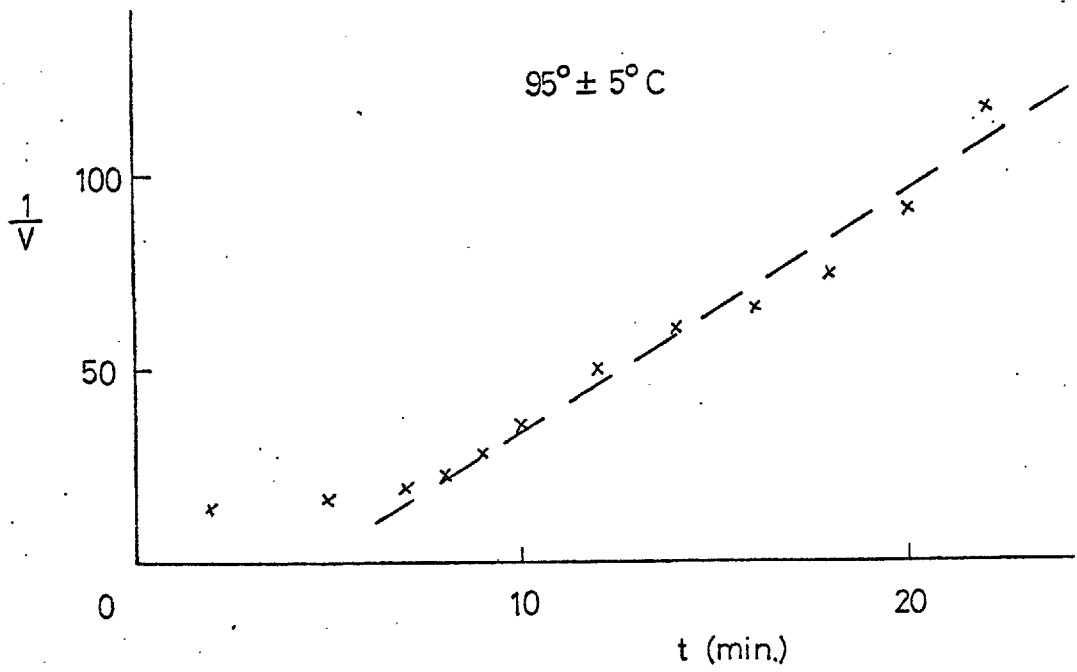


Fig. 6-4 Charge Decay from Corning 7059 Glass:
plot of inverse probe potential, $\frac{1}{V}$ against time

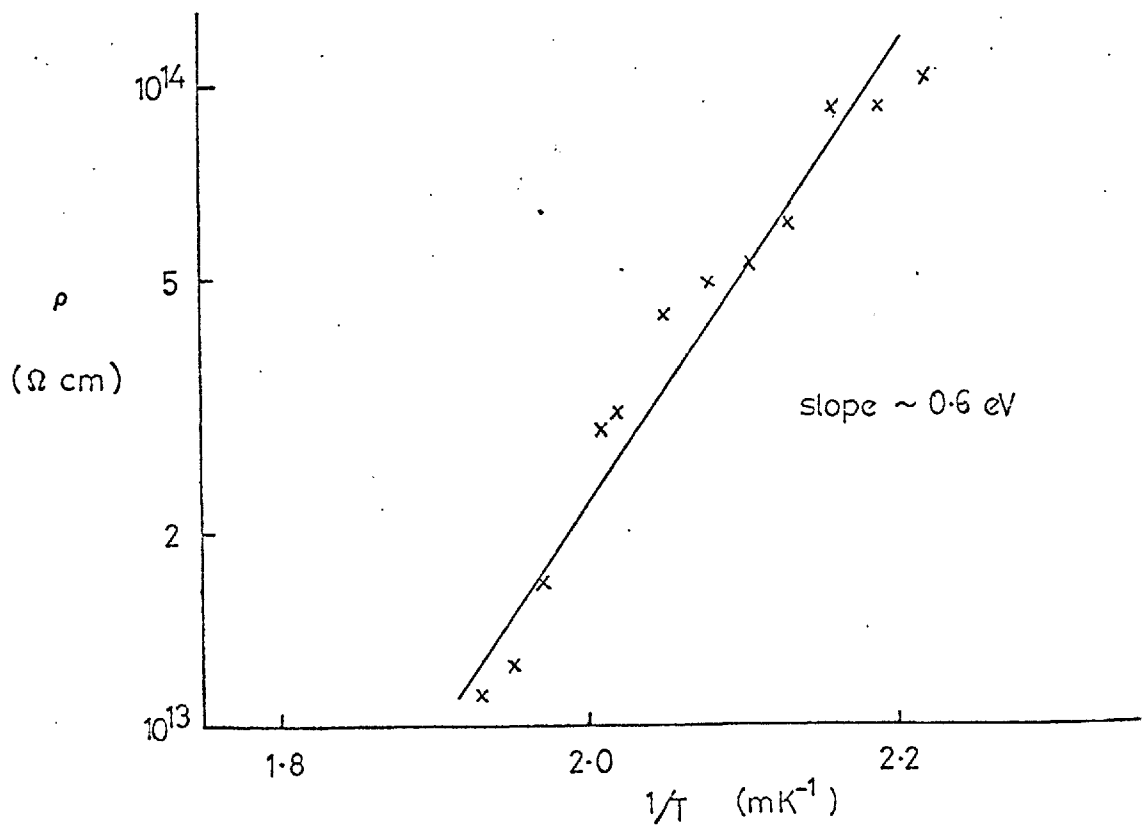


Fig. 6-5 Temperature Dependence of Resistivity of Corning 7059 Glass:
plot of bulk resistivity, ρ vs. inverse temperature

The source-substrate distance was kept to 10 -15 cm; the substrate was surrounded by earthed shields so that a charged particle emitted from the source was very unlikely to reach the substrate. From the above measurements, the rate of charging of the substrate could not exceed 10^7 e cm^{-2} per second. In fact, no measureable charging was detected by the probe, even with the ionisation gauge switched on.

(2) Charge emission during stripping

When a mica crystal is cleaved, or a polymer film is stripped from its substrate, the emission of electrons and of light are frequently observed (see Deryagin et al. 1957). Apart from visual observation, two other methods were used to test this possibility.

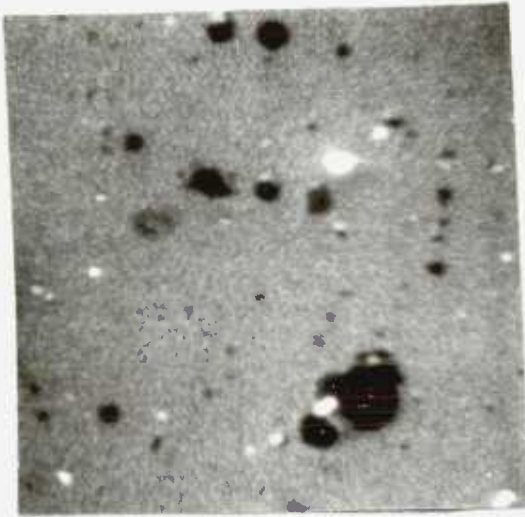
The first method uses the fact that the interface as a whole should be electrically neutral. Thus, if the charges on the film and substrate are not equal and opposite, some charge must have been emitted into the gap or leaked away through the materials. The total charge on the metal film can be measured by the charge or current flow method (see Sect. 6.1.3); the charge on the insulator is determined by scanning the insulator with the probe. The two measurements usually agree within the experimental accuracy ($\sim 20\%$). The amount of charge - if any - emitted from the interface is therefore insignificant.

The second test consists of placing a biased electrode near the area of the substrate from which the film is stripped. Any charges emitted from the gap between the film and substrate while the film is being stripped could therefore be collected by the electrode. In fact, no measureable current (noise level $\simeq 10^{-14} \text{ A}$ on electrometer) was detected for either polarity of bias voltage.

6.1.6 Microscopic Observations of Film and Substrate Surfaces

The condition of the substrate surface is known to have a considerable influence on the adhesion of thin films. The glass substrates were examined in an optical and a scanning electron microscope (SEM) before film deposition and after film stripping; for observations in the SEM the glass surfaces were coated with a thin carbon film to prevent surface charging in the electron beam. The surfaces which had been cleaned by the procedure described in Section 5.3.1 showed only few contaminant particles. Figure 6-6 shows a SEM photograph of the substrate surface after stripping a film from it; the surface has a number of irregularities, occasionally areas where the film remained attached to the substrate (this was apparent in optical micrographs). Similarly, the 'substrate side' of the stripped film shows indentations of several microns diameter (see Fig. 6-7). These observations suggest that the stripping does not always occur at the interface, possibly due to the roughness of the substrate or the presence of contamination. Although these flaws represent only a small percentage of the interfacial area, they could cause the observed variations in the stripping force over a substrate; this effect is commonly referred to as 'mechanical interlocking' of the film and substrate.

During the stripping process the film is bent through a right angle close to the line of detachment. In this region the film may be severely deformed by the applied stripping force. Figure 6-8 shows a SEM photograph of the film during a stripping experiment; the radius of curvature of the film, with a small applied force, is about 40 μm . For the film shown in Fig. 6-8 (film thickness 0.2 μm) the strain due to bending is about half a percent.



5 μ m

Fig. 6-6 (left) Scanning electron micrograph of glass surface after film stripping.

Fig. 6-7 (right) SEM micrograph of film surface after stripping.



Fig. 6-8 SEM micrograph of film during stripping.

6.1.7 Sputtered Films

The adhesion of sputtered gold films on Corning 7059 glass was investigated. The films were deposited in an argon r.f. plasma (argon pressure 2 mtorr, sputtering power 1 kW). The average stripping energy for these films (thickness 0.5 - 1 μm) was around 4 J m^{-2} , i.e. several times greater than for evaporated films, with variations up to 8 J m^{-2} ; a large reduction in the adhesion was observed over areas of the substrate which were visibly contaminated, e.g. showing drying marks on the substrate surface.

Over regions of strong adhesion (stripping energy $\sim 8 \text{ J m}^{-2}$) evidence of inelastic deformations of the film was found: the stripping force and current flow from the film were recorded simultaneously (see Fig. 6-9). The current shows a sharp pulse at the same instant as an abrupt drop in the stripping force occurs; subsequently the stripping force rises to a maximum and falls gradually until the next pulse occurs. The stripping process was seen to follow a stop-go sequence, in which the film goes through a strain cycle. Initially, elastic energy is stored in the film due to bending and tensile stresses. Since the film adheres strongly to the substrate, the increasing applied force causes a sharp kink, at which plastic deformation of the film eventually occurs. Thus, the applied force reaches a maximum and falls as plastic flow occurs; the film does not break as a result of this deformation (possibly due to work hardening), but is detached abruptly from the substrate. The SEM photograph (Fig. 6-10) shows the sharp kinks in the stripped film (thickness 1 μm) with a curvature of about 20 μm .

The electrical charge on the substrate after stripping was close to the value for evaporated films ($2 \times 10^{10} \text{ e cm}^{-2}$); the incidence of charged particles during sputtering thus does not affect the charging process.

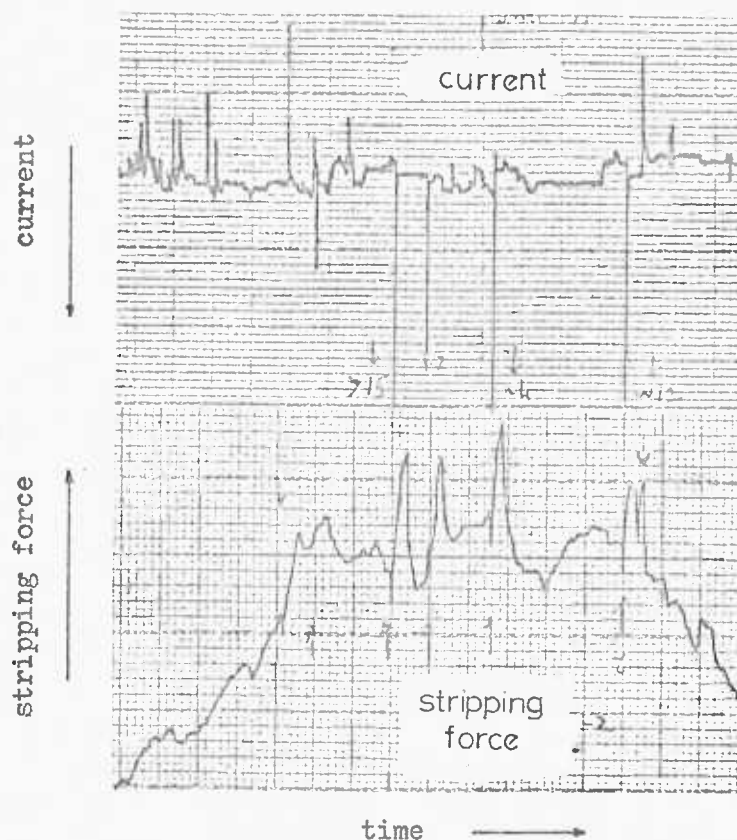


Fig. 6-9 Simultaneous records of current flow and stripping force for sputtered Au film (stripping speed: $10 \mu\text{m sec}^{-1}$)



Fig. 6-10 Scanning electron micrograph of stripped film (sputtered Au/ Corning 7059 glass)

6.2 Discussion: Adhesion to Glass Substrates

The experimental results for thin films on glass substrates are discussed in this section. The validity of the stripping method in giving a true measure of thin film adhesion is assessed. This forms the basis for a comparison between the experimental values and the theoretical calculations (Chap. 2) of the adhesion. The electrostatic component of adhesion is calculated from the charge measurements and the mechanisms of charge transfer across the metal-glass interface are discussed.

6.2.1 Reversibility of the Film Stripping Process

The experiments of repeated stripping of a film (Sect. 6.1.2) give a direct indication of the extent to which the stripping process is reversible. Consider the stages leading up to the separation of the film from the substrate: the stripping force acts on both the film and the substrate; the weaker component, i.e., the film and especially its interface with the substrate, may be deformed considerably. Under tensile stress, metal films do not behave completely elastically (Menter and Pashley 1959); at strains exceeding about 1 % they are found to be deformed plastically (Neugebauer 1960) as a result of dislocation movement. The film-substrate interface contains numerous structural defects which impede the motion of dislocations. Thus, the energy stored in the system as the stripping force is increased, may be released by a fracture along the interface (adhesive fracture) before the film is deformed plastically. In this case, the stripping process is almost completely reversible: the stripping energy is then practically equal to the adhesion energy (see Sect. 5.1).

The evaporated films (Au, Ag and Cu) showed no visible signs of irreversible deformations resulting from the stripping process. The films are strained mainly by being bent through a right angle, but, as Fig. 6-8 shows, the strain is normally less than 1 % . In the case of sputtered gold films the plastic deformation of the film due to bending was observed directly (see Sect. 6.1.7). The adhesion of the sputtered films was so large that the film was deformed irreversibly before stripping occurred. More strongly adhering films (e.g. evaporated films of aluminium on glass) tend to break rather than being detached from the substrate.

If no irreversible processes occur during or after stripping, then the stripping energy should remain unchanged on subsequent stripping after re-attaching the film to its substrate. In practice, although no energy may be dissipated while stripping the film, the exposure of the surfaces to the ambient will result in irreversible changes. At a pressure of 1 μ torr a complete monolayer of gas molecules may be adsorbed on a surface within a second. Thus, when a stripped film is reattached to its substrate, the interfacial separation will be increased by at least two monolayers of molecules. The adhesion of the film will then be determined in part by the dispersion properties of the adsorbed gases. In the case of oxygen or water vapour (both are strongly adsorbed on glass), the van der Waals interaction with the film is not weakened significantly; the van der Waals adhesion is therefore not necessarily reduced by the adsorption. However, any chemical bonding that may have contributed to the adhesion initially, is now lost. The adsorbed gases may also change the contact potential across the interface (see Sect. 3.2.5) and will thus affect the electrostatic adhesion.

The repeated stripping experiments (Sect. 6.1.2) show a decrease in the stripping energy (S) after each repetition of stripping the same area of a film. There is no abrupt drop in the value of S after the first stripping; the energy dissipated in irreversible processes is only about 10 % of S . As Fig. 6-2 shows, the stripping energy decreases monotonically with the (cumulative) time during which the film and substrate are separated (i.e. the exposure time). The gradual decrease in S is not related to the number of repetitions of stripping and is therefore unlikely to be due to non-elastic deformations of the film. The dependence of S on the exposure time may be a result of the slow adsorption of gas molecules which weaken the van der Waals adhesion of the film. In fact, a mass spectrometer analysis of the gases in the vacuum chamber showed the presence of hydrocarbons (constituents of diffusion pump oil) of about 0.1 μ torr partial pressure. These heavy gas molecules may be adsorbed slowly, thus reducing the adhesion of the film very gradually (e.g. a 3nm layer of adsorbed molecules will reduce the van der Waals adhesion energy to about 1 % of its initial value).

The electrostatic adhesion between the film and substrate could, in principle, account for the slow decrease in stripping energy. The electrical charge at the interface may leak away while the film and substrate are separated. If the charge is not replenished when the film is re-attached, then the electrostatic adhesion (proportional to the square of the charge density) decreases with the cumulative exposure time. However, it will be seen below (Sect. 6.2.3) that the magnitude of the electrostatic adhesion is too low to account for the variation in stripping energy. On the other hand, the electrostatic forces may have an important effect on the re-attachment of the film. Since the electrostatic forces have a long range of action

(see Sect. 2.2), the film will be pulled back towards the substrate. At a separation of a few nanometers the van der Waals forces begin to contribute to bring the surfaces into contact. The repeated stripping experiments suggest that, in spite of surface irregularities, the film is brought back into atomic contact with the substrate over macroscopic areas of the interface.

We can conclude from this discussion that very little of the stripping energy is dissipated irreversibly during the first stripping of a film. The stripping process itself is therefore nearly reversible and the stripping energy can be equated with the adhesion energy of the film to a good approximation (better than 10 %). The irreversible part of the experiment is largely due to the adsorption of gas molecules on the freshly formed surfaces.

6.2.2 Charge Transfer across the Film-Glass Interface

In Section 3.2.5 it was shown that the transfer of electrons across metal-insulator interfaces depends on the contact potential difference between the two materials. The contact p.d. and the metal work function at this interface cannot, however, be measured directly; if we assume that the metal work function in vacuo (ϕ_m) - which can be measured experimentally - has a value close to that at the metal-insulator interface, then ϕ_m is approximately linearly related to the contact p.d.. The electron transfer will then depend on the value of ϕ_m .

In Figure 6-11 the charge density (σ) measured on Corning 7059 glass after removing the metal film has been plotted as a function of the metal work function ϕ_m . The values of ϕ_m were taken from published data for metal films on glass substrates (measurements in high vacuum). The charge density shows a strong dependence on ϕ_m ,

tending to become more positive with increasing ϕ_m ; a similar relationship exists between σ and the metal electronegativity X_m ($X_{Au} = 2.4$, $X_{Ag} = X_{Cu} = 1.9$). Such a variation is expected for an electron transfer process, but cannot easily be explained by an ionic mechanism.

The magnitudes of charge density lie in the range of $\pm 10^{10}$ to $10^{11} \text{ e cm}^{-2}$; a reversal of the sign of the charge can be expected around 4.6 eV. Over the range of the experimental values, the charge density varies by about $2 \times 10^{11} \text{ e cm}^{-2}$ per eV of work function difference. Because of the uncertainty in the values of ϕ_m , it is not possible to deduce the form of the variation with charge density. A tentative value of the electron states density at the glass surface can, however, be deduced by comparison with the models developed in Section 3.2.5. Assuming the surface states density (N_s) is small, the density of localised states in the glass is (from Eq.(3.50) and Fig. 3-12) of the order of 10^{16} cm^{-3} . Alternatively, if we assume that only surface states are filled by the charge transfer process, then our measurements indicate a surface states density of about $2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$.

The above values can be compared with the results of the charge decay measurements (Sect. 6.1.4). A theory of the decay of excess charges from insulator surfaces has been developed by Wintle (1970) (see also Keiji Kanazawa et al. 1972). It is shown that, assuming the equilibrium density of charge carriers in the insulator is small compared with the excess charge, the surface electric field due to that charge decays exponentially with time. If a potential probe is used to measure the surface charge, as in our experiments, the decay of the probe potential V shows two distinct regions:

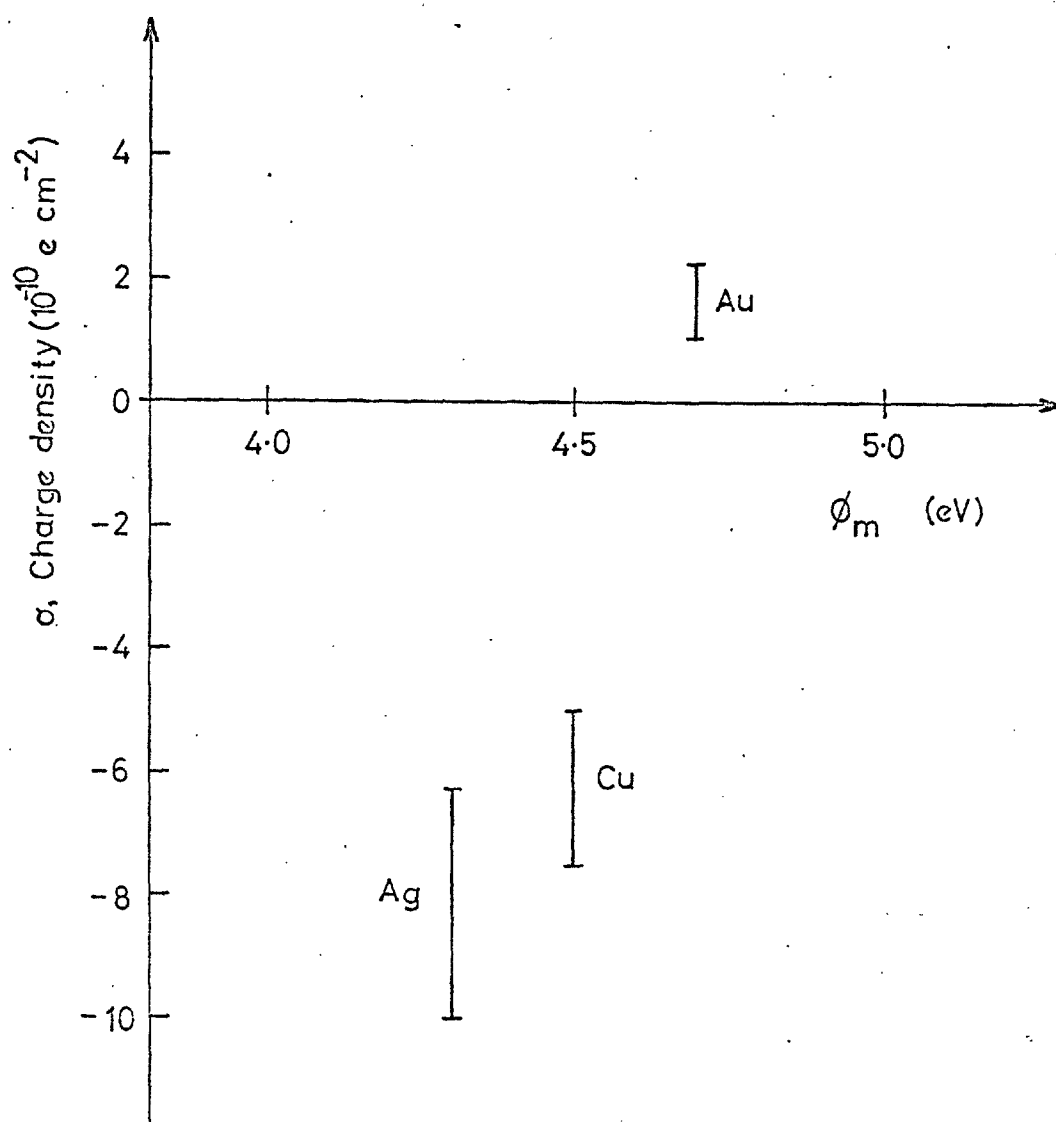


Fig. 6-11 Charge Transfer across Metal-Glass Interface:
plot of charge density σ on Corning 7059 glass
against metal work function ϕ_m

[values of ϕ_m : for Au from Hopkins et al. 1964
for Ag from Hopkins and Riviere 1964
for Cu from Riviere 1957]

(a) initial decay, for a time (t) which is shorter than the time taken by the charge to traverse the insulator (transit time τ), i.e. for

$$t < \frac{d^2}{V_0 \mu} = \tau \quad (6.1)$$

the probe potential V decays from its initial value V_0 as

$$V = V_0 \left(1 - \frac{\mu V_0}{2 d^2} t \right) \quad (6.2)$$

where μ is the charge mobility in an insulator of thickness d .

(b) further decay, after a time $t > \tau$, proceeds as

$$V = \frac{d^2}{2\mu t} \quad (6.3)$$

Thus, the decay is initially linear with time, but after the transit time τ (defined by Eq.(6.1)) the charge, being proportional to the probe potential, decays hyperbolically. This behaviour has been observed experimentally, notably for polymers (e.g. Ieda et al. 1967). In our experiments, the charge decay from glass surfaces was found to become hyperbolic after about 200 seconds ($\approx$ transit time) at $95^\circ \pm 5^\circ\text{C}$, as shown in Fig. 6-4. Using Eq. (6.3), the charge mobility in glass is about $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at that temperature.

This result enables us to estimate the density of localised states in glass, assuming the conduction of charge through the amorphous insulator occurs by a hopping mechanism. The mobility of charge in a solid with N_t trapping states per unit volume has been given

$$\mu \sim \frac{e \nu}{kT N_t} \exp - \frac{\Delta E}{kT} \quad (6.4)$$

where ΔE is the activation energy for conduction and ν is the jump frequency between traps ($\nu \sim 10^{13} \text{ s}^{-1}$). For $\Delta E = 0.6 \text{ eV}$, as determined from conduction measurements (see Fig. 6-5), the trap density is about 10^{16} cm^{-3} .

The above model for the conduction processes in glass is obviously oversimplified. The electrical properties of glass are not known in detail and must depend to some extent on the structure and composition of the particular glass under investigation. A hopping model has been suggested for the conduction in alkali-free glass (Gough et al. 1969); trapping states are thought to arise from local deviations in charge neutrality in the solid. This type of model may well be appropriate for the conduction in Corning 7059 glass, which contains few mobile ions. In fact, the trap density estimated in this way agrees closely with the value deduced from the surface charge measurements.

We can now discuss the charge transfer process in more detail: The metal-insulator contact is formed when the substrate is at a temperature above 100°C . The conductivity of Corning 7059 glass is sufficiently high at such temperatures for a transfer of electrons to occur, such that an equilibrium distribution of charges at the interface is obtained. When the sample cools to room temperature this distribution may change such as to maintain the equilibrium conditions. However, below about 80°C the conductivity is very low, so that effectively no further charge movement can occur. At room temperature, the charge at the interface may therefore not be in thermal equilibrium.

During the separation of the interface the charge distribution is taken still further out of equilibrium; as a result, the charge tends to flow back across the interface (see Sect. 3.2.2). However,

because of the low conductivity in the bulk of the insulator, only charges in surface states can tunnel back across the interface at separations up to about 1 nm. It was suggested in Section 3.2.2.1 that the resulting reduction in surface charge density may be up to an order of magnitude. The charge originally present at the metal-glass interface may therefore have been as high as $10^{12} \text{ e cm}^{-2}$ per eV of work function difference.

Our results can be compared with those of Davies (1967a) for Corning 7059 glass; the surface charging of glass by mechanical contact with bulk metal electrodes was attributed to electronic processes (see Sect. 3.2.5.3) and a value of 4.3 eV was suggested for the work function of Corning 7059 glass. Qualitatively, these results are in agreement with ours, but the charge densities are about an order of magnitude smaller in Davies' experiments. This difference may be due to the relatively small area of direct contact obtained between two bulk solids, the surfaces of which are (inevitably) rough on an atomic scale; on the other hand, the interfacial area between a thin film and a substrate may be greater than the geometrical area.

The value of the work function of Corning 7059 glass expected from our results (see Fig. 6-11) is about 4.6 eV. Considering the uncertainty in the values of the metal work functions, this value is in reasonable agreement with that of Davies (1967a); the effect of temperature on the charge distribution (discussed above) does not appear to be very significant. For comparison, the work function of borosilicate glass determined by photoelectric threshold measurements (Nelson 1963) is 4.6 eV.

6.2.3 Geometrical Factors in Adhesion Measurements

The electrostatic and van der Waals components of adhesion were calculated in Chapter 2 by considering the work done in separating two parallel surfaces against the adhesion forces. In the stripping experiments, however, the film is bent through a right angle as it is being separated from its substrate. The effect of this change in geometry on the theoretical expressions for the adhesion energy must be considered.

Van der Waals adhesion

Let us assume that the film is bent through a right angle, forming a quadrant of a cylinder of radius R , as shown in Fig. 6-12a. For simplicity, the Hamaker expression for the van der Waals component of adhesion (see Eq. (2.34)) may be used. The van der Waals force on an elementary strip of the film (of area δA) at a separation z from the substrate surface is

$$\delta F(z) = \frac{A_{ij}}{6z^3} \delta A \cos \alpha \quad (6.5)$$

where α is the angle between the film and substrate at the element considered; A_{ij} is the Hamaker constant for the two solids. The separation z is related to the angle α by the expression

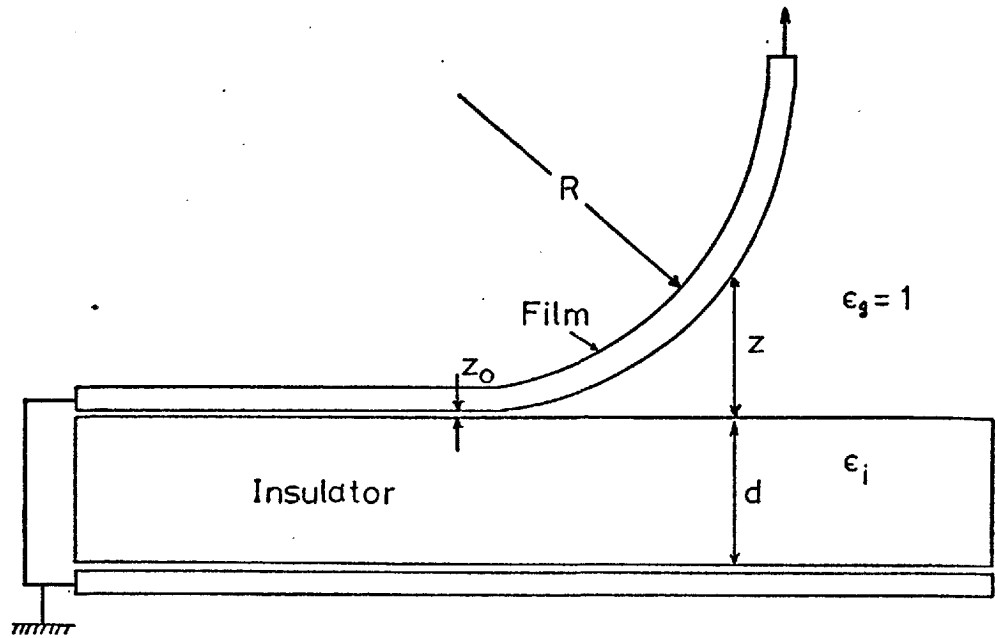
$$z = z_0 + R(1 - \cos \alpha) \quad (6.6)$$

where z_0 is the adhesion distance (see Fig. 6-12a).

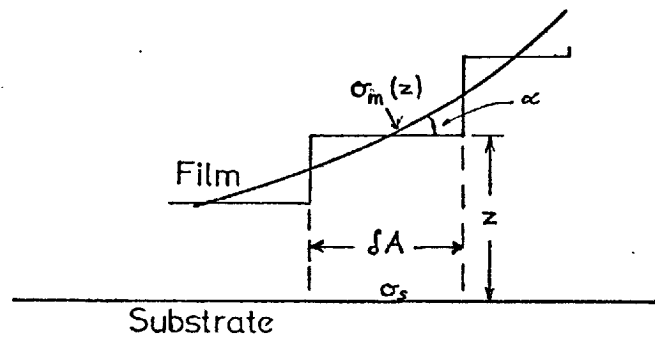
The total adhesion energy of the film is given by the work done in removing the film to infinity:

$$W_{vdW} = \int_{z_0}^{\infty} P(z) dz \quad (6.7)$$

where $P(z)$ is the adhesion force per unit area of the film at a separation z . It is apparent from Eq. (6.5) that the force



(a) Curvature of film during stripping



(b) Elementary 'parallel-plate' capacitor formed by the film and substrate

Fig. 6-12 Geometry of Film Stripping

on the film contributes to the adhesion energy, only if it has a non-zero component perpendicular to the substrate surface. The limits of integration in Eq. (6.7) should therefore be taken only between $z = z_0$ and $z = z_0 + R$; thus, from the above equations,

$$W_{\text{vdW}} = \int_{z_0}^{z_0+R} A_{ij} \frac{R - (z - z_0)}{6 z^3 R} dz \quad (6.8)$$

$$= \frac{A_{ij}}{12 z_0^2} \left(\frac{R}{z_0 + R} \right) \quad (6.9)$$

This expression differs from that for the parallel plate geometry (Eq. (2.34)) by the factor $R/(z_0 + R)$; the two cases converge if the value of R is much greater than the adhesion distance z_0 . This is to be expected to occur since the range of dispersion forces is very short: most of the work done in separating the film from the substrate is due to the area of the film closest to the substrate; this area approximates to a plane, since the radius of curvature of the film during stripping is much greater ($\sim 10 \mu\text{m}$) than the adhesion distance ($< 0.5 \text{ nm}$). The precise shape of the film during stripping is therefore unimportant as far as the van der Waals adhesion energy is concerned.

Electrostatic adhesion

Consider, as above, the cylinder-plane geometry for a film stripped from an insulating substrate of thickness d ; as in Section 2.2.2.4 we assume that the insulator is initially sandwiched between two metal film which are electrically connected. The insulator surface is charged to a constant density σ ; the charge induced on the film, $\sigma_m(z)$, during stripping decreases with increasing separation from the substrate. The electrostatic force attracting the film to the substrate at a separation z is given by

$$F_z = \frac{1}{2\epsilon_0} \int_S (\underline{E} \cdot \underline{D}) \cos \alpha \, dS \quad (6.10)$$

the integration being taken over the film area S ; $\underline{E}$ and $\underline{D}$ are the electric field and displacement at the film surface. The electric field can be regarded as being approximately uniform in the region where the separation z is small compared with the radius of curvature of the film (R). For this region, the system may be regarded as consisting of a series of elementary parallel plate capacitors (see Fig. 6-12b); the force exerted on an area δA of the film towards the substrate is then, using Eq. (6.10)

$$\delta F_z = \frac{1}{2\epsilon_0} \left(\frac{\sigma_m(z)}{\cos \alpha} \right)^2 \delta A \quad (6.11)$$

As in Section 2.2.2.4, the charge induced on the film can be related to the constant surface charge on the insulator:

$$\sigma_m(z) = \sigma_s \cos \alpha \frac{2z_0 + d/\epsilon_i}{z + z_0 + d/\epsilon_i} \quad (6.12)$$

The work done in removing the film to a separation z against the electrostatic forces is given by

$$W_{el}(z) = \frac{\sigma_s^2}{2\epsilon_0} \int_{z_0}^z \left(\frac{2z_0 + d/\epsilon_i}{z + z_0 + d/\epsilon_i} \right)^2 dz \quad (6.13)$$

$$= \frac{\sigma_s^2}{2\epsilon_0} (2z_0 + d/\epsilon_i) \left(\frac{z - z_0}{z + z_0 + d/\epsilon_i} \right) \quad (6.14)$$

This expression holds for small separations $z \ll R$; if the insulator thickness is large, i.e. $z \ll d/\epsilon_i$, then Eq. (6.14) reduces to

$$W_{el}(z) = \frac{\sigma_s^2}{2\epsilon_0} z \quad (6.15)$$

An estimate of the electrostatic work of adhesion (W_{el}) can be obtained from Eq. (6.14), using the uniform field approximation. The electrostatic forces cease to contribute to the adhesion of the film at a separation exceeding the value $z = z_0 + R$; thus, from Eq. (6.14) with $R \gg z_0$,

$$W_{el} = \frac{\sigma_s^2 d}{2 \epsilon_i \epsilon_0} \left(\frac{R}{R + d/\epsilon_i} \right) \quad (6.16)$$

This expression is obviously very approximate since the electric field is uniform only at separations which are much smaller than R ; nevertheless, Eq. (6.16) shows the importance of the film-substrate geometry in determining the electrostatic work of adhesion. Comparison with Section 2.2.2.4 shows that W_{el} for the cylinder-plane geometry differs by a factor $R/(R + d/\epsilon_i)$ from the parallel-plate case (Eq. (2.82)).

Equation (6.16) has been used in Figure 6-13 to plot W_{el} as a function of the ratio $\epsilon_i R/d$ for various values of the surface charge density σ_s . In the stripping experiments, the radius of curvature of the film (see Sect. 6.1.6) is smaller than the effective thickness of the glass substrate ($d/\epsilon_i = 0.14$ mm); the work of adhesion is reduced by about an order of magnitude from the theoretical maximum (parallel-plate case).

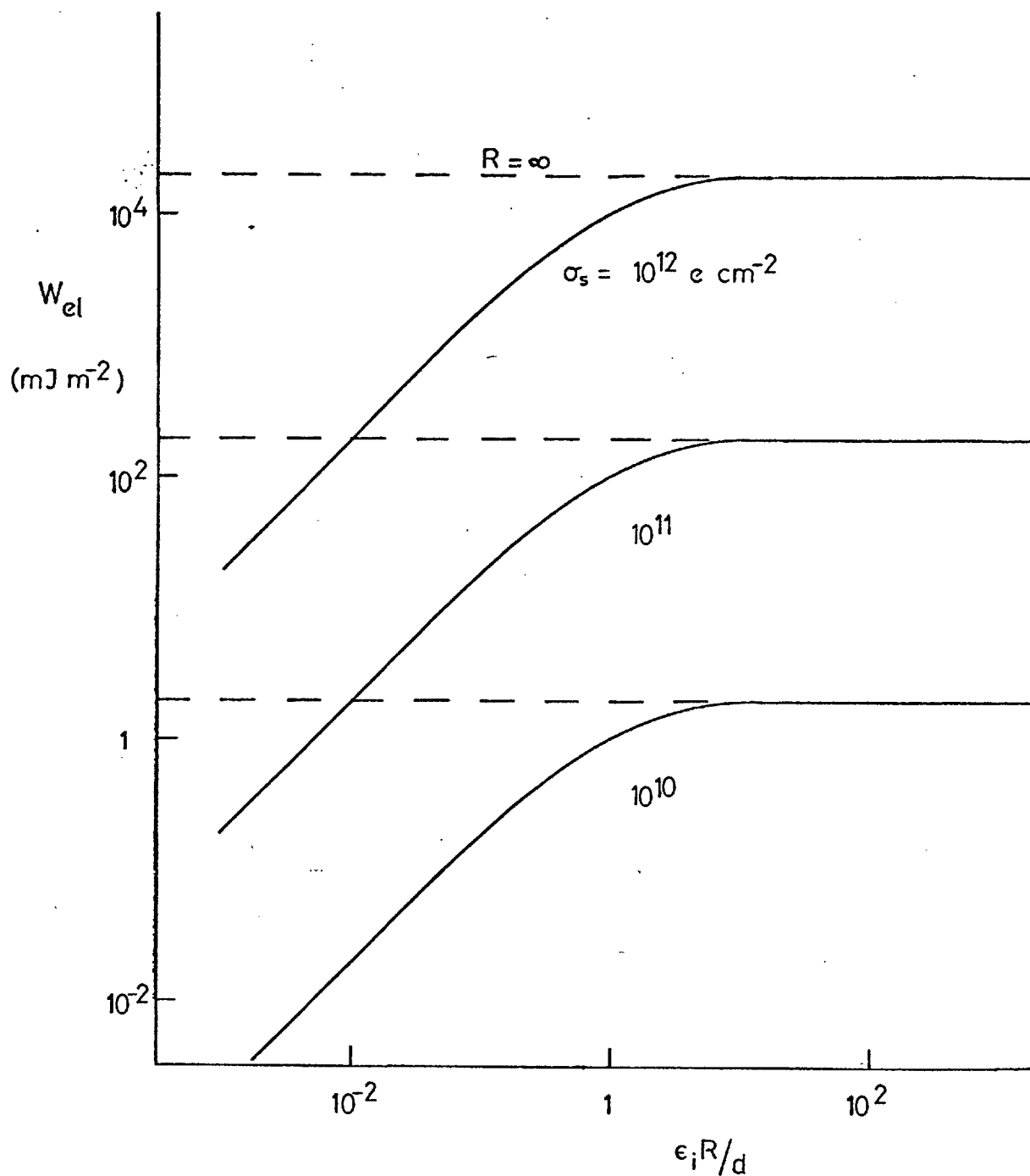


Fig. 6-13 Dependence of Electrostatic Adhesion on Film Curvature, (R)
 plot of W_{el} against $\epsilon_i R/d$ for $d/\epsilon_i = 0.1 \text{ mm}$
 at various charge densities σ_s .

6.2.4 Comparison between Theoretical and Experimental Adhesion

On the basis of the preceding sections we can now make a detailed comparison between the experimental results and the theoretical predictions for the adhesion of thin films on glass. The adhesion parameters are compared in Table 6-2: the van der Waals adhesion energy was calculated in Chapter 2 from the continuum approximation; the electrostatic work of adhesion (W_{el}) has been determined from the measured charge densities (see Table 6-1) with the geometrical modifications discussed in Sect. 6.2.3. The experimental stripping energies (Table 6-1) are shown for comparison.

According to the conclusions of Section 6.2.1, the reversibility of the stripping process implies that the stripping energy is equal to the total adhesion energy of the film. In fact, the stripping energies shown in Table 6-2 are about three times greater than the corresponding van der Waals energies. On the other hand, the relative values for gold, silver and copper films are similar in theory and experiment: the values for copper films are about 60 % of those for gold and silver films.

The electrostatic contribution estimated for the parallel-plate case reaches up to 40 % of the van der Waals energy for silver and copper films. However, in practice, the geometry of the film during stripping is such as to reduce the electrostatic work of adhesion (see Fig. 6-13). The radius of curvature of the films is between 10 and 100 μm (see Sect. 6.1.6); as shown in Table 6-2, the electrostatic contribution is then reduced to a few percent of the van der Waals adhesion.

Table 6-2

Adhesion on Corning 7059 Glass

Film	<u>Au</u>	<u>Ag</u>	<u>Cu</u>
Stripping energy (mJ m ⁻²)	1100 ± 200	1000 ± 200	750 ± 50
Van der Waals energy (mJ m ⁻²)	390	310	185
Electrostatic	R = ∞		
work of adhesion	100μm		
(mJ m ⁻²)	10μm		
	5	115	80
	2	48	33
	0.4	8	6

There are two possible ways of explaining the discrepancy between the experimental and theoretical results: either the theory is incorrect or the interpretation of the experimental results is invalid. It is frequently argued that adhesion measurements involving a separation of the interface cannot be interpreted in terms of the adhesion forces between the two materials. The reason is that, on breaking the bonding between the materials, a part of the work done on the system is dissipated irreversibly (see Sect. 4.1); secondly, it is held (e.g. Bickerman 1968) that the fracture does not always occur at the interface, but in the weaker of the two materials, and that therefore the theories of adhesion are irrelevant to the experiment.

Our results for thin films on glass have shown that the stripping process is practically reversible (see Sect. 6.2.1) and that, therefore, the stripping energy can be equated with the adhesion energy. The observations of the substrate surface on a microscopic scale (see Sect. 6.1.6) showed that adhesive break occurs over most of the interfacial area. More sophisticated apparatus would be required to determine the locus of failure on an atomic scale. The contamination of the substrate surface (in high vacuum) makes the interface the weakest region, and a fracture is most likely to occur in the interfacial plane. Our measurements are therefore directly related to the adhesion of the film.

The reason for the disagreement between theory and experiment must thus be of a theoretical nature: either the theories of adhesion due to electrostatic and van der Waals forces (as outlined in Chap. 2) are too inaccurate, or there is a significant contribution due to a different adhesion mechanism.

The electrostatic contribution to the adhesion of the film is calculated from the charge remaining on the substrate after

separation of the interface. However, in Section 6.2.2 it was concluded that during film stripping the charge may have been reduced by an order of magnitude by the time the separation exceeds 1 nm. The work done in the separation to 1 nm has therefore been underestimated by two orders of magnitude, but the effect on the total electrostatic work of adhesion is negligible (see Eq. (6.16)). A significant effect could arise from a discharge at greater separations (e.g. Paschen discharge at a few μm); in fact, this effect lies at the basis of the explanation of electrostatic adhesion due to Deryagin and co-workers (see Deryagin et al. 1957). However, this kind of discharge is unlikely to occur in a high vacuum (see Sect. 3.2.2.2) and was not observed in our experiments (see Sect. 6.1.5).

The calculation of the van der Waals adhesion is based on the continuum approximation, using an idealised structure for the glass surface and the metal film. This method cannot be accurate to more than an order of magnitude; in fact, the comparison with the summation method of calculating the adhesion on mica substrates (see Sect. 2.1.2.1) showed that the continuum approximation tends to underestimate the adhesion. The van der Waals adhesion to glass may therefore be expected to be somewhat stronger than the values in Table 6-2 suggest.

It was shown in Section 2.1.2.1 that the van der Waals adhesion is largely due to the surface atoms and ions. The structure and composition of the glass surface is therefore very important. Any surface contamination will influence the van der Waals (and possibly, the electrostatic) adhesion. This may be the reason for the large variations in stripping energy and charge over a given sample. The contamination effect could thus swamp any dependence of the adhesion on the parameters of film deposition and stripping.

6.2.4.1 Chemisorption

In this section the possibility of short-range interactions contributing to the adhesion of the film are discussed. Short-range (chemical) forces between two atoms arise from the overlap of the electron distributions of the atoms; the strength of the resulting bond depends on the specific properties of the interacting electrons. The binding energy of chemisorbed atoms or molecules on solid surfaces is typically several electron-volts.

A simple description of the chemisorption of atoms on the surfaces of solids can be given in terms of solid state theory (see Hayward and Trapnell 1964). It is supposed that surface electron states (or 'dangling bonds') exist on a surface; the origin of surface states is discussed, for example, by Many et al. (1965). An atom can be chemisorbed by a transfer of an electron to or from such a state, if it is available. The chemisorption properties are thus determined by the number of available surface states, rather similar to the processes at metal-semiconductor interfaces (see Sect. 3.2.4). For example, surfaces with high densities of electron states, such as metals (especially those of transition elements), tend to chemisorb readily.

Chemisorption thus appears to be very similar to the process leading to electrostatic adhesion. The difference is that chemisorption is the result of the specific ('chemical') interactions between two atoms, electrostatic adhesion is a macroscopic phenomenon, based on classical (continuum) electrostatics. However, for particular cases the two descriptions overlap: the electrostatic adhesion arising from the transfer of electrons from the surface states of one solid into those of the other, can be regarded as the macroscopic analogue of chemisorption.

In a high vacuum (~ 1 μ torr) the surfaces of glass are covered with an adsorbed layer of gases, especially chemisorbed oxygen and water vapour (see Holland 1964). A thin film which is evaporated on to this surface is thus deposited on to the contaminant layer and cannot therefore be bound to the substrate by chemical forces. This conclusion is confirmed by our experimental results, which indicate adhesion values that are typical for van der Waals bonding (≤ 0.5 eV per atom). Furthermore, the stripping process could not be reversible if chemical forces contributed significantly to the adhesion of the film.

If the substrate surface were completely 'clean', then the incident atoms could be bound chemically, assuming that chemisorption sites were available. This may occur if the incident atoms have sufficiently high energy to displace the contaminant layer and to be themselves chemisorbed. A process of this kind is possible for sputtered atoms which have energies of several electron volts when incident on the substrate (Stuart et al. 1969); the incident atoms are therefore implanted into a surface layer of the substrate. As a result, chemical bonds may be formed, so that the sputtered film adheres strongly to the substrate.

Our experiments (Sect. 6.1.7) showed a high stripping energy ($\approx 5 \text{ J m}^{-2}$) for sputtered films on glass. The stripping process is not reversible in this case so that an interpretation of the results in terms of the adhesion of the film is not possible (in any case, adhesion is difficult to define for a diffuse interface). However, the results suggest a high binding energy (2 to 3 eV per atom), in the region of chemical bonding.

6.2.4.2 Comparison with previous measurements

The adhesion of gold films on soda glass substrates has been measured by Chapman (1969, 1971) using the stripping method. At rates of stripping in the range of 0.1 to 10 mm min^{-1} , the stripping energy was found to lie in the region of 500 mJ m^{-2} . Our measurements for gold films on borosilicate glass gave rather higher values (see Table 6-2) under similar conditions. A preliminary measurement of the adhesion of silver films on soda glass gave a stripping energy of $800 \pm 200 \text{ mJ m}^{-2}$ and charge density of $10^{10} \text{ e cm}^{-2}$ (electrostatic adhesion $< 1\%$). The difference in results may be due to surface contamination remaining after cleaning the substrates; the adhesion is very sensitive to surface contamination, as pointed out earlier.

Benjamin and Weaver (1961) investigated the adhesion of metal films to glass by the scratch test. These measurements indicated a weak adhesion for gold, silver and copper films (increasing in that order); an aging effect was observed in the case of silver and copper, the 'scratch' adhesion rising to very high values. This aging was attributed to the formation of an intermediate oxide layer at the interface (see Kamovski and Estill 1964), so that the film is bound increasingly by chemical forces.

The adhesion was measured in this work for films up to three months after deposition. No aging effect was observed for Au, Ag and Cu films - this result is in agreement with those obtained by the pull test (Butler et al. 1970, Lin 1971). The aging effect observed by the scratch test may be a consequence of oxidation of the outer film surface.

6.2.5 Summary

In the above sections the adhesion of metal films (Au, Ag and Cu) to glass substrates was discussed in the light of the experimental results. It was found that the work done in stripping a film has two major components: the work done against electrostatic forces, dependent on geometrical factors, and the contribution due to van der Waals forces. Although, in theory, the electrostatic adhesion reaches up to about 100 mJ m^{-2} , for the specific conditions of our experiments, the work done against electrostatic forces is only a small percentage of the stripping energy ($\sim 1 \text{ J m}^{-2}$). Chemical forces do not contribute significantly to the adhesion of the film, because of the presence of contamination at the interface. The largest component of adhesion is therefore due to van der Waals forces. The theoretical values of van der Waals adhesion are much smaller than the experimental values; this discrepancy is attributed to the inaccuracy of the theoretical calculations, since the stripping method was found to give a direct measure of thin film adhesion.

The charge transferred across the film-glass interface arises from electronic processes. The details of the charge transfer mechanism require further investigation, particularly since the transferred charge could not be measured directly. However, the charge effect can be explained tentatively by a process involving the localised states in a surface layer of the substrate.

6.3 Adhesion to Ionic Crystals

6.3.1 Results for Mica Substrates

The adhesion of thin films of gold, silver and copper to mica substrates was investigated by the stripping method. The films were evaporated at temperatures up to 300°C on to air-cleaved mica surfaces ((001) plane of mica parallel to surface). Electron diffraction showed that the films were orientated to some degree (diffraction pattern of discrete spots with hexagonal symmetry) with the (111) plane of the metal parallel to the substrate surface.

The films were stripped from the mica substrates using the procedure described in Section 5.3. In Figure 6-14 the results are shown for the stripping energy plotted as a function of the stripping speed over the range of 0.5 to 100 mm sec^{-1} . The values of stripping energy lie in the range of 1 to 3 J m^{-2} , with no obvious dependence on the stripping speed.

There are several indications that the films are stripped from their substrates with a thin layer of mica adhering to them. Over a given substrate the stripping force has discontinuous jumps, typically by some 50 %; some specimens showed a small periodic variation in stripping force. The films tended to rupture along cleavage steps on the substrate surface.

Direct observations of stripped films in the scanning electron microscope showed that a thin layer of mica is frequently cleaved off with the film. On the other hand, over some areas of the substrate only the film is stripped; for example, a stripped silver film showed oxidised areas on the surface after prolonged exposure to the atmosphere, while some areas had remained unaffected.

As with glass substrates, some experiments were performed in which the same area of a film was re-stripped several times. For a gold film the stripping energy was found to drop from about 4 J m^{-2} to 1 J m^{-2} on first re-stripping.

Extensive measurements were carried out of the electrical charge on the substrate surfaces. The mica surfaces were electrically neutral after cleavage in air; vacuum cleavage generally resulted in positive charging ($> 10^{10} \text{ e cm}^{-2}$). The charges remaining on the substrate after removing the films were always positive, varying in density between 10^{10} and $5 \times 10^{11} \text{ e cm}^{-2}$. Strong variations were found in the charge density over a given substrate, with a tendency for thinner substrates (thickness $< 100 \text{ }\mu\text{m}$) to be more highly charged. The charge densities did not vary systematically with the deposited film or the speed of stripping.

6.3.2 Discussion

The cleavage properties of mica have been investigated by several workers (see Bowden and Tabor 1964). The cleavage energy has been measured by splitting mica sheets; Orowan (1933) determined the cleavage energy of mica in vacuo to be in the region of 5 J m^{-2} , whereas when measured in air (atmospheric pressure) it is only 350 mJ m^{-2} (see Bailey 1957). This reduction in cleavage energy is believed to be due to gases trapped between sheets of the mica crystal when exposed to the atmosphere.

In the stripping experiments the externally applied force acts on both the film and the substrate. Thus, if the cleavage energy of mica is less than the adhesion energy of the film, then a layer of mica may be split off with the film, the fracture thus

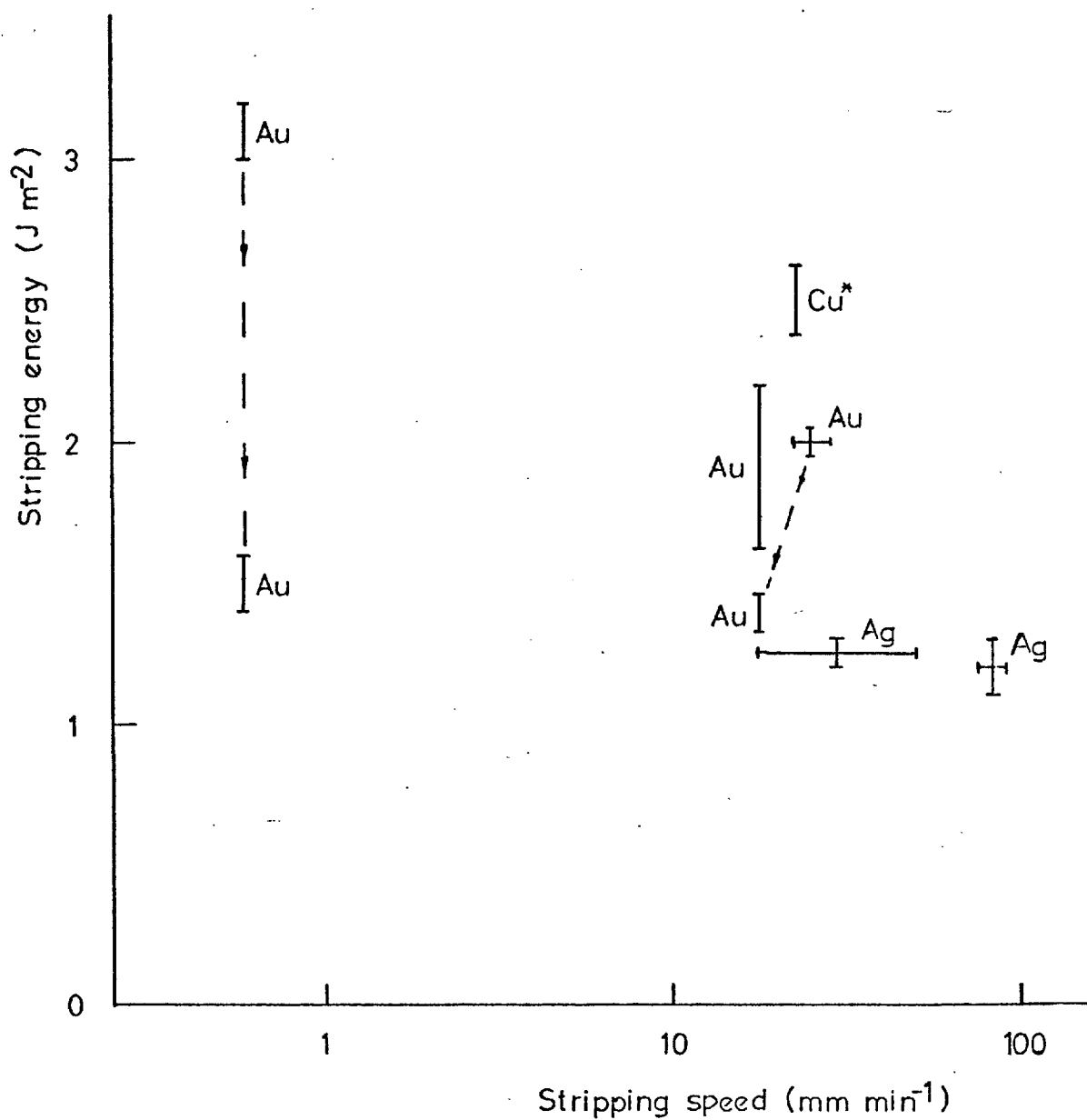


Fig. 6-14 Stripping of Films from Mica
plot of stripping energy against speed
(* tape-backed film)

occurring in the substrate. For our experiments, an adhesive fracture is more likely if the adhesion energy of the film is less than 5 J m^{-2} . In fact, the theoretical calculations of the van der Waals adhesion of Au, Ag and Cu films (Sect. 2.1.2.1) give values around 1 J m^{-2} , as shown in Table 6-3. An adhesive fracture would therefore be expected to occur unless the electrostatic adhesion is very large. However, the mica surface has a large number of cleavage steps (as observed above) at which the cleavage energy may be reduced by the presence of trapped gases. This fact may explain why a layer of mica is split off over some areas during film stripping: over these areas the stripping force has an additional component for bending the mica layer which is cleaved off. The lowest values of stripping energy (around 1 J m^{-2}) will therefore be observed over areas of adhesive fracture; these values are shown in Table 6-3.

The cleavage plane of mica contains a hexagonal arrangement of potassium ions, as shown in Figure 2-4; if more than half of the K^+ sites (about $4 \times 10^{14} \text{ cm}^{-2}$) on the cleavage surface are occupied, then the surface has a net positive charge. Metsik (1960) has observed patches of opposite charge ($\sim 10^{11} \text{ e cm}^{-2}$) on the vacuum cleaved surface of mica, indicating a variation in the number of surface K^+ ions. On the other hand, our experiments gave only positive charges on mica after cleavage in a vacuum of 1 μtorr . The spatial resolution of the charge probe is such that patches of opposite charge of 1 mm^2 area could easily be detected. The absence of charge on air-cleaved surfaces may be a result of gas adsorption (especially hydroxyl ions) or of gas discharge between the surfaces during cleavage (see Sect. 3.2.2.2).

Table 6-3Adhesion on Mica

Film:	<u>Au</u>	<u>Ag</u>	<u>Cu</u>
Stripping energy (mJ m^{-2})	1400 ± 200	1200 ± 200	[2500]*
Van der Waals energy (mJ m^{-2})	1360	1090	970
Charge density ($10^{-10} \text{ e cm}^{-2}$)	1 to 50		
Electrostatic work of adhesion (mJ m^{-2})	5 to 100		

* tape-backed film

The presence of positive charges on the mica surface is thus to be expected if the stripping process causes a cleavage of the substrate. Surprisingly, no significant difference in charging was observed on areas of adhesive stripping. Since no dependence on the material of the film was observed, the charge transfer between the film and substrate is unlikely to be due to electrons. The surface charging may therefore be an ionic effect, due to the preferential adsorption of mobile ions (e.g. K^+ ions from mica) at the surface.

Whatever the mechanism of charging, the existence of a net electrical charge on the mica surface suggests that there is an electrostatic contribution to the stripping energy. Assuming the surface charge remains constant during the stripping of the film, then the electrostatic work of adhesion, calculated from Eq. (6.16), lies in the range of 5 to 100 $mJ\ m^{-2}$. As shown in Table 6-3, this contribution represents up to about 10 % of the stripping energy.

The cleavage of mica has been shown to be a reversible process (see Bowden and Tabor 1964); the cleavage energy is reduced by the adsorption of gases on the mica surfaces. Assuming that, similarly, the film stripping process is reversible (in the absence of gas adsorption), then the stripping energy can be equated with the adhesion energy of the film to mica. The stripping energies are within about 10 % of the calculated values of van der Waals adhesion (see Table 6-3); the electrostatic component does not affect this agreement significantly.

6.3.3 Adhesion to Rocksalt

The adhesion of gold, silver and copper films to air-cleaved rocksalt crystals was investigated. The substrate surface, prepared by cleavage parallel to the (100) plane, contains a high density of cleavage steps. It was found as a result to be extremely difficult to prevent the unsupported films from breaking at the cleavage steps during stripping; even at the lowest speeds of stripping ($2 \mu\text{m sec}^{-1}$) the stripping experiments were usually unsuccessful. (Similar difficulties were encountered with metal films on substrates of magnesium oxide crystals) Most of the stripping results were therefore obtained with films which were supported by an adhesive tape. The stripping energies are consequently rather high (see Table 6-4) and, as discussed in Section 4.1, the values are not a direct measure of the adhesion of the films to rocksalt.

Reliable values were obtained for the stripping energy of an unsupported copper film, as shown in Table 6-4. Gold and silver films appeared to have weak adhesion so that they could have been stripped successfully in the absence of cleavage steps.

The rocksalt surfaces were practically uncharged ($< 10^6 \text{ e cm}^{-2}$) after cleavage in air. For all three metal films, the charge remaining on the substrates after stripping was normally positive, ranging from 10^9 to $4 \times 10^9 \text{ e cm}^{-2}$. The surface charge tended to decay at a rate of about 15 % per hour at room temperature.

6.3.4 Discussion

The high density of cleavage steps resulting from the cleavage of rocksalt crystals created serious experimental problems, although relatively clean surfaces were obtained in this way. In the cases

Table 6-4

Adhesion on Rocksalt

Film	<u>Au</u>	<u>Ag</u>	<u>Cu</u>
Stripping energy (mJ m ⁻²)	[2000]*	[2500]*	400 - 700
Van der Waals energy (mJ m ⁻²)	555	406	218
Charge density (10 ⁻¹⁰ e cm ⁻²)		0.1 to 0.3	
Electrostatic work of adhesion (mJ m ⁻²)		≤ 0.5	

* tape-backed film

where the film could be stripped, the steps cause a mechanical interlocking between film and substrate, thus raising the stripping energy. The values obtained for the stripping energy of unsupported films will therefore be higher than the adhesion energy. In fact, the stripping energy of copper films is about twice the calculated value for the van der Waals adhesion (see Table 6-4). The electrostatic contribution, as deduced from the charge measurements (and using Eq. (6.16)), is negligible ($< 1 \text{ mJ m}^{-2}$).

The surface energy of rocksalt crystals has been measured by gas adsorption methods (Benson et al. 1956) to be 276 mJ m^{-2} . The cleavage energy ($= 2 \times \text{surface energy}$) is therefore comparable with the stripping energy for unsupported films. At cleavage steps on the rocksalt surface a layer of the substrate may therefore be stripped off with the film, as in the case of mica substrates.

The cleavage of rocksalt in vacuo is known to result in surface charging (Ryan and Grossman 1968); the electrical charge may be associated with lattice defects (vacancies, dislocations) which are created by the cleavage (Bethge 1969). In our experiments, no charging was observed before film deposition on to air-cleaved crystals. The charge on the substrates observed after film stripping could therefore arise from a cleavage, rather than from a charge transfer between the film and substrate. This conclusion is supported by the fact that the magnitude of the surface charge is not dependent on the metal, as would be expected for an electron transfer across the interface.

6.3.5 Summary

The adhesion of evaporated metal films to ionic crystals has been investigated. The substrates of mica and rocksalt were prepared by cleavage in the atmosphere; this procedure provided relatively clean, uncharged surfaces, but resulted in experimental difficulties due to cleavage steps on the surfaces. For metal films on mica, the film stripping tended to cause a cleavage of the crystalline substrate, rather than an adhesive fracture; the films on rocksalt crystals tended to break at cleavage steps. The experimental adhesion results for mica substrates were found to be in close agreement with the theoretical values of the van der Waals adhesion. For rocksalt substrates most results were obtained with tape-backed films so that the interpretation of the adhesion of the films is only tentative.

The charge remaining on ionic crystals after removing the films was not related to the material of the film. In most cases, this was due to the cleavage of the substrate during film stripping, which, in the case of mica, caused high charge densities. The resulting electrostatic adhesion is up to about 100 mJ m^{-2} , or 10 % of the total adhesion energy. For rocksalt substrates the electrostatic component is negligible.

CHAPTER VII

CONCLUSIONS

It has been the aim of this work to investigate the importance of electrical charge effects in the adhesion of thin films. A theoretical description of electrostatic adhesion shows that the charge transferred across the interface between two solids can give rise to strong adhesion forces. In the case of a contact between a metal and a semiconductor, the charge transfer can be described in terms of the electronic properties of the solids; for a metal-insulator contact this may not always apply, and ionic effects can be important. Generally, the charge transfer is unlikely to exceed a magnitude of $10^{13} \text{ e cm}^{-2}$ which, depending on the type of solids in contact, results in an electrostatic adhesion energy up to a few 100 mJ m^{-2} . The theoretical calculations of the van der Waals adhesion predict values which are of the same order as, or greater than, the electrostatic adhesion for metal films on ionic substrates.

The measurements for metal films (gold, silver and copper) on glass substrates show that the stripping method gives a direct measure of the adhesion of the films. This fact makes the stripping method, with its extreme simplicity, a useful way of measuring the adhesion of thin films which are weakly bound to their substrates. On the other hand, the adhesion results for metal films on ionic crystals cannot always be interpreted unambiguously, since a thin layer of the crystalline substrate may be cleaved off with the stripped film.

In all measurements of the electrical charge on insulating substrates it was found that the substrate surfaces were charged after film stripping. The charge transfer between metal films and Corning 7059 glass substrates was explained in terms of electronic processes. The resultant electrostatic adhesion can (in theory) exceed 100 mJ m^{-2} , but for the practical geometry of the experiments the electrostatic work of adhesion is only a small percentage of the total adhesion energy. The crystalline substrates (mica and rocksalt) were, in most cases, charged as a result of cleavage; the electrostatic component was significant (a few percent) only for mica substrates.

The van der Waals forces give rise to the largest component of the adhesion for the films and substrates investigated in this work. The calculation of the van der Waals forces underestimates the adhesion glass and rocksalt, but gives good agreement with the experimental results for mica. The discrepancy is attributed to the inaccuracy of the calculations and to the presence of contamination at the interface; accurate theoretical predictions are not possible unless the structure of the interface is known in detail. Chemical forces were found to increase the adhesion to glass substrates, only for films deposited by sputtering.

As a practical application, the electrostatic adhesion of thin films appears to offer a possibility of controlling the adhesion through the electronic properties of the film and substrate. Although theoretically possible, for the materials studied in this work, the electrostatic component is far too small to change the total adhesion significantly. An effective way of improving adhesion could be obtained by providing a chemical interaction between the film and substrate (see Mattox 1965).

CHAPTER VIII

FURTHER WORK

8.1 Charge Transfer Mechanisms

In this work some insight has been gained into the mechanisms of charge transfer between metals and insulators. In the case of glass substrates, it was shown that electronic processes are responsible for the surface charging. However, it was not possible in our experiments to measure directly the contact p.d. or the charge at the interface. If direct measurements were possible, further information could be obtained about the electronic states at the insulator surface.

In certain cases this information can be deduced from experiments with thin film insulators. For example, the space charge layer at the insulator surface has a capacitance which can be determined from measurements on a metal-insulator-metal thin film sandwich structure (see Simmons et al. 1970).

Further possibilities can be explored with the use of metal-insulator (thin film) - semiconductor structures (MIS). An electrical charge in the insulator will induce a charge on the semiconductor surface; this results in a change in the surface conductivity of the semiconductor and in the capacitance of the device (see Grove et al. 1965, Kalter et al. 1971). The change in surface conductivity on removing the metal film from a MIS structure can be used to deduce the electrostatic adhesion of the film (see Krotova et al. 1967).

We have performed some preliminary experiments with evaporated metal films on substrates of oxidised silicon (1 μm oxide layer on n-type silicon single-crystal: samples kindly provided

by Dr. M. Pepper, Plessey). The charge remaining on the substrate after film stripping was found to depend on the metal in magnitude (up to $5 \times 10^{11} \text{ e cm}^{-2}$) and in polarity (positive for gold, negative for silver films); the corresponding electrostatic adhesion is about 1 % of the stripping energy ($\approx 800 \text{ mJ m}^{-2}$). For charge densities exceeding $10^{12} \text{ e cm}^{-2}$, the electrostatic component could raise the adhesion of the film substantially; this effect could thus be of importance in the fabrication of MIS devices.

8.2 Adhesion Measurements

The adhesion between two solids depends strongly on the characteristics of the interface. In our work this fact was apparent through the effect of contamination of the substrate surface. A great deal of information about adhesion could be gained from a detailed knowledge of the structure and composition of the substrate surface and the deposited film. By experimentation in ultra-high vacuum the surfaces can be characterised chemically (by Auger spectroscopy) and structurally (by LEED); the adhesion of discontinuous films can be measured (by the vibration method, see Sect. 4.1.2) to obtain information about adhesion in relation to the structure of the interface and the nucleation properties of thin films.

PUBLICATIONS

The following papers were published, or are about to be published, on the work for this thesis and are included as part of this thesis:

- (1) 'Charge Effects in Thin Film Adhesion'
(1972) Thin Solid Films 13, 157
(with B.N. Chapman)
- (2) 'Charge Effects at the Film-Substrate Interface'
(1973) to be published in 'Vacuum'
(with B.N. Chapman)

REFERENCES

- Anderson J.C. (1972) Thin Solid Films 12, 1
- Arridge R.G.C. (1967) Brit. J. Appl. Phys. 18, 1311
- Bailey A.I. (1957) Proc. 2nd Cong. on Surface Activity, Vol. 3, p. 406,
(London, Butterworth)
- Bauser H., Klöpfer W. and Rabenhorst H. (1970) Adv. Static
Electricity 1, 2
- Beams J.W., Freazeale J.B. and Bart W.L. (1955) Phys. Rev. 100, 1657
- Belser R.B. and Hicklin W.H. (1956) Rev. Sci. Instrum. 27, 293
- Benjamin P. (1898) 'A History Of Electricity' (N.Y., Wiley)
- Benjamin P. and Weaver C. (1959) Proc. Roy. Soc. A 252, 418
- (1960) *ibid* A 254, 163
- (1960a) *ibid* A 254, 177
- (1961) *ibid* A 261, 516
- (1963) *ibid* A 274, 267
- Benson G.C. and Claxton T.A. (1968) J. Chem. Phys. 48, 1356
- Benson G.C., Schreiber H.P. and van Zeggeren F. (1956)
Canad. J. Chem. 34, 1553
- Bethge H. (1969) J. Vac. Sci. Technol. 6, 460
- Bickerman J.J. (1968) 'The Science of Adhesive Joints' (N.Y., Academic Press)
- Böhme G., Kling W., Krupp H., Lange H. and Sanstede G. (1964)
Z. Angew. Phys. 16, 486
- Böhme G., Krupp H. and Schnabel W. (1969) in 'Molecular Processes on
Solid Surfaces' p. 611, ed. E. Drauglis (N.Y., McGraw Hi.
- Boksenberg A., Boyd R.L.F. and Jones I.C. (1968) Nature 220, 556
- Born M. and Mayer J.E. (1932) Z. Phys. 75, 1
- Bowden F.P. and Tabor D. (1964) 'Friction and Lubrication of Solids'
Part II (O.U.P.)
- Bredov M.M. and Kshemianskaia I.Z. (1957) Sov. Phys. - Tech. Phys. 2, 844

- Brindley E.W. and Hoare E.E. (1935) Proc. Roy. Soc. A 152, 342
- Brown R. (1970) in 'Handbook of Thin Film Technology' Ch. 6, eds. L.I. Maissel and R. Glang (N.Y., McGraw Hill)
- Butler D.W., Stoddart C.T.H. and Stuart P.R. (1970) J. Phys. D: Appl. Phys. 3, 877
- (1971) in 'Aspects of Adhesion' Vol. 6, p. 55, ed. D.J. Alner (University of London Press)
- Campbell D.S. (1970) in 'Handbook of Thin Film Technology' Ch. 12, eds. L.I. Maissel and R. Glang (McGraw Hill, N.Y.)
- Casimir H.B.G. and Polder D. (1948) Phys. Rev. 73, 360
- Challande R.F. (1970) Adv. Static Electricity 1, 156
- Chapman B.N. (1969) Ph.D. Thesis, Imperial College, London
- (1971) in 'Aspects of Adhesion' Vol. 6, p. 43, ed. D.J. Alner (Univ. London Press)
- Cohen M.H. (1970) J. Non-Cryst. Solids 2, 432
- Cowley A.M. and Sze S.M. (1965) J. Appl. Phys. 36, 3212
- Cunningham R.G. and Hood H.P. (1970) J. Colloid Interf. Sci. 32, 373
- Dalgarno A. (1967) Adv. Chem. Phys. 12, 143
- Davies D.K. (1967a) IPPS Conf. Ser. No. 4, 'Static Electrification' p. 29 (London, IPPS)
- (1967b) J. Sci. Instrum. 44, 521
- (1969) J. Phys. D: Appl. Phys. 2, 1533
- (1970) Adv. Static Electricity 1, 10
- de Boer J.H. (1936) Trans. Faraday Soc. 32, 10
- Debye P. (1920) Phys. Z. 21, 178
- Deryagin B.V. (1955) Research 8, 70
- Deryagin B.V., Aleinikova I.N. and Toporov Y.P. (1968) Powder Technology 2, 154
- Deryagin B.V., Krotova N.A., Karassev V.V. and Kirillova Y.M. (1957) Proc. 2nd Int. Cong. on Surface Activity, Vol. 3, p. 417 (London, Butterworth)

- Deryagin B.V. and Landau L. (1941) *Acta Physicochim.*, USSR, 14, 633
- Deryagin B.V. and Metsik M.S. (1960) *Sov. Phys. - Solid State* 1, 1393
- Deryagin B.V. and Smilga V.P. (1960) *Proc. 3rd Int. Cong. on Surface Activity*, Vol. 2, Sect. B, p. 349
(1967) *J. Appl. Phys.* 38, 4609
- Deryagin B.V. and Zimon A.D. (1961) *Kolloidn. Zh.* 23, 544
- Duke C.B. (1969) 'Tunneling in Solids' (N.Y., Academic Press)
- Eisenschitz R. and London F. (1930) *Z. Phys.* 60, 491
- Eley D.D. (1961) 'Adhesion' (O.U.P.)
- Fauré R., Carlan A., Crebassa J., Desrousseaux G. and Robrieux B.
(1972) *Thin Solid Films* 9, 329
- Foord T.R. (1969) *J. Phys. E: Sci. Instrum.* 2, 411
- Fowler R.H. and Nordheim L. (1928) *Proc. Roy. Soc. A* 119, 173
- Frenkel J. (1926) *Z. Phys.* 26, 117
(1946) 'The Kinetic Theory of Liquids' (O.U.P.)
- Fröhlich F. and Suisky D. (1964) *Phys. Stat. Sol.* 4, 151
- Gardon J.C. (1967) in 'Treatise on Adhesion and Adhesives' Vol. 1, p. 269
ed. R.L. Patrick (N.Y., Dekker)
- Good R.J. (1967) *ibid* p. 9
- Gough E., Isard J.O. and Topping J.A. (1969) *Phys. Chem. Glasses* 10, 89
- Gregory J. (1969) *Adv. Colloid Interf. Sci.* 2, 396
- Grossman J.J. (1968) *J. Vac. Sci. Technol.* 6, 233
- Grove A.S., Deal B.E., Snow E.H. and Sah C.T. (1965)
Sol. State Electron. 8, 145
- Gubkin A.N., Mitronina V.S., Sergienko V.F. and Subbotin M.I. (1959)
Instrum. and Exptal. Techniques No. 4, p. 113
[engl. transl. (1960) p. 631]
- Gundry P.M. and Tompkins F.C. (1968) in 'Experimental Methods in Catalytic Research' p. 100 (N.Y., Academic Press)
- Hamaker H.C. (1937) *Physica* 4, 1058

- Harper W.R. (1951) Proc. Roy. Soc. A 205, 83
- (1967a) 'Contact and Frictional Electrification' (O.U.P.)
- (1967b) IPPS Conf. Ser. No. 4 'Static Electrification'
p. 3 (London, IPPS)
- Hawley R. and Zaky A.A. (1967) Prog. in Dielectrics 7, 115
- Hayakawa T. (1957) Bull. Chem. Soc. Japan 30, 236
- Hayward D.O. and Trapnell B.M.W. (1964) 'Chemisorption' (London, Butterworth)
- Heavens O.S. (1950) J. Phys. Radium 11, 355
- Helmholtz H. (1853) Poggendorfer Annalen 89, 211
- Henish H.K. (1957) 'Rectifying Semiconductor Contacts' (O.U.P.)
- Henry P.S.H. (1953) Brit. J. Appl. Phys., Suppl. 2, S 31
- (1957) J. Text. Inst. 48, P 5
- Henry W.G. and Rogers J.L. (1956) Phil. Mag. 1, 223
- Hersh S.P. and Montgomery D.J. (1955) Text. Res. J. 25, 279
- Hill R.M. (1967) Thin Solid Films 1, 241
- (1972) Thin Solid Films 12, 367
- Holland L. (1964) 'The Properties of the Glass Surface' (London, Chapman
and Hall)
- Hopkins B.J., Mee C.H.B. and Parker D. (1964) Brit. J. Appl. Phys. 15, 865
- Hopkins B.J. and Riviere J.C. (1964) *ibid* 15, 941
- Hughes K.A. and Secker P.E. (1971) J. Phys. E: Sci. Instrum. 4, 362
- Inculet I.I. and Wituschek E.P. (1967) IPPS Conf. Ser. No. 4
'Static Electrification' p. 37 (London, IPPS)
- Ieda M., Sawa G. and Shinohara U. (1967) Japan. J. Appl. Phys. 6, 793
- Jonscher A.K. (1971) J. Vac. Sci. Technol. 8, 135
- Kaelble D.H. (1967) in 'Treatise on Adhesion and Adhesives' Vol. 1,
p. 170, ed. R.L. Patrick (N.Y., Dekker)
- Kalter H., Schatorjé J.J.H. and Kooi E. (1971) Phillips Res. Rept. 26, 181
- Kamovski M.M. and Estill W.B. (1964) Rev. Sci. Instrum. 35, 1324
- Keesom W.H. (1921) Phys. Z. 22, 129
- Keiji Kanazawa K., Batra I.P. and Wintle H.J. (1972) J. Appl. Phys. 43, 719

- Kelvin, Lord (1898) *Phil. Mag.* 46, 82
- Kliever K.L. and Köhler J.S. (1965) *Phys. Rev.* 140, A 1226
- Krotova N.A., Polyakov A.M. and Ssokolina G.A. (1967) in 'Chemistry, Physics and Application of Surface Active Substances' Vol. 2, p. 115 (London, Gordon and Breach)
- Krupp H. (1967) *Adv. Colloid. Interf. Sci.* 1, 111
- (1971) *Inst. Phys. Conf. Ser. No. 11 'Static Electrification'* p. 1 (London, Inst. Phys.)
- Kurtin S., McGill T.C. and Mead C.A. (1969) *Phys. Rev. Lett.* 22, 1433
- Landolt-Börnstein (1950) 'Zahlenwerte und Funktionen' Band I, Teil 1
- (1967) *ibid*, Band II, Teil 10, 6th edn. (Berlin, Springer)
- Lebedev A.A. (1940) *Bull. Acad. Sci. USSR, Sci. Phys.* 4, 584
- Lenel Z. (1933) *Phys. Chem. B* 23, 379
- Lennard-Jones J.E. (1931) *Proc. Phys. Soc.* 43, 461
- Lewis B. (1967) *Thin Solid Films* 1, 85
- Lewis B. and Campbell D.S. (1967) *J. Vac. Sci. Technol.* 3, 258
- Lifshitz E.M. (1956) *Sov. Phys. JETP* 2, 73
- Lin D.S. (1971) *J. Phys. D: Appl. Phys.* 4, 1977
- Loeb L.B. (1958) 'Static Electrification' (Berlin, Springer)
- Llewellyn-Jones F. (1967) 'Ionisation and Breakdown' (London, Methuen)
- London F. (1930) *Z. Phys.* 63, 245
- (1937) *Trans. Faraday Soc.* 33, 8
- Macky W.A. (1928) *Proc. Roy. Soc. A* 119, 107
- Many A., Goldstein Y. and Grover N.B. (1965) 'Semiconductor Surfaces' (Amsterdam, North Holland)
- Margenau H. (1939) *Rev. Mod. Phys.* 11, 1
- Margenau H. and Kestner N.R. (1969) 'Theory of Intermolecular Forces' (Oxford, Pergamon)
- Mattox D.M. (1965) Scandia Corp. Monograph SC-R-65-852
- May W.D., Smith W.D.P. and Snow C.O. (1957) *Nature* 179, 494

- Mayer J.E. (1933) J. Chem. Phys. 1, 270
- Mead C.A. (1966) Solid State Electron. 9, 1023
- Medley J.A. (1953) Brit. J. Appl. Phys., Suppl. 2, S28
- Menter J.W. and Pashley D. W. (1959) in 'Structure and Properties of Thin Films' p. 111, eds. C.A. Neugebauer, J.D. Newkirk and D.A. Vermilyea (N.Y., Wiley)
- Metsik M.S. (1960) Sov. Phys. - Solid State 1, 991
- Montgomery D.J. (1959) Solid State Phys. 9, 136
- Moses S. and Witt R.K. (1949) Ind. Chem. Eng. 41, 2334
- Mott N.F. (1969) Festkörperprobleme 9, 22
- Mott N.F. and Davis E.A. (1971) 'Electronic Processes in Non-Crystalline Solids' (Oxford, Clarendon Press)
- Mott N.F. and Gurney R.W. (1948) 'Electronic Processes in Ionic Crystals' 2nd edn. (O.U.P.)
- Müller H. (1936) Proc. Roy. Soc. A 154, 624
- Nelson R.C. (1963) J. Appl. Phys. 34, 629
- Neugebauer C.A. (1960) J. Appl. Phys. 31, 1096
- Orowan E. (1933) Z. Phys. 82, 239
- Orr W.J.C. (1939) Trans. Faraday Soc. 35, 1247
- Overbeek J.T.G. (1952) in 'Colloid Science' Vol. 1, ed. H.R. Kruyt, p. 115 (Amsterdam, Elsevier)
- Pauling L. (1967) 'The Nature of the Chemical Bond' 3rd edn. (N.Y., Cornell Univ. Press)
- Pirene J. and Katheuser E. (1964) Physica 30, 2005
- Poepfel R.B. and Blakley J.W. (1969) Surf. Sci. 15, 507
- Reedyk C.W. and Perlman M.M. (1968) J. Electrochem. Soc. 115, 49
- Rhoderick E.H. (1970) J. Phys. D: Appl. Phys. 3, 1153
- Rhodin T.N. (1949) Disc. Faraday Soc. 5, 215
- Rhodin T.N. and Walton D. (1964) in 'Single Crystal Films' p. 31 eds. M.H. Francombe and H. Sato (N.Y., Pergamon)
- Richtmyer F.K., Kennard E.H. and Lauritsen T. (1955) 'Introduction to Modern Physics' 5th edn. (N.Y., McGraw Hill)

- Riviere J.C. (1957) Proc. Phys. Soc. 70, 676
- Robins J.L., Rhodin T.N. and Gerlach R.L. (1966) J. Appl. Phys. 37, 3893
- Rose G.S. and Ward S.G. (1957) Brit. J. Appl. Phys. 8, 121
- Ross S. and Olivier J.P. (1964) 'On Physical Adsorption' (N.Y., Intersci.)
- Ryan J.A. and Grossman J.J. (1968) Sci. J. 4, 41
- Ryan J.A., Grossman J.J. and Hansen W.M. (1968) J. Geophys. Res. 73, 6063
- Schaffert R.M. (1962) IBM J. 6, 192
- Schnabel W. (1969) Dissertation, Karlsruhe University
- (1970) Adv. Static Electricity 1, 33
- Schottky W. (1914) Phys. Z. 15, 872
- (1935) Z. Phys. Chem. B 29, 335
- Sessler G.M. and West J.E. (1971) Rev. Sci. Instrum. 42, 15
- Shaw P.E. and Jex C.S. (1928) Proc. Roy. Soc. A 118, 97
- (1928) *ibid* A 118, 108
- Shockley W. (1939) Phys. Rev. 56, 317
- Simmons J.G. (1968) Phys. Rev. 166, 912
- (1970) in 'Handbook of Thin Film Technology' Ch. 14
eds. L.I. Maissel, R. Glang (N.Y., McGraw Hill)
- Simmons J.G., Nadkarni G.S. and Lancaster M.C. (1970) J. Appl. Phys.
41, 538
- Skinner S.M., Gaynor J. and Sohl G.W. (1956) Mod. Plastics, Feb., p. 127
- Skinner S.M., Savage R.L. and Rutzler J.E. (1953) J. Appl. Phys. 24, 438
- Sparnaay M.J. (1967) Adv. Colloid Interf. Sci. 1, 277
- Stuart R.V., Wehner G.K. and Anderson G.S. (1969) J. Appl. Phys. 40, 803
- Sundahl R.C. (1972) J. Vac. Sci. Technol. 9, 181
- Tabor D. and Winterton R.H.S. (1969) Proc. Roy. Soc. A 312, 435
- Tessman J.R., Kahn A.H. and Shockley W. (1953) Phys. Rev. 92, 890
- Trautweiler F. (1968) Photog. Sci. Eng. 12, 98
- van Turnhout J. (1970) Adv. Static Electricity 1, 56

- Verwey E.J.W. and Overbeek J.T.G. (1948) 'Theory of the Stability of Lyophobic Colloids' (Elsevier, Amsterdam)
- Vick F.A. (1953) Brit. J. Appl. Phys., Suppl. 2, S 1
- von Engel A. (1962) 'Ionisation of Gases' (O.U.P.)
- Walton D., Rhodin T.N. and Rollins R.W. (1963) J. Chem. Phys. 38, 2698
- Weingärtner G., Tödheide-Haupt U. and Ruppel W. (1968)
Z. Angw. Phys. 25, 257
- Wintle H.J. (1970) J. Phys. E: Sci. Instrum. 3, 334
- Wyckoff R.W.G. (1968) 'Crystal Structures' Vol. 4, 2nd edn. (N.Y., Wiley)
- Young D.M. and Crowell A.D. (1962) 'Physical Adsorption of Gases'
(London, Butterworth)
- Zachariasen W.H. (1932) J. Am. Chem. Soc. 54, 3341
-

CHARGE EFFECTS IN THIN FILM ADHESION*

H. GRAF VON HARRACH AND B. N. CHAPMAN

Materials Section, Department of Electrical Engineering, Imperial College, London SW7 2BT (Gt. Britain)

(Received May 18, 1972)

The adhesion of thin films is usually attributed to van der Waals and chemical forces. In this work the importance of an electrostatic contribution to the adhesion of metallic thin films to insulating substrates has been investigated. The transfer of charge across a film-substrate interface can lead to the formation of an electrical double layer; the resultant electrostatic attraction can contribute to the adhesion of the film. The magnitude of this attractive force can be comparable with that due to van der Waals forces. For two weakly adhering solids where the adhesion is determined only by long-range forces, the electrostatic component may therefore be significant.

Vacuum-deposited metallic films are peeled from their substrates (amorphous or crystalline insulators) *in vacuo* (10^{-6} torr) and the work done in this process is used to obtain a measure of the film adhesion. Using a highly sensitive probe technique, the sign and magnitude of the charge remaining on the substrate is determined subsequently at various substrate temperatures. Results obtained over a range of ambient conditions show charge densities of $\pm 10^{10} - 10^{11}$ electronic charges cm^{-2} ; comparison with the measured work of peeling suggests an electrostatic component of adhesion of a few percent. However, the possibility of charge decay during peeling of the film cannot be excluded, so that this value must be regarded as a minimum. A model is proposed for the mechanism of charge transfer during formation and separation of the interface.

1. INTRODUCTION

The structure of a thin film and the durability of any thin film device are both strongly influenced by the adhesion to the substrate; thin film adhesion is therefore a parameter of great importance.

An electrostatic component of adhesion^{1, 2} can arise from an exchange of charge across the interface between any two solids. If electrons are transferred across the interface the process will tend towards thermal equilibrium where the Fermi levels of the two solids are equalised. The electrical double layer thus formed exerts an electrostatic force of adhesion across the interface. The transfer

* Paper presented at the International Conference on Thin Films, "Application of Thin Films", Venice, Italy, May 15-19, 1972; Paper 10.1.

of charge between a metal and an insulator has been demonstrated experimentally³⁻⁵; the observed linear dependence of the charge on the work function of the contact metal indicates that electrons are involved in the transfer process.

2. ELECTROSTATIC AND PHYSICAL ADHESION

In this paper an investigation of the electrostatic adhesion of metal thin films to insulating substrates is reported. The magnitude of this effect can be estimated by considering the two solids in contact after a charge transfer σ per unit area across the interface (Fig. 1). By analogy with a parallel plate condenser,

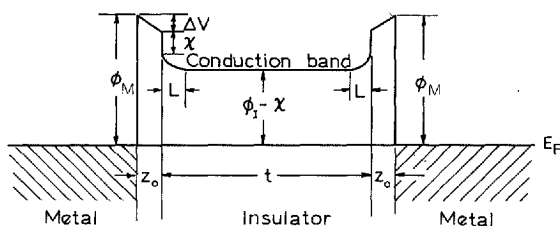


Fig. 1. Band diagram of metal-insulator-metal system at equilibrium ($\phi_M > \phi_i$).

the attractive force between the charge layers is

$$P_0 = \sigma^2 / 2\epsilon_0 \quad (1)$$

per unit area of interface. Hence, for a charge transfer of $10^{11} - 10^{13}$ electronic charges per cm^2 , the resulting force is about $10^4 - 10^8 \text{ dyn cm}^{-2}$. Physisorption forces⁶ are usually greater than 10^8 dyn cm^{-2} ; however, at small separations z ($< 500 \text{ \AA}$), these forces decay as z^{-3} , whereas the electrostatic forces remain practically constant.

In our experiments the work required to remove a thin film from its substrate has been measured, so that the adhesion energy is the more relevant parameter. The insulator of thickness t and relative permittivity ϵ is initially sandwiched between two interconnected, earthed films of the same metal (see Fig. 1); the interconnection reduces the probability of discharge during stripping (see below). If one film is removed to infinity the work done against electrostatic forces is

$$W_{\text{el}} = \int_{z_0}^{\infty} P(z) dz \quad (2)$$

where z_0 is the initial metal-insulator separation. For an immobile charge in the insulator (see Section 4), the electrostatic attraction $P(z)$ per unit area at separation z is given by

$$P(z) = \frac{\sigma^2}{2\epsilon_0} \left(\frac{t/\epsilon + 2z_0}{t/\epsilon + z + z_0} \right)^2 \quad (3)$$

assuming a uniform electric field in the gap and a space charge layer thickness $L \ll t$. Hence, the electrostatic adhesion energy is

$$W_{\text{el}} = \frac{\sigma^2}{2\epsilon_0} \left(\frac{t}{\epsilon} + 2z_0 \right) \quad (4)$$

If $z_0 \ll t/\epsilon$

$$W_{el} \approx \sigma^2 t / 2\epsilon\epsilon_0 \quad (5)$$

For surface charge densities of $10^{11} - 10^{13}$ electron charges per cm^2 and an insulator with $t/\epsilon = 10^{-2}$ cm, eqn. (5) gives an electrostatic adhesion of $10^2 - 10^6$ erg cm^{-2} . For comparison, physical adhesion energies are typically^{7, 8} a few hundred ergs per square centimetre. It should be noted that under conditions other than those above, the electrostatic adhesion energy may be much greater.

3. EXPERIMENTAL DETAILS

Metal thin films are evaporated in a conventional vacuum system onto both surfaces of insulating substrates heated to $200^\circ - 400^\circ \text{C}$; both films are earthed. Without breaking the vacuum, an adhesive tape is attached at one end of the sample as shown in Fig. 2(a), and parallel lines are scribed to define the area

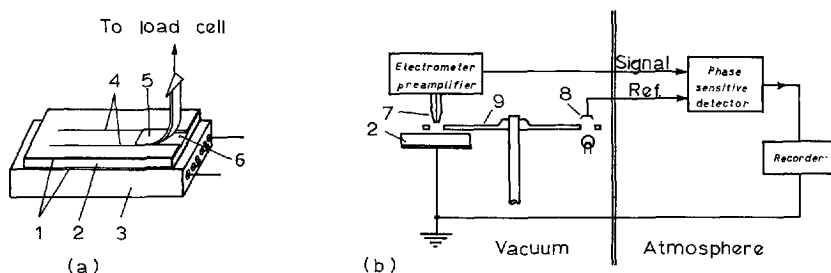


Fig. 2. (a) Film stripping set-up; (b) charge measurement system: 1, earthed metal films; 2, insulating substrate; 3, substrate heater; 4, scribed lines; 5, adhesive tape; 6, stripped area; 7, probe; 8, photo-detector; 9, earthed shutter.

of unbacked film to be removed⁹; strength requirements on the unbacked film impose a minimum of about 200 nm thickness. The film is stripped from its substrate at constant speed ($0.1 - 10 \text{ cm min}^{-1}$) and at angles near 90° to the substrate; the stripping energy (the work of stripping unit film area) can be calculated⁹ from the force measured by a load cell.

The measurement of the charge on the insulator surface is carried out by a potential probe apparatus (Fig. 2(b)) based on that of Davies¹⁰. The method relies on the induction of charge in a probe placed close to the charged surface¹¹. The chopped probe signal is amplified by an electrometer (Fig. 2(b)), the output of which is fed into a phase-sensitive detector. A scan of the charge distribution across the insulator surface can be recorded by monitoring the rectified detector output. The apparatus has been described in detail elsewhere¹².

4. RESULTS AND DISCUSSION

Table I shows the results obtained for gold, silver and copper films on borosilicate glass (Corning 7059). The measured charge densities, ranging from 10^{10} to 10^{11} electronic charges cm^{-2} (both signs), depend strongly on the

TABLE I

<i>Metal film</i>	<i>Film work function (eV)</i>	<i>Charge density (nC cm⁻²)</i>	<i>Electrostatic adhesion energy (erg cm⁻²)</i>	<i>van der Waals adhesion energy (erg cm⁻²)</i>	<i>Stripping energy (erg cm⁻²)</i>
Au	4.7 ^(1.3) 5.3 ^(1.4)	+2.6 ± 1	5	950	1400 ± 300
Cu	4.5 ^(1.3)	-10 ± 2	80	400	800 ± 200
Ag	4.3 ^(1.5)	-13 ± 3	115	800	1000 ± 200

contact metal. Samples which were exposed to the atmosphere before film stripping, unlike those above, gave positive charges for all three metals; for several hours after stripping the film (at 20 °C) the surface charge remained constant, implying a negligible mobility in the insulator. An approximate value of the electrostatic adhesion energy (W_{el}) can be obtained by applying eqn. (5) to the practical situation; the values of W_{el} shown in Table I have been calculated from the measured charge densities (σ) with $t/\epsilon = 0.14$ mm.

The adhesion energy of a thin film to its substrate can be defined⁹ as the work done in reversibly removing unit area of the film to infinity. When a film is stripped irreversible processes obviously occur, depending on the rate of stripping, ambient pressure etc.⁹ The measured stripping energies (Table I) are therefore greater than the adhesion energies; the corresponding van der Waals adhesion energies shown in Table I (calculated in ref. 8) are indeed somewhat smaller. The electrostatic adhesion energies reach up to 20% of the van der Waals energies.

The charge transfer process at a metal-insulator interface can now be discussed with reference to the experimental conditions. If the charge mobility in the insulator is sufficiently high (e.g. at raised temperature, as in our experiments) the equilibrium situation (see Fig. 1) is reached rapidly and the charge density transferred depends on the metal work function^{3, 4}. During separation of the interface the reverse charge transfer can occur², but since our films were stripped at room temperature, this charge leakage may be small. Nevertheless, the measured charge densities and the corresponding electrostatic adhesion energies represent minimum values.

A comparison of the above results (Table I) with those of Davies³ for the charge densities generated on glass (Corning 7059) by mechanical contact with metal electrodes at room temperature is shown in Fig. 3. The work functions of metal films on glass¹³⁻¹⁵ have been used for this plot (the higher value for Au was measured¹⁴ in mercury-free vacuum systems).

5. CONCLUSIONS

The results show that there is an electrostatic component of adhesion which may be of some significance. Our results to date are in accord with a charge transfer model based on electronic properties.

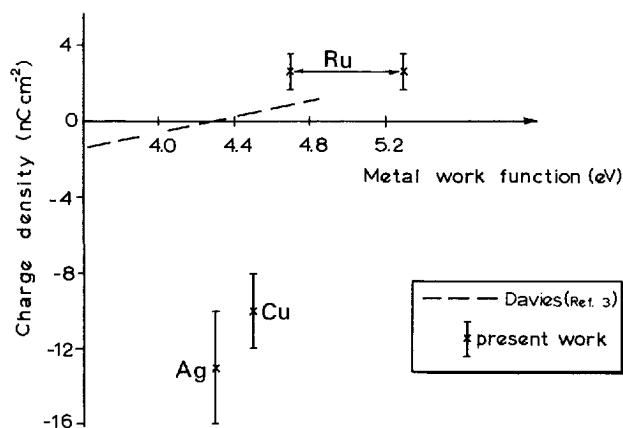


Fig. 3. Plot of charge density against metal work function.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the Science Research Council for supporting this work, and to The Clothworkers' Company for a grant to one of us (H. G. v. H.).

REFERENCES

- 1 B. V. Deryagin, N. A. Krotova, V. V. Karashev, Y. M. Kirillova and I. N. Aleinikova, in J. H. Schulman (ed.), *Proc. 2nd Intern. Congr. on Surface Activity*, Vol. 3, Butterworths, London, 1957, p. 417.
- 2 B. V. Deryagin and V. P. Smilga, *J. Appl. Phys.*, **38** (1967) 4609.
- 3 D. K. Davies, *Static Electrification*, I.P.P.S. Conf. Series No. 4, I.P.P.S., London, 1967, p. 29.
- 4 D. K. Davies, *Brit. J. Appl. Phys., Series 2*, **2** (1969) 1533.
- 5 R. G. C. Arridge, *Brit. J. Appl. Phys.*, **18** (1967) 1311.
- 6 H. Krupp, *Adv. Colloid Interface Sci.*, **1** (1967) 111.
- 7 P. Benjamin and C. Weaver, *Proc. Roy. Soc.*, **A252** (1959) 418.
- 8 B. N. Chapman, *Ph. D. Thesis*, Imperial College, London, 1969.
- 9 B. N. Chapman, in D. J. Alner (ed.), *Aspects of Adhesion—6*, Univ. London Press, London, 1971, p. 43.
- 10 D. K. Davies, *J. Sci. Instr.*, **44** (1967) 521.
- 11 H. J. Wintle, *J. Phys. E.*, **3** (1970) 334.
- 12 H. Graf von Harrach and B. N. Chapman, to be published.
- 13 J. C. Riviere, *Proc. Phys. Soc.*, **70** (1957) 676;
B. J. Hopkins, C. H. B. Mee and D. Parker, *Brit. J. Appl. Phys.*, **15** (1964) 865.
- 14 A. A. Holscher, *Surface Sci.*, **4** (1966) 89;
E. E. Huber, *Appl. Phys. Letters*, **8** (1966) 169.
- 15 B. J. Hopkins and J. C. Riviere, *Brit. J. Appl. Phys.*, **15** (1964) 941.

Charge effects at the film – substrate interface

received 10 July 1972

H Graf von Harrach and B N Chapman, Materials Section, Department of Electrical Engineering, Imperial College, London SW7 2BT, England

The measurement of the electrical charge generated at the surface of an insulating solid by the incidence of particles or radiation, or by contact with other solids, can provide information about surface properties. The contact charge transferred across metal–insulator interfaces has been measured by a probe technique after separation of the interface. The charge on borosilicate glass ($\sim 10^{11}$ electron charges cm^{-2}) depends strongly on the contact metal. The results are interpreted in terms of an electron transfer model.

Introduction

The study of solid surfaces frequently involves the incidence of particles or radiation. Electrical charges generated by these interactions on metal and semiconductor surfaces will be lost by conduction, but on the surfaces of insulating solids they may be stored for a long period of time. By the measurement of the surface charge and its temporal and spatial variation, the information stored on insulating surfaces may be extracted.

Another way of generating surface charges is by contact with solid surfaces. In this work the transfer of electrical charge across the interface between metal thin films and insulating substrates has been studied as part of an investigation of electrostatic effects in thin film adhesion¹. A simple apparatus has been designed to measure the charge density remaining on the insulator surface after removing the metal film *in vacuo*; the apparatus is capable of determining the charge density generated by any method. On the basis of the results of these charge measurements we have been able to describe the charge transfer process in terms of an electronic model.

The measurement of surface charge

A number of methods of charge measurement rely on the principle of induction: when a conductor is brought up to a charged surface, a charge of opposite polarity is induced on the surface of the conductor; since the induced charge depends linearly on the surface charge, its magnitude and polarity can be determined. This principle is used by the Faraday cylinder to measure the charge on a solid of any shape; Kelvin² applied it to the measurement of the contact potential difference between two conducting surfaces.

The charge on an insulating surface can be measured by a metal probe placed at a height h from the surface, as shown in Figure 1. If the potential V induced on the probe due to a charge density σ_s is measured by an electrometer of input capacity C_1 , ($C_1 \gg$ the total capacitance between probe and earth) then it can be shown that:³

$$V = \frac{\sigma_s A}{C_1(1 + \epsilon h/t)} \quad (1)$$

where t and ϵ are the insulator thickness and relative permittivity, and A is the probe area. Equation (1) holds for small probe heights compared with the charged area, i.e. if the electric fields in the gap and the insulator are uniform. The probe potential V is then directly proportional to the surface

charge density σ_s . If the insulator contains a volume distribution of charge, $\rho(x)$, then σ_s has to be replaced by an effective surface charge:

$$\sigma = \sigma_s + \epsilon_0/t \int_0^t dx \int_0^x \rho(x) dx$$

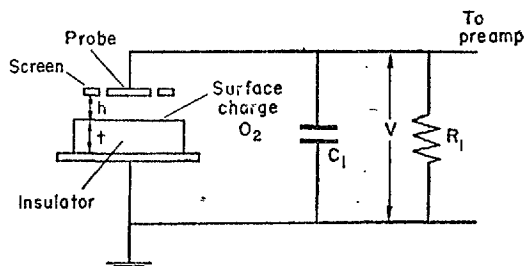


Figure 1. Schematic diagram of probe-insulator arrangement.

Charge measurement apparatus

Various types of charge measuring systems rely on the general principle described above⁴. Since, in practice, the electrometer has a finite input resistance, the charge induced on the probe will leak away to ground. Equation (1) above holds exactly only for infinite resistance, therefore the probe potential has to be measured within a time which is short compared with the decay time constant. This is achieved either by using a time constant of $\approx 100^5 - 7$ or by modulating the probe signal.⁸⁻¹⁰

Our apparatus (Figure 2) is based on the method of Davies⁸. An earthed metallic shutter is rotated between the stationary probe and the insulator surface, such that a probe signal of amplitude V and pulse width ~ 1 ms is generated. The signal is fed into a phase sensitive detector (synchronized with the shutter

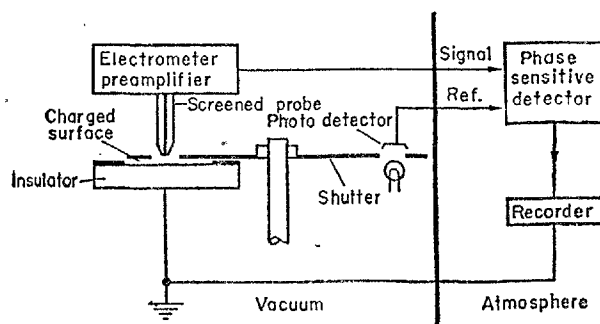


Figure 2. Charge measurement system.

frequency), the rectified output of which can be monitored continuously. The system is linear to an accuracy of about 2 per cent up to probe heights of 1.7 mm; the smallest detectable charge corresponds to 10^7 electron charges cm^{-2} at $t/\epsilon=0.1$ mm.

By displacing the sample beneath the probe at a constant separation, the charge distribution can be determined by measuring the output dependence on the width of a charged area. This is shown in Figure 3, where the output from narrow strips charged to a constant density (e.g. conducting strips with

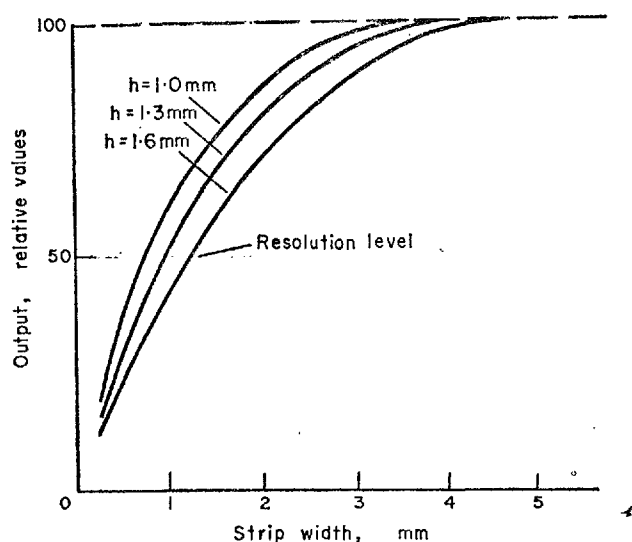


Figure 3. Probe resolution—at probe heights $h=1.0, 1.3, 1.6$ mm.

bias voltage) has been plotted against the strip width at various probe heights (h). The resolution, given by the half-height level, is of the same order as h , i.e. about 1 mm.

Contact charging of insulator surface

The electrostatic charging of insulating surfaces by contact with solids has been investigated extensively in the past^{11,12}. Recent experiments^{8,13,14} have suggested that the contact electrification can be explained in terms of an electronic theory: when two solids with different electron populations are placed in contact, an exchange of charge across the interface occurs, tending to equalise the populations; the process will tend towards a situation of thermal equilibrium in which the Fermi levels of the two solids are aligned. If the equilibrium situation is achieved, then the charge transferred should depend on the work function difference of the two solids^{14,15}.

For a metal-insulator contact, the process of charge transfer is usually extremely slow at room temperature¹⁶ since the insulator mobility is negligibly small. But at elevated temperatures when the mobility is comparatively high, an equilibrium situation may be reached, as shown in Figure 4.

Experimental procedure and results

Experiments have been carried out with metal films on borosilicate glass (Corning 7059). Identical films (thickness 0.2 – 0.5 μm) are evaporated in a vacuum of 1 – 10 μtorr on to both faces of a glass slide heated to a temperature above 200°C . The two films are earthed to avoid stray charging. Without breaking the vacuum, a film is removed by mechanical stripping¹⁷ from its substrate at 20°C . The charge remaining on the glass surface is subsequently measured by the system described above.

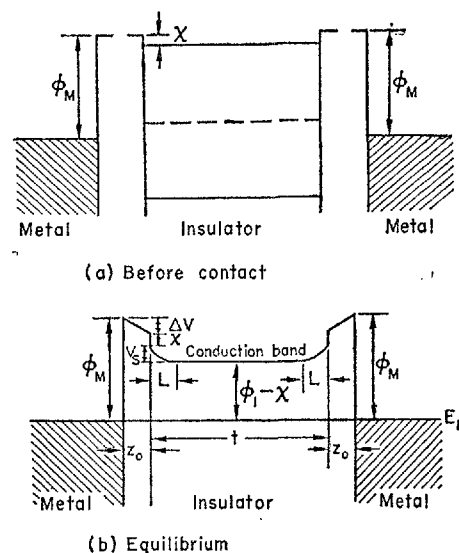


Figure 4. Band diagrams of metal-insulator-metal system.

Before film deposition the substrate surface is uncharged ($<10^8$ electron charges cm^{-2}); after removing the film a charge depending strongly in polarity and magnitude on the contact metal is measured on the glass surface. The charge densities generated on glass by Au, Ag and Cu films correspond to 10^{10} – 10^{11} electron charges cm^{-2} , with variations of up to 50 per cent over a given substrate. These values appear to be independent of the evaporation parameters, and even the charge generated by sputtered gold films is of the same order as that resulting from evaporated films.

The charge densities generated by gold, silver and copper films on borosilicate glass have been plotted in Figure 5 as a function of the metal work function ϕ_M ; the values for ϕ_M have been taken from the literature (for Au: Hopkins *et al.*¹⁸, Holscher¹⁹; for Ag: Hopkins and Riviere²⁰; for Cu: Riviere²¹). Figure 5 shows a rapid change towards more positive charge as the metal work function increases.

Discussion

The results (Figure 5) suggest a correlation between the measured surface charge and the work function of the contact metal. When the metal-insulator interface is formed, the insu-

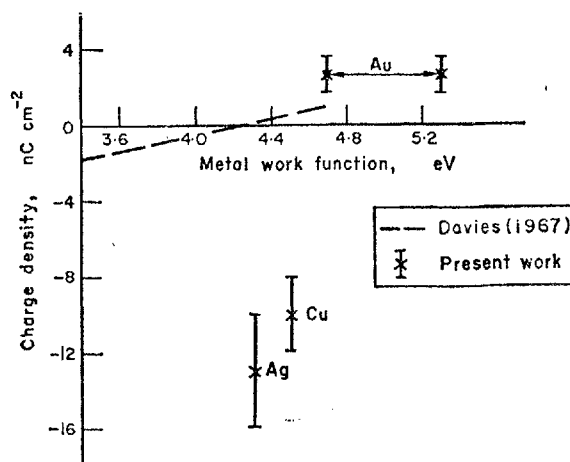


Figure 5. Plot of charge density on glass vs work fn.

ator is at a temperature above 200°C, at which the charge mobility in the insulator is considerable (e.g. a surface charge decays within seconds). Furthermore, the thin film is in atomic contact with the substrate surface; the charge transfer process across the interface is therefore likely to equalize the Fermi levels of the two materials, as discussed above.

Our results may be compared with those of Davies¹⁴ for the charge generated on borosilicate glass at 20°C by mechanical contact with bulk metal electrodes. Davies found a linear dependence of the transferred charge on the metal work function, but as shown in Figure 5, the charge densities are an order of magnitude smaller than our results. The differences may be due to the smaller real contact area resulting from mechanical contact or due to the temperature dependence of the charge mobility and, possibly, of the insulator work function. For both methods of contact charging an electron transfer into surface states^{16,22} could contribute to the total charge transfer.

When the metal-insulator interface is separated, a field emission across the gap ($\lesssim 1$ nm) may occur, such as to reduce the surface charge. Although this process is impeded by the low charge mobility in the insulator, the resulting loss of surface charge may not be negligible. A simple measure of the charge loss may be obtained by measuring the charge at the insulator surface before and after separation of the interface; these measurements are now in progress.

Conclusions

The electrical charge generated at the surface of insulating

solids may be used to obtain information about the electronic properties of insulator surfaces. Our measurements of the charge transferred across the metal-insulator interface have shown a correlation between the charge at the insulator surface and the metal work function. An interpretation of these results in terms of an electron transfer model has been discussed.

References

- ¹ H Graf von Harrach and B N Chapman, *Proc Int Conf on Thin Films*, Venice, May 1972; to be published in *Thin Solid Films*.
- ² Lord Kelvin, *Phil Mag*, 46, 1898, 82.
- ³ H J Wintle, *J Phys, E: Scient Instrum*, 3, 1970, 334.
- ⁴ J van Turnhout, *Advan Static Electricity*, 1, 1970, 56.
- ⁵ K A Hughes and P E Secker, *J Phys E: Scient Instrum*, 4, 1971, 362.
- ⁶ Sessler and West.
- ⁷ T R Foord, *J Phys E: Scient Instrum*, 2, 1969, 411.
- ⁸ D K Davies, *J Phys E: Appl Phys*, 2, 1969, 1533.
- ⁹ C W Reedyk and M M Perlman, *J Electrochem Soc*, 115, 1968, 49.
- ¹⁰ A Boksenberg *et al*, *Nature*, 220, 1968, 556.
- ¹¹ L B Loeb, *Static Electrification*, Springer, Berlin (1958).
- ¹² W R Harper, *Contact and Frictional Electrification*, Oxford University Press (1967).
- ¹³ R C G Arridge, *Br J Appl Phys*, 18, 1967, 1311.
- ¹⁴ D K Davies, *IPPS Conf Ser No 4, Static Electrification*, p 29, London, IPPS (1967).
- ¹⁵ F A Vick, *Br J Appl Phys (Suppl 2)*, 4, 1953, S1.
- ¹⁶ H Bauser *et al*, *Advan Static Electricity*, 1, 1970, 2.
- ¹⁷ B N Chapman, in *Aspects of Adhesion—6* (edited by D J Alner), p 43, University of London Press (1971).
- ¹⁸ B J Hopkins *et al*, *Br J Appl Phys*, 15, 1964, 865.
- ¹⁹ A A Holscher, *Surface Sci*, 4, 1966, 89.
- ²⁰ B J Hopkins and J C Riviere, *Br J Appl Phys*, 15, 1964, 941.
- ²¹ J C Riviere, *Proc Phys Soc*, 70, 1957, 676.
- ²² H Krupp, *Inst Phys Conf Ser No 11, Static Electrification*, p 1, London Inst Phys (1971).