PERSPECTIVE OF ADHESION OF THIN FILMS

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1. Introduction

The durability of thin films deposited on substrates is of primary importance in many diverse technological areas such as cladding, electroplating, decorative coatings of various sorts, solid lubrications, paints and integrated electronic and optical devices. One of the main factors that controls film durability is the adhesion between the substrate and its surface coating. The properties of the coating itself are obviously important, but the strength and durability of any coating are equally dependent upon the adhesion between the coating and the substrate, the most important factor. The importance of adhesion of thin films [39] is emphasized by the following:

1. Thin films (usually less than one micron thick) are so thin and fragile that they must be supported by a more substantial substrate, and the degree to which the film shares the strength of the substrate depends upon the adhesion between them.
2. The durability, longevity and wear of thin films are largely dependent upon the adhesion between the film and substrate.
3. The kinetics of the growth and structure of the films formed by vacuum deposition are largely influenced by the adhesion between films and their substrates.
4. Adhesion is important in surface chemistry and physics since it directly depends on interatomic and intermolecular forces.
5. Strongly adhering thin films are used as protective overcoats against corrosion.

The importance of adhesion in general is due to its widespread application in industry, chemistry and electronics. An understanding of thin-film adhesion and of its control possibilities is therefore of considerable importance.

2. General

Since adhesion phenomena are encountered in many fields, the term "adhesion" has several different meanings and definitions. Adhesion may simply signify the sticking together of two similar or dissimilar materials, or the state of two surfaces held together by interfacial forces which may consist of valence forces and/or interlocking forces. Adhesion as indicated by Good [1], is the mechanism by which mechanical force or work is transferred from one solid to another, in tension or in shear, without interfacial slip or inelastic displacement of one body with respect to the other. An alternative general definition of adhesion is that of molecular contact between the two phases. Recently [39], two general terms relevant to adhesion measurements have been introduced, such as:

ADHEREND a general term for a solid substrate to which other materials adhere;

ADHERATE — the material which adheres to an adherend. Examples of adherates are thin films, paints and coatings. ADHESIVE is a special kind of adherate in that it adheres to two adherends instead of one.

It is very important. to differentiate between an adherate-adherend combination called "adhering system" and an adhesive joint (expressed in short form as "adhint" [2]) because in the former there is only one interface and two bulk phases, whereas in the latter there are two interfaces and three bulk phases. In an adhering system, adhesion can be expressed in terms of forces or work of attachment, or in terms of forces or work of detachment. For the former manner, the correct expression should be "basic adhesion", "fundamental adhesion", "true adhesion" or "interfacial adhesion". On the other hand, Chapman [3] classified adhesion of thin films into:

i. Interfacial adhesion, the simplest one, where two distinct materials meet at a well-defined interface.

ii. Interdiffusion adhesion, which results from a solid state interdiffusion between the two materials. In this case, a discrete interface is replaced by a gradual and continuous transition from one material to the other.

iii. Intermediate layer adhesion, where the materials are bonded together via one or more layers of compounds of the materials with each other or with the surrounding gases; oxides are particularly common. Again, there is no single, well-defined interface.

All these different types of adhesion are further complicated in practice because surfaces are never perfectly smooth, and some degree of mechanical interlocking takes place.

The interfacial adhesion or basic adhesion signifies the interfacial bond strength between two materials in contact with each other. Basic adhesion is simply the summation of all intermolecular or interatomic interactions. These interactions could be electrostatic, chemical, or Van der Waals type. Unless there is a well-defined interface between the adhering systems, the term "basic adhesion" is meaningless. Basic adhesion is strictly an interfacial property and depends exclusively on the surface characteristic of adhering systems. Basic adhesion [39] should be independent of the thicknesses of adherate, and adherend, specimen size, specimen geometry, temperature, measurement technique, manner of applying external forces, manner of performing the test, test rate, and bulk properties of adhering systems.

On the other hand, practically, adhesion can be measured in terms of forces or work needed for detachment or separation of the adhering systems. The separation may take place at the interface, or in the interfacial region (also called interphase), or in the bulk of the weaker adhering phase. Separation in the bulk is termed cohesive failure. The cohesive failure of a thin coating or adhesive is, however, unlikely to be the same as the cohesive failure of the same material in bulk.

The interfacial region or interphase possesses a certain thickness, and its mechanical properties are different from those of the other phases. Interphases may be present on the adhering phases (for example, oxide on metal, oil layer in a surface), or they may be formed by interaction of the adhering phases (for example, diffusion-type interphase in a metal-metal system.).

In real adhering systems, there can be many interfaces and interphases in addition to the two bulk phases, and separation could be at any of the interfaces or in any of the interphases or in one of the two bulk phases. If the separation occurs at an interface or in an interphase, then it is suggested that the measured adhesion be labeled "practical adhesion".

It is suggested to formulate the relationship between practical adhesion and basic adhesion as follows:

1. If there exists a sharply defined interface between the two adhering phases and the separation is clearly at this interface, then "practical adhesion is a function of basic adhesion and other factors" [39].

2. If the separation is in the interfacial region, then "practical adhesion is a function of interatomic or intermolecular bonding within the interfacial region and other factors".

These other factors include intrinsic stresses (which depend, among others, upon the adherate thickness), presence or absence of sites of easy failure, the mode of applying external stress, that is, the technique of measuring practical adhesion, the failure mode, etc.

3. Origin and nature of adhesion forces

The variation in the degree of adhesion between thin metal films and substrates has been attributed to the formation of an oxide layer between the metal films and the substrates. Backus [5] showed films of oxygen-active metals to have stronger adhesion to glass than films of the noble metals. The film adhesion is generally attributed to a bond with an oxide layer and the energy of adhesion is felt to be closely related to the change in the free energy of oxide formation. Bateson [6] has discussed the adhesive properties of metallic films in relation to the surface chemistry of glass and suggested formation of an oxide bond by the reaction of the impinging atoms with the hidroxyle groups present at the glass surface. Benjamin and Weaver [7], concluded from their studies that for many metals on glass the initial adhesion could be considered as Van der Waals bonding but the adhesion subsequently increased with time, reaching a final value much beyond that could be attributed to Van der Waals forces alone. This was due to the gradual formation of an oxide layer at the metal/glass interface. They concluded also that both the energy of film adhesion and the heat of condensation of the vapor atoms could be related to, and explained by, the Van der Waals forces at the film-substrate interface. The general picture emerges, however, that the oxygen-active metals form chemical bonds with the substrates and are strongly adhesive, whereas those which form only physical bonds are easily removed. The bond appeared to be a two-stage process of physical adsorption usually known as Van der Waals interaction, practically known as London [8], Debye [9] or Kessom [10] effect followed by chemical interactions known as covalent, ionic and metallic bonding.

For low values of adhesion, the absorbed atoms keep their electron shells intact and the forces holding them on the surface are of the Van der Waals type. This situation holds up to values of approximately 0.4 eV and the atoms are said to be physisorbed on the substrate. Above 0.4 eV sharing of electrons can occur, and the atoms are now said to be chemisorbed.

It is to be noted that, if materials with different work functions are initially in close contact, the charges present on the materials will cause an electrostatic attraction to exist between the surfaces. Separation work must overcome these forces. Such effects apply to the adhesion of thin films. So, in certain cases, adhesion at the metal-insulator interfaces has been attributed to an electric double layer produced by charge transfer [11] (electronic charges). The electrical double layer thus formed will develop an electrostatic force of adhesion across the interface. Further, the presence of electrostatic charges during the deposition of evaporated and sputtered films also appears to influence their adhesion. Derjaguin and Smilga [12] developed an electronic theory of adhesion involving the presence of an electric double layer on the interface between two surface.

4. Electrostatic phenomena in adhesion

An electrostatic component of adhesion may arise from an exchange of charge across the interface between two surfaces. As mentioned above, the electronic theory of adhesion developed by Derjaguin and Smilga [12], showed that the electrostatic forces generated by the double electric layer formed on the interface are the main factors of adhesion between two surfaces. The electronic theory of adhesion considers the adherate-adherend system (film-substrate) as a capacitor which is charged due to the contact. The separation of the double charge layer in a stripping process such as breakage of the bond is similar to the separation of the plates of a parallel plate condenser, and a potential difference develops which increases until a discharge occurs at different separations depending on the nature and pressure of the ambient gas. The electrostatic theory of adhesion supposes the work of adhesion to vary with the nature and pressure of the gas. Skinner et al. [11] were unable to detect surface charges of the magnitude which Derjaguin et al. [12] thought were involved.

So far it has not been possible to directly confirm or refute the existence of a double charge layer in thin film systems. But Chapman [13] investigated the electrostatic adhesion of thin metal films to insulating substrates and estimated the magnitude of this effect by considering the two surfaces in contact after a charge transfer σ per unit area across the interface. Then by analogy to a parallel plate condenser, the resulting attraction force will be $\sigma^2/2\epsilon_0$ per unit area (ϵ_0 is the permittivity of free space). For a charge transfer of 10^{11}—10^{13} electronic charges cm^{-2}, the resulting attraction force is about 10^3—10^7 Nm^{-2}.

5. Factors influencing adhesion of thin films

A number of parameters and factors influencing thin film adhesion are known, such as the substrate cleaning procedure, the rate of deposition, the film thickness, the type of substrate, the substrate temperature, the purity of source material and the pressure in the evaporator during deposition. Good adhesion is simple to achieve by cleaning the substrate surface so that the film and the substrate really do contact. Solvent cleaning usually removes only oils and greases, leaving more tenacious materials such as surface oxides which may prevent interdiffusion.

One can remove such deposits by chemical or sputter etching (taking care that cone growths and other topography changes do not occur). Cleaning the substrate surface prior to deposition was found necessary for good adhesion in the occurrence of surface contamination. One may expect that glow discharge and ion bombardment cleaning would have a further influence on thin film nucleation and growth. These initial stages of nucleation and subsequent growth would influence in turn, the adhesion and cohesion failure mechanisms of a thin film.

In the case of interdiffusion or compound interfaces, adhesion can often be improved by substrate heating.

Sometimes very little heating is required; gold can be evaporated onto silicon (provided the oxide surface is removed) at 50 °C to produce excellent adhesion via a diffuse interface extending through many atomic layers. Intermediate layer adhesion occurs naturally for some materials, such as aluminium on glass.

Intermediate oxide layers can also be achieved by depositing an oxygen-active metal onto an oxide surface.

Sputtered films are often stated to be more adherent than evaporated films because the sputtered atoms are ejected from their target source with much more energy than those from an evaporation source. In sputter deposition, secondary target electrons bombard the substrate and are responsible for a good deal of substrate heating which will promote and influence interfacial reaction and interdiffusion as well; the associated charge will also have a marked effect on nucleation and this should have an influence on the adhesion of a thin film.

6. Measurement of thin film adhesion

One of the particular difficulties with thin film adhesion is its inaccessibility to measurement. At this time, there is still no generally acceptable method of measurement. So, it is important to define carefully the purpose of the measurement and to select the correct method for each particular case under investigation, and this will decide which methods are suitable and which are not. In any case, a review of the techniques for measuring practical adhesion has been given by Campbell [15]. Recently Mittal [4] has comprehensively and critically reviewed the adhesion measurement techniques for thin films. Before dealing with these techniques, it is necessary to mention that an ideal test for measuring practical adhesion should be:

a) reproducible;
b) quantitative;
c) nondestructive;
d) easily adaptable to routine testing;
e) relatively simple to perform;
f) little time-consuming;
g) applicable to a wide range of adherate thicknesses;

h) independent of operator's experience;
i) applicable to all combinations of adherates and adherends;
j) valid over a wide range of specimen sizes;
k) applicable to products and processes;
l) suiting to measure a wide range of practical adhesion strengths;
m) simple to interpret;
n) amenable to standardization.

No single test method uniting these ideal conditions has been realized in practice.

The techniques for measuring thin film adhesion fall into two main groups:

a) Nucleation methods
b) Mechanical methods.

6.1. *Nucleation methods*

In a recent review, Campbell [15] has given a detailed explanation and interpretation of these methods which are based essentially upon the measurement of:

a) nucleation rate;
b) measurement of island density;
c) critical condensation;
d) residence time of the depositing atoms.

On an atomic scale, the removal of a film consists in breaking the bonds between the individual atoms of the film and the substrate so that macroscopic adhesion can be considered as the summation of single atomic forces. In principle, therefore, it should be possible to relate the adsorption energy of a single atom on the substrate to the total adhesion of the film.

Nucleation methods of measuring the adsorption energy are fairly complicated and generally of limited applicability. Nucleation methods are not the tests for measuring adhesion; this type of work has led to a better understanding of thin film formation and structure. Also, these techniques are not applicable to completed films.

6.2. *Mechanical methods*

These methods of measuring adhesion which use some means of removing the film from the substrate are more obvious and direct, and various reviews have been given of the methods available [16, 17]. At this time, there is still no generally acceptable method of measurement. As no method of universal applicability has been found so far, it is important to select the correct method for each particular case under investigation.

So, a short survey of the simplest and most common mechanical methods for measuring adhesion will be given.

6.2.1. The direct pull method

This is perhaps the simplest of all methods for measuring adhesion [18 to 23]. The basic principle of the method is to apply a tensile force to directly pull the film off, normal to the substrate surface by means of some kind of pulling device. The normally applied force required to remove the film is then measured.

If the failure occurs at the substrate — film interface, this force is taken to be the "force of adhesion". This method can be applied not only to study the adhesion of thin films, but also to measure the strength and the adhesive properties of, for instance, cemented or soldered joints. The direct pull-off method suffers from the following difficulties:

a) Simple tensile tests are difficult to perform, and most of the present techniques involve a complex mixture of tensile and shear forces, which renders the interpretation of the results more difficult.

b) Alignment must be perfect to insure uniform loading across the interface.

c) Such tests are limited in validity by the strength of available adhesives or solders.

d) There is always a possibility of:

i) adhesives or solvent to penetrate and to affect the film-substrate interface.

ii) Stresses produced during setting of cement or adhesive.

iii) Non-uniform stress distribution or stress concentration over the contact area during the pulling process.

All of these factors affect the final adhesion strength measured.

The so-called topple test used by Butler [24] is closely related to the pull test. In this method a rod is attached to the film but the force is not applied in the normal direction but in a lateral direction. Butler has described such an apparatus (Figs 1, 2) and points out that this method is superior to the direct pull-off method since:

a) This arrangement offers less substrate distortion since no resultant overall force normal to the plane of the substrate develops.

b) For this apparatus alignment is not as critical as in the case of the direct pull-off method.

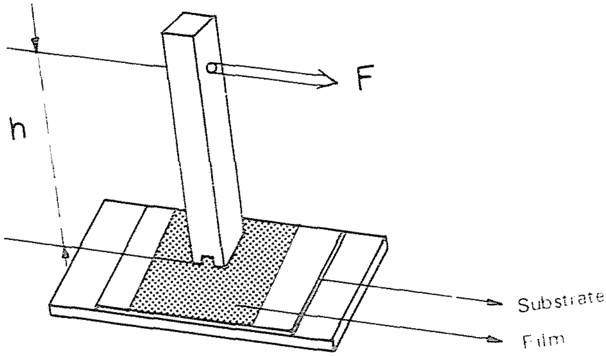

Fig. 1. Lateral Force as a Measure of Adhesion
(From reference 24)

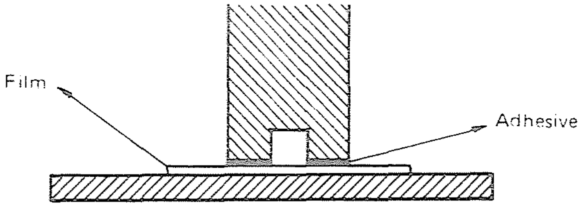

Fig. 2. Topple Test of Thin-Film Adhesion
(From reference 24)

6.2.2. *The scratch method*

This technique for measuring adhesion was first used quantitatively by Heavens [25], and later developed mostly by Weaver and co-workers [26 to 33]. The quantitative value for adhesion of thin films to a substrate is obtained by smoothly drawing a hard, rounded stylus subject to gradually increasing loads across the film until a critical load value where the film is completely removed from the substrate, resulting in a clear channel. The critical load where the clear track is formed is taken as the measure of adhesion.

The critical load has been shown to be reproducible for coatings deposited onto the same substrate under identical conditions and to be an excellent quantitative indicator of adhesion quality. The load is progressively increased to a value where the film is detached by the moving point, and this critical load value is the measure of the film-substrate adhesion. Butler et al. [35] were the first to investigate the reliability of the scratch test, by using the scanning electron microscope, and have concluded the scratching process to be much more complex than was previously realized and the mechanism to vary from system to system. The fundamental difficulty was to find out how a compressive force normal to the substrate could produce film detachment but it was observed that the process always involved plastic deformation of the substrate by the point and this deformation produced a shearing force at the film-substrate interface around the rim of the identation produced by the point. A simple relationship between the applied load and the shearing force was developed, so that adhesion could be calculated as a shearing force. The analysis of this shearing force coupled with experimental results demonstrated effectively that the critical load was determined by the characteristics of the film-substrate interface, varying with any change in one or the other and yet showing no direct correlation with the mechanical properties of either.

6.2.3. The peel method

This test was originally suggested by Strong.[36] Adhesive tape is pressed onto the film and then torn off. When the tape is pulled off, the film is either wholly removed, partially removed, or left behind on the substrate. This method is obviously not quantitative, but it does yield useful qualitative information [37]. If the film is removable, however, it is possible to turn the measurement into a quantitative one. A schematic diagram of the apparatus is seen in Fig. 3.

The film can be peeled from the substrate in two ways:

a) by directly holding onto the film, and

b) by applying some sort of backing material to the film, and then holding onto the backing. The actual peel test involves peeling of a specified width of the film at a specified angle. In this technique, it is impossible to specify the area involved at any instant, so the force used in peeling has little significance. The results are expressed as energy or work done per unit area. So the peeling test

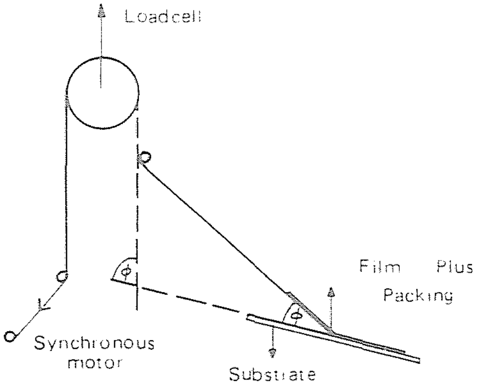

Fig. 3. Schematic Diagram for Stripping or Peeling Experiments. (From Handbook of Thin-Film Technology) [15]

results are not directly comparable to the results obtained using other techniques which provide adhesion values in terms of force per unit area. In order to make any useful measurement the film must be completely removed from the substrate, which limits the applicability of this technique to interfaces of relatively poor adhesion. The method has been refined and made quantitative by measuring the force during removal of the film, and thus obtaining the peeling energy. The influence of the tape itself on the measurement can be reduced by transmitting the peeling force to the film via a short piece of tape but performing the actual measurements only on the unsupported film [38]. The force can also be transmitted to the film by attaching a release strip which can be lifted with a razor blade. These methods have so far been used exclusively for measurements of the adhesion of metal films.

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Summary

Adhesion of evaporated films is an important parameter in both optical and electronic applications. In conformity with its importance, a general review is given of the adhesion of thin evaporated films; its relevance, origin and nature of adhesion forces, some evidence of the electrostatic component of adhesion, and many factors influencing the adhesion of thin films are discussed in detail. In addition, experimental methods for measuring adhesion are reviewed.

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