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ADHESION*

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Summary

Adhesion is defined as the work necessary to separate the coating–substrate interface; most available methods measure the load required to strip off the coating. The many quantitative and qualitative methods used are presented and the origins of adhesion are discussed. The parameters influencing the adhesive strength are reviewed: substrate preparation, coating technique, residual pressure in the vacuum chamber and substrate temperature are all found to be significant, and aging effects which can raise or lower the adhesion can also be observed. Many variables affect the measured adhesion and mean that only a partial analysis is possible in general at the present time. This leaves a wide field open for further studies.

1. Introduction and definition

The problems of adhesion of coatings with thicknesses between 0.05 and 50 μm are discussed in this paper. In most applications these coatings are not self-supporting but rather are applied to the surface of a solid body. This solid either can simply function as a substrate or can have specific properties which are improved in some way by the application of the coating. Improvement of the surface is thus defined as an intentional and exact alteration of the optical, electrical, chemical or mechanical properties of the solid surface.

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In all these cases sufficiently good adhesion between the partners is of paramount importance to the usefulness of such a system. These coatings can be produced by various technologies such as physical vapour deposition (PVD) in a vacuum or chemical vapour deposition (CVD) from the gaseous phase. The preparation and the production technology can greatly influence the way in which the materials adhere. What then exactly is adhesion?

Newer physics, chemistry and technical dictionaries define adhesion as "... the bond or the strength of the bond between two materials or two bodies; also the bond of individual molecules to the interface surfaces" [1 - 3]. The ASTM defines adhesion as the "Condition in which two surfaces are held together by either valence forces or by mechanical anchoring or by both together." [4]. These bonding forces could be van der Waals' forces, electrostatic forces and/or chemical bonding forces which are effective across the interface.

In this paper the word adhesion will be used as a synonym for "the adherence" of a film to its substrate and, in its broader sense, for the "adhesive strength". Adhesion is defined by the work necessary to separate atoms or molecules at the interface. A distinction can be made between the maximum possible adhesion (basic adhesion) of a system which represents the maximum attainable value on the one hand and the experimentally measured adhesion [5, 6] on the other.

The macroscopic experimentally measured adhesion values are determined by the basic adhesion, the mechanical properties of the film and the fracture mechanism in the separation process [7, 8]. The relation between the experimentally measured adhesion EA and the basic adhesion BA is given by

$$\mathrm{EA} = \mathrm{BA} - \mathrm{IS} \mp \mathrm{MSM} \tag{1}$$

where IS is the internal mechanical stress and MSM is the method-specific error of measurement. The basic adhesion cannot usually be determined because the size of the measurement error can seldom be estimated.

The experimentally measured adhesion is given in units of force or energy per unit surface area. A relation between the energy W_{ad} of adhesion and the force of adhesion can only be derived when a reasonable and conclusive estimate of the path followed by the adhesive force $F(x)$ over the dividing distance x between the film and the substrate surface can be made [6]:

$$W_{\mathrm{ad}} = \int F(x)\,\mathrm{d}x \tag{2}$$

The strength of the adhesion across the interface can be distributed very unevenly because the structures of the substrate surface and of the film are often heterogeneous. Contaminants covering very small areas and monomolecular contaminants on the substrate surface can also cause local changes in the adhesive strength. Thus the experimentally determined adhesion values should be regarded as average values across the interface surfaces investigated.

2. Methods of measurement

The individual methods of measurement used to determine the degree of adhesion can be classified and subdivided according to various criteria, *e.g.* mechanical and non-mechanical methods. An example of a simple qualitative test is shown in Fig. 1.

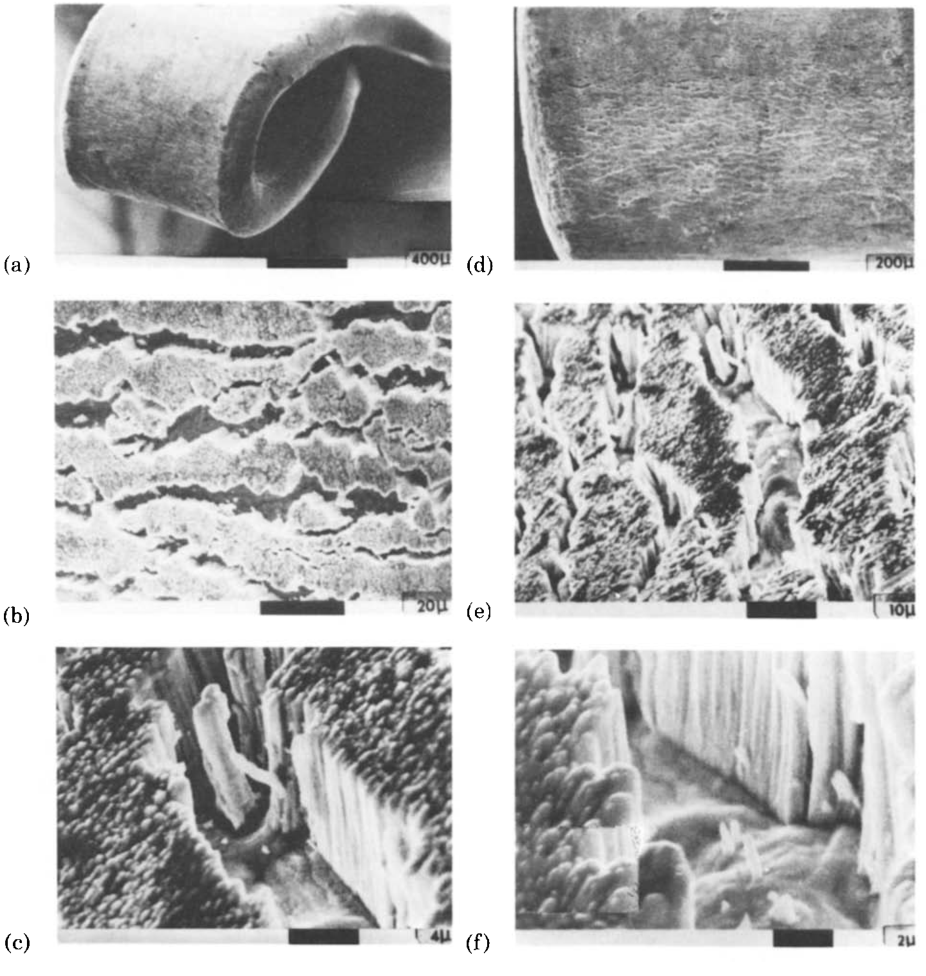

Fig. 1. Qualitative test to check film adhesion by bending. The scanning electron micrographs (a) - (f) were obtained at various magnifications. The specimen examined is an Ni–Fe substrate coated with a rhenium film 10 μm thick which had been applied by ion plating. When the specimen is bent to a radius of 0.6 mm [9] the close-packed crystallite columns develop cracks as the substrate is stretched. The micrographs show that the film has not separated from the substrate. Therefore the adhesion is good.

In the practical application of a measuring method it is important to know, among other things, whether the method can be carried out without destroying the test objects and whether it can provide reproducible results and the size of the method-specific error of measurement. The simplicity of the measurement apparatus and the time necessary to make the measurement should also be taken into account.

Another practical consideration is the use of a measurement method that simulates as closely as possible the type of stress to which the coating/substrate system will be subjected in service. Tables 1 and 2 list a number of methods of measuring the adhesion of thin films which have appeared in the literature.

TABLE 1

Mechanical methods of determination

Qualitative	*Quantitative*
Scotch tape test [6, 10 - 14]	Direct pull-off method [8, 19 - 33]
Abrasion test [12, 15]	Moment or topple test [34 - 37]
Bend and stretch test [8, 16]	Electromagnetic tensile test [38]
Shearing stress test [16 - 18]	Laser spalation test [39]
	Ultracentrifuge test [6, 16, 40 - 44]
	Ultrasonic test [6, 70]
	Peeling test [6, 45 - 48]
	Tangential shear test [49, 50]
	Scratch test [44, 46, 51 - 67]

TABLE 2

Non-mechanical methods of determination

Qualitative	*Quantitative*
X-ray diffraction test [65]	Thermal method [68, 69]
	Capacity test [6, 71]
	Nucleation test [46]

2.1. Mechanical methods

In mechanical methods adhesion is measured by applying a force to the coating/substrate system under examination. This force causes a mechanical stress at the interface which should remove the film from the substrate once the stress has been increased to an appropriate level. The definitions given here for "mechanical stress" are those commonly used in the field of physics and are thus different from those definitions which have become established in thin film literature. The stress can be either tensile perpendicular to the interface or shearing parallel to the interface. In practical applications a combination of these two types of stress usually occurs. That force or energy at which the separation of film and substrate first takes place is taken as an index of the experimentally measured adhesion [6].

In addition to the stress produced by external forces, very strong internal stresses inherent in the film (intrinsic stress) also affect the interface and influence the experimental adhesion measurement results in an undetermined way. In extreme cases very strong internal stresses alone can lead to detachment of the film [72, 73] or to cohesive failures in the substrate [74].

In general, failure and thus separation can appear in any of five regions (Fig. 2) [75]. Region 1 is the inside of the film and region 5 is the bulk material of the substrate which is sufficiently distant from the interface. If the separation occurs in one of these two regions then failure is cohesive. On an atomic scale, region 3 can be either a very sharply defined interface or a very diffuse interface layer. In order to be able to measure the adhesion, the separation must take place in this region [75, 76]. Even with a material transition of the monolayer-on-monolayer type, the changes in some physical characteristics (*e.g.* elasticity and electrical interface phenomena) take place continuously. When there is an interface layer (*e.g.* through diffusion) the transitional area increases in size. For this reason a distinction is made between the mechanical behaviour of the interface layers in regions 2 or 3 and that of the inner regions of film 1 or substrate 5 [75, 76].

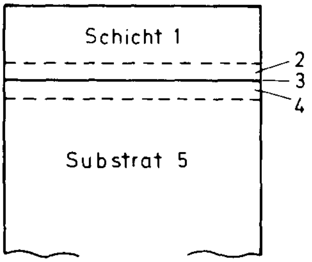

Fig. 2. The five regions [75] in which separation can take place.

A separation exclusively at the interface is assumed to be improbable according to the "weak boundary theory" [77, 78]. Rather, the separation should always occur in the bulk regions of coating or substrate (cohesive failure) or in a finitely thick "weak layer" (interface layer) between the two substances. A failure within the weak interface layer is regarded as an adhesive failure. The weak layer can be a brittle oxide layer or an absorbed and occluded layer of gas and/or some other kind of contamination.

The basis of another theory [79] is the triggering of a fracture at pre-existing cracks in the substrate or within the film according to the so-called Griffith–Orowan criterion [19, 80]:

$$\sigma^2 = \text{constant} \times EG/l \qquad (3)$$

where E is the modulus of elasticity, G is the work per unit surface area required for crack propagation, l is the length of the longest cracks in existence and σ is the force per unit surface area required for crack propagation. The crack thus formed grows in a direction normal to that of the applied mechanical stress. The actual fracture is assumed to be a transformation of energy either into dissipative energy (*e.g.* heat) stored as elastic deformation or supplied externally. It must also be assumed that an energy transfer takes place from the area around the fracture to the fracture zone.

Fracture can also extend across several of the given regions. If the separation of the coating from the substrate takes place inside or around the interface layer, the force or energy necessary for the separation is a measure of the experimentally measured adhesion [76]. However, if the separation takes place deep inside the film or substrate, it is a cohesion fracture, *i.e.* the adhesion forces are stronger than the cohesion forces. From a qualitative point of view, the adhesion is considered to be bad if a separation in the interface layer can be caused. However, if a separation occurs in the bulk, the adhesion is good. Quantitative values can only be obtained when the force used to lift the coating can be measured. Individual measurement methods are distinguished from one another by the way the load is coupled to the sample system and then by the way in which it is applied. These criteria allow a division into methods which can remove the coating through (a) a force applied perpendicularly to the interface layer or (b) a force applied at various angles to the interface layer.

An upper limit of the transferable force, and thus a maximum measurable adhesion value, results from the fact that in almost all the measuring methods (with the exception of, for example, ultracentrifuge or heat expansion methods) a traction piece must be attached mechanically. Thus this limit is dependent on the load capacity or degree of fixation of the method-specific attachment (*e.g.* gluing or soldering).

Because of the varying attachment techniques and the individual transfer devices (Scotch tape, needles for scratching etc.) further uncontrolled stresses can be caused in the interface layer in addition to the controlled mechanical stress produced externally. Such additional stress can be caused, for example, by drying, polymerizing or stiffening of the glue layer or the solder layer used for the traction piece. It can also occur because of plastic–elastic deformation of the traction piece itself during a test.

The experimentally determined adhesion values are thus not free from effects due to the measurement method used. Therefore it is unfortunately not always possible to compare measurements obtained by different methods.

2.2. Non-mechanical methods

With the exception of the nucleation method, non-mechanical methods to measure adhesion are not very well developed, and their field of application is severely limited. These methods can, in any case, be used for basic investigations. Even the nucleation method is too complicated for use for technological applications because it requires too much equipment and takes too much time. For this reason we shall not discuss it in more detail here.

3. Causes of adhesion

3.1. Interface layer

The quality of adhesion between solids, *e.g.* between a film and its substrate, depends to a large extent on the microstructure of the interface layer that is being formed. The following types of interface layers can be distinguished [8, 69, 81].

3.1.1. Mechanical interface layer

This type of interface layer forms on rough porous substrates. The film material fills the pores and other morphologically advantageous places when there is sufficient surface mobility and wetting, and a mechanical anchor is formed. The adhesion depends on the physical characteristics (particularly the shear strength and the plasticity) of the combination of materials.

3.1.2. Monolayer on monolayer

This interface is characterized by an abrupt transition from the film material to the substrate material. The transition region has a thickness 2 - 5 Å. Interfaces of this type form when no diffusion occurs; there is little or no chemical reaction and the substrate surface is dense and smooth.

3.1.3. Chemical bonding interface layer

This type of interface layer is characterized by a constant chemical composition across several lattices. The formation of the interface layer results from the chemical reactions of film atoms with substrate atoms which may also be influenced by the residual gas. A distinction is made between intermetallic bonds and alloys and chemical bonds such as oxides, nitrides etc.

3.1.4. Diffusion interface layer

This interface layer is characterized by a generalized constant change in the lattice and the composition in the film–substrate transition area. At least partial solubility is required for diffusion between the film and the substrate material to take place. The necessary energy (1 - 5 eV) must be supplied from elsewhere, *e.g.* when copper is evaporated onto an unheated gold substrate the heat of condensation is sufficient for diffusion to take place. Diffusion layers have advantageous characteristics as transitional layers between very different materials, *e.g.* for reducing mechanical stresses resulting from thermal expansion.

3.1.5. Pseudodiffusion interface layer

This type of layer can be formed by implantation at high particle energies or by sputtering and ion plating of the substrate materials with simultaneous condensation of the film material. Pseudodiffusion interface layers have the same advantageous characteristics as diffusion interface layers, but in contrast with the latter they can be formed from materials that do not mutually diffuse. Ion bombardment before coating can increase the "solubility" in the interface layers, thus increasing the diffusion by producing a higher concentration of point defects [82] and stress gradients [83].

One type of interface layer seldom occurs alone. In normal practice, combinations of the various types of interface layers often occur simultaneously.

3.2. Types of bonding

Adhesion forces lying between 0.1 and 10 eV can be classified as follows: physisorption, chemisorption and chemical bonding.

The charging effect [37] can also be classified as physisorption. When two materials with very different electron affinities are combined, an electrical double layer forms which also contributes to the adhesion. Physisorption contributes up to approximately 0.5 eV to the adhesion. The force lies between 10^4 and 10^8 dyn cm^{-2}.

The interaction between film and substrate atoms which is described as chemisorption can result in strong bonds when electrons are shifted or exchanged. In true chemical bonding such as covalent and ionic bonding as well as in metal bonding the bonding forces are very strong, depending on the degree of electron transfer. In covalent and ionic bonding the resulting bonds tend to be brittle, whereas in metal bonding ductile alloys are often produced. The energy contributed to the adhesion from chemical bonds ranges from 0.5 to about 10 eV. The forces are greater than or equal to 10^{11} dyn cm^{-2}.

This apparently clear picture of differing interface layers and types of interaction is complicated by the fact that surfaces do not behave uniformly because they are under the influence of the so-called active and passive centres. Active centres include grain boundaries, dislocations, vacancies or crystallite faces with varying free energies and activation energies of chemisorption. Passive centres, which are analogous to active centres, are surface areas which have already been covered with foreign material so that little or no chemisorption can take place.

It should be noted that the quality of adhesion improves with time in some cases (*e.g.* silver on glass). This phenomenon can be explained in terms of the slow (diffusion) formation of an oxygen-bonded interface layer. Other investigations made using the scratch test [82, 84] of the changes in adhesion that take place with time for metal films on polymer substrates have shown that there is a marked improvement in the adhesion of the gold film over a period of time. In this case the major part of the improvement in adhesion was attributed to the slow formation of an electrostatic double layer. This was proved by bombarding the film with ions from a glow discharge which broke down the double layer, whereupon the adhesion returned to its original lower value [82]. This series of experiments showed that the electrostatic components contribute significantly to adhesion.

This observation confirms that adhesion seldom comes about only through reciprocal action but rather that it is determined by the combined effects of various intermolecular atomic interactions.

4. Parameters influencing adhesion

The adhesion of thin films is influenced by a large number of parameters. Some of these are defined by the choice of materials for the coating and the substrate. The others are influenced by the preparation of the substrate, the coating process and the handling of the film–substrate combination after the coating process is completed.

4.1. Coating and substrate materials

In most cases the substrate is given and fixed, and the coating is applied to change certain of its characteristics, *e.g.* antireflection coating of lenses, corrosion protection of a metal or improvement of hardness. The choice of material combinations in each case is often quite limited because of the application for which the system is intended. The choice of the combination of substances (if the film is to be evaporation coated) determines whether the interface layer will be of the diffusion type or the chemical bond type, or whether weak reciprocal action forces will be effective across the interface. If it is expected that the adhesion between the chosen materials will be weak, then the adhesion can be improved by the addition of an appropriate intermediate layer (compound system). The most common application of intermediate layers is to improve the adhesion of gold films on oxide substrates, *e.g.* glass. Metals such as chromium which oxidize and alloy easily are usually used as the intermediate layer. The chromium adheres very well to the substrate because of oxidation, and the chromium and gold form a diffusion interface layer which also has very good adhesion [85]. The adhesion of evaporated aluminium films on glass can be greatly improved by using nickel or chromium in a similar way [56]. The evaporation coating of metal alloys with low internal stresses (*e.g.* 75% Ti and 25% Cr) is a special case whereby the components of the alloy themselves often have a very high internal stress [86].

4.2. Substrate preparation

The formation of an interface layer and thus the adhesion are greatly influenced by the physical and chemical structure of the substrate surface and the neighbouring areas as well as by the morphology of the surface (planicity, waviness and roughness).

The chemical composition of a surface itself is almost always different from that of the bulk of the material. Prior treatment of the surface, *e.g.* cutting and polishing, changes not only the mechanical structure but also the chemical structure of the surface. This can have both positive and negative effects on adhesion. For example, a layer comprising the polishing agent (usually an oxide), reaction products, water and glass particles (Beilby film) forms on the substrate surface when glass is polished [87]. Therefore the substrate should be prepared in such a way as to provide a defined and reproducible surface. There are many physical and chemical cleaning and preparation methods that are capable of doing this. The desired cleaning is often achieved by using a cleaning process which has a combination of individual steps. When working out a cleaning process it must be remembered which contaminants are to be cleaned from which surface materials (metal, ceramic etc.).

4.3. Influence of the coating method

The formation of the interface layer is very strongly influenced by the coating process. In the case of films deposited by physical vapour deposition a distinction is made between three different methods of applying the coating (evaporation in a high vacuum, sputtering and ion plating), and the formation of an interface layer and the adhesion are influenced by the energy of the vapour particles condensing on the substrate as well as by the residual gas pressure (see Fig. 3).

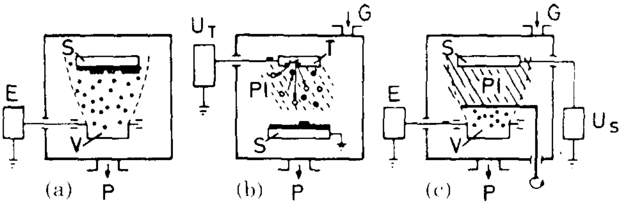

Fig. 3. Schematic diagram of the principle of physical coating processes [18]: (a) evaporation coating in a vacuum; (b) cathode sputtering; (c) ion plating. P, pumping system; V, evaporator; S, substrate; T, target; E, energy supply to evaporator; Pl, plasma; G, controlled gas supply; U_T, negative target voltage (cathode voltage); U_S, substrate voltage.

The average kinetic energy of the vapour particles on evaporation is 0.1 - 0.2 eV. From this low energy it must be concluded that only lightly adsorbed foreign material films with absorption energies of less than 0.1 eV can be removed in this process and that vapour particles cannot in general be implanted under the substrate surface. Therefore the nuclei generally form on or in an absorption layer adhering to the substrate which can function both as a weak boundary layer and as an adhesion layer through chemical bonding.

In cathode sputtering the film material energy is rather higher (1 - 10 eV) [7].

In ion plating a combination of evaporation (because of the high deposition rate) and sputtering (because of the high particle energy) allows particle energies greater than 100 eV to be obtained [88]. Here condensation on the substrate takes place under the simultaneous influence of ions and highly energized neutral particles (plasma) at pressures between 10^{-3} and 10^{-2} mbar. The highly energized particles can remove most of the absorption layer when they arrive at the surface. In addition, sputtering of the substrate surface (particularly for ion plating) and implantation of particles of the film material can also occur. Thus a reciprocal action between the film and the substrate material is possible, *e.g.* a chemical reaction, or perhaps forced diffusion (pseudodiffusion). These are the reasons why films deposited by sputtering and ion plating generally adhere much better than evaporated films.

In addition to the kinetic energy level of the film material, the pressure and composition of the residual gas in the coating equipment also determine the characteristics and adhesion of the film.

If the film is produced by evaporation in a high vacuum, the pressure should be kept below 10^{-5} - 10^{-6} mbar. If this is not done the low energy vapour particles will be dispersed too much in the residual gas at the usual distance between evaporator and substrate (0.5 m). Although 0.5 m corresponds to a mean free path λ at a pressure of 10^{-4} mbar, calculated from the simplified equation

$$\frac{N}{N_0}=\exp\left(-\frac{1}{\lambda}\right) \tag{4}$$

this means that only 40% of the vapour atoms reach the substrate without collisions with the residual gas particles which result in a reduction of energy and a change of direction [89].

Furthermore, the nucleation behaviour depends on the composition of the residual gas absorption layers (particularly condensed water vapour) on the substrate surface which affects the adhesion. It should be noted that, in addition to the microstructure and the molecular structure of the evaporated films, the adhesion is also influenced by the angle at which the vapour particles hit the substrate. No difference in adhesion can be observed for perpendicular angles of incidence θ between 0° and about 48°, but at values of θ of 60° the film microstructure becomes porous and the adhesion is greatly reduced [48].

When the pressure is high (10^{-2} - 10^{-1} mbar) during evaporation coating the proportion of vapour particles reaching the substrate and condensing there is so small, because of the scattering resulting from collisions with residual gas molecules, that the adhesion is bad. In contrast, a sufficient number of highly energized vapour particles reach the substrate and condense there despite multiple collisions when sputtering or ion plating is used.

Sputtering gold films onto glass substrates using oxygen as the sputtering gas is a special case. If argon is used as the noble gas atmosphere, then the adhesion of the gold is only marginally better than that of evaporated films. If a mixture of oxygen and argon is used, the adhesion improves in proportion to the oxygen content of the sputtering gas mixture. When the oxygen content of the gas mixture is only 20%, the film adheres so strongly that it can no longer be removed from the substrate without destroying it [51]. However, good adhesion is obtained when gold films are ion plated onto glass in an argon atmosphere [90].

The substrate temperature has a very strong effect on adhesion. Thus the re-evaporation rate, the surface mobility, the diffusion and the propensity of the atoms to chemical reactions are strongly affected by the substrate temperature. This indicates that the varying adhesion values obtained are dependent on the substrate temperature, and this can be explained in terms of reactions between the film and the substrate material [27], which in turn are dependent on the substrate temperature.

4.4. Aging

In many cases the film–substrate system is not totally stable once the coating process has ended, and it continues to change physically and chemically until it reaches a stable condition [88]. The adhesion of the film to its substrate often undergoes marked changes during this time.

Three processes, which generally progress slowly, are responsible for this aging: chemical reactions in the interface layer area; solid body diffusion across the interface layer; changes in the crystal structure (recrystallization through self-diffusion). These processes are strongly dependent on temperature. Their speed usually increases with increasing temperature [55, 58, 91].

5. Final comments

There are two important aspects of the adhesion of thin films.

From the academic aspect adhesion itself is an interesting phenomenon. Of special interest are the nature and degree of the forces reacting across the interface which actually effect this adhesion (basic adhesion).

From the pragmatic aspect the total adhesive strength of the entire film to the substrate in a practical system has to be considered. Mechanical measuring methods tend to be developed with this in mind. However, the results are influenced and falsified by a multitude of unknown method-specific measurement errors so that the basic adhesion can only be calculated approximately. This does not, however, make these measurements less valuable for practical application. Only through the introduction and expansion of modern investigatory methods will it be possible to carry out research on more complex surface and interface processes. At present the difficulty lies in the fact that a great deal of information on the chemical composition and geometry of the interface layer, the bonding energy between film atoms and substrate atoms, the dipole moments of absorbed complexes, the distribution of electrical conditions, oscillations, surface area diffusion and the kinetics of sorption processes and surface reactions is required. A complete analysis of these effects is not possible at present. This means that only partial solutions to the problems of adhesion can be made while certain limiting conditions are imposed.

This gives the scientist a wide field to work on before he can explain the processes at the interface and deduce from them the laws that could lead to an improvement of adhesion. Those working in practical applications should develop more sophisticated testing methods which allow the energy applied to be measured exactly so that it can be compared with the values deduced theoretically.

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