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Interfacial Adhesion in Metal/Polymer Systems for Electronics

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ABSTRACT

The effects of the different surface modification methods on the adhesion of electroless and sputter-deposited metals to dielectric polymers were investigated. The adhesion of Cu and Cr/Cu metallizations to the epoxies, liquid crystalline polymer and inorganic-organic hybrid polymer was measured with the newly developed pull test method. The microstructure and chemical state of the surfaces were characterized with the help of X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle measurements. The adhesion not only depends on the surface pretreatments but also the metallization techniques. The investigation revealed that plasma, reactive ion etching (RIE) and wet-chemical treatments induced clearly different physico-chemical changes on the polymer surfaces that strongly affected the adhesion of the metals to the polymers. The wet-chemical treatment produced large numbers of microcavities to anchor deposited electroless copper. The dependence of the adhesion on the surface roughness in the electroless copper/polymer systems confirmed the dominant role of the mechanical interlocking. The plasma and RIE treatments were very effective in improving the wettability of the polymer by increasing the surface polarity. It led to considerably better adhesion of sputter-deposited copper to the polymer than the chemical treatment. The enhancement of the surface polarity of the polymer and the enlarged surface contact area due to the increased roughness were the most important factors in the adhesion. SEM of the fracture surfaces showed that the failure modes of the copper/polymer systems were predominantly cohesive in nature within the polymer. By performing the theoretical and experimental investigations into controlling adhesion mechanisms in the metal/polymer systems, a better fundamental understanding of the adhesion between metals and polymers in the high-density built-up modules has been achieved.

PREFACE

This work has been carried out in the Laboratory of Electronic Production of Technology, Helsinki University of Technology, during the period 1999-2002.

I am most grateful to my supervisor, Professor Jorma Kivilahti for providing me with the opportunity to work on this interesting subject. His continuous encouragement, guidance and support have been of great value to me. His vision of the future and his advice has had a remarkable influence on my entire career in research in this field of technology.

I wish to thank all the co-authors of the publications included in this thesis and all the people working in the Laboratory of Electronics Production Technology. I would especially like to mention Markus Turunen, Risto Tuominen, Dr. Tomi Laurila, Pekka Marjamäki and Dr. Kejun Zeng for their suggestions during many useful discussions, Dr. Kari Lounatmaa for his contribution to the SEM examinations as well as Pia Holmberg and Pirjo Kontio for their practical assistance. Thanks also go to Dr. Victor Ovchinnicov from the Microelectronics Center for his assistance in the plasma treatments. I would also like to thank all my friends with whom I spent some very relaxing moments.

I wish to express my warm gratitude to my parents, brother and sister for their love and support.

Finally, I would like to thank my husband Zhijian for his endless love, support and patience and my lovely daughter Minjing for sharing so many wonderful times during the years.

Espoo, September 2003
Jun Ge

Contents:

List of abbreviations and symbols

AFM	Atomic force microscopy
EDS	Energy Dispersive Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
FE	Field emission
HDI	High density interconnect technology
IMB	Integrated module boards
LCP	Liquid crystal polymer
PCB	Printed circuit board
PVD	Physical vapor deposition
Ra	Average roughness
RIE	Reactive ion etching
RF	Radio frequency
RMS	Root mean square roughness
SEM	Scanning electron microscopy
SPM	Scanning probe microscopy
WBL	Weak boundary layer
XPS	X-ray photoelectron spectroscopy
r	Distance between interacting atoms or molecules (m)
G	Gibbs' free energy
μ_i	Chemical potential of components i
n_i	Number of moles of components i
P	Pressure
V	Volume
T	Absolute temperature
S	Entropy
γ	Surface free energy
A	Surface area.
γ_S	Surface energy of the solid surface
γ_L	Surface tension of the liquid
γ_{SL}	Interfacial surface free energy between the solid and the liquid
KE	Kinetic energy of the emitted electron
$h\nu$	Energy of the X-ray source
BE	Binding energy of the electron in the atom
ϕ	Work function
Z	Average height
Zn	Measured height relative to the minimum value, which is equal to 0
N	Number of data points in the area of analysis
θ	Contact angle

List of Publications

Appendix I	J. Ge, R.Tuominen, and J.K. Kivilahti, "Adhesion of Electrolessly-Deposited Copper to Photosensitive Epoxy" Journal of Adhesion Sci. Technol, 15 (2001) 1133.
Appendix II	J.Ge and J.K. Kivilahti, "Effects of Surface Treatments on the Adhesion of Cu and Cr/Cu metallizations to a Multifunctional Photoresist", Journal of Applied Physics, 92 (2002) 3007.
Appendix III	J. Ge, M.P.K. Turunen and J.K. Kivilahti, "Surface Modification of a Liquid Crystalline Polymer for Copper Metallization", Journal of Polymer Science Part B: Polymer Physics, 41 (2003) 623.
Appendix IV	J. Ge, M.P.K. Turunen and J.K. Kivilahti, "Surface Modification and Characterization of Photodefinable Epoxy/Copper Systems", Thin Solid Films, 440 (2003) 198.
Appendix V	J. Ge, M.P.K. Turunen, M. Kusevic and J.K. Kivilahti, "Effects of Surface Treatment on the Adhesion of Copper to a Hybrid Polymer Material", Journal of Materials Research, 18 (2003) 2697.

The research program relating to this thesis was planned by the author together with a co-author, J.K. Kivilahti. The author has played a major role in all aspects of the research work, carrying out most of the experimental work and analyzing the results. The adhesion test method was developed by the author in collaboration with co-authors Risto Tuominen and J.K. Kivilahti. The evaluation of the surface free energy of the polymers needed in this work was carried out jointly by the author and co-author Markus Turunen. The author wrote the manuscripts, all of which have been discussed in detail with the co-authors.

1. Introduction

The increased miniaturization and functionality of electronic products and the broader bandwidths that will be needed for future wireless communication demand the utilization of the most advanced interconnection, packaging and substrate technologies. An example of such technologies is the integrated module board (IMB) technology that is employed in the integration of thin flexible silicon chips and deposited passive components inside high-density build-up substrates [1, 2]. This can be carried out using either the fully additive or semi-additive techniques utilizing photodefinable polymers and metal deposition processes [3, 4]. Likewise, to overcome signal integrity problems and other system performance limitations encountered in very high frequency applications, an increasing amount of research is being carried out into the development of optical interconnections at the printed circuit board level [5-8]. But the technologies enabling the integration of optical and electrical functions in the same polymer substrate require, among other things, the use of the most advanced photodefinable materials like inorganic-organic hybrid polymer materials. It should be noted, however, that good adhesion between polymers and metals in built-up structures is crucial for the successful implementation of distruptive technologies and for the reliability of future electronic devices.

Even though good photopolymer materials exhibiting excellent combinations of physical and chemical properties have been developed, the polymers are inherently hydrophobic, low surface energy materials, with generally quite weak metal/polymer interfacial adhesion. This has been a dominant problem that has limited the more widespread use of such materials in electronics. To achieve sufficient adhesion of metals to polymers, the polymer surfaces are usually modified by a wet-chemical treatment or a dry process such as plasma, UV/Ozone and laser treatments [9-19]. Ideally, the modifications occur only at the polymer surfaces without affecting the desired bulk properties.

The polymer surfaces are generally metallized with electroless copper in printed circuit board applications. Investigations of various electroless copper/polymer systems have shown that, in order to achieve good adhesion, the surface of the polymers must be roughened in order to produce sufficient mechanical interlocking sites [20, 21]. However, there are an increasing number of applications in which roughened polymer surfaces have a deleterious effect on electrical performance, especially in high-frequency broadband wireless communication [22, 23]. In addition, all the available photopolymers cannot be easily micro-roughened. The alternative metallization method used in this thesis was the sputter-deposition. This high-energy method leads to good adhesion, even on a relatively smooth polymer surface. This, in turn, is essential for the good electrical performance needed in high-frequency electronics applications.

Previous attempts to measure the adhesion of metals to polymers have focused on techniques such as the scotch tape test, 90° peel test and stud pull test. Even though the peel test is simple to execute, peel strength represents the combined effect of adhesion and mechanical forces and is very sensitive to variation in test parameters (e.g., angle, rate, etc.). On the other hand, typical pull tests measuring tensile strength use a stud attached to the surface with adhesive, which sets a limit to the pull strength. Therefore, developing a new adhesion test method that avoids the problems mentioned is one of objectives of this work.

In order to get a better understanding of the effects of the different surface modifications and copper deposition methods, it is very useful to employ surface analysis and microstructural methods such as scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact angle measurements. By providing information about the chemical compositions of a few atomic layers of the polymer surfaces, the topographies of the polymer surfaces and the failure modes of the metal/polymer systems, the factors controlling interfacial adhesion can be investigated.

The theoretical and experimental approach was used to discover adhesion mechanisms in multilayer structures for predicting and improving adhesion between dissimilar materials. The results reported in this thesis, and the increased understanding of the adhesion in various metal/polymer systems that can be derived from them, are useful not only for the good adhesion and fabrication process control in the specifics of the systems, but also for other applications at polymer interfaces beyond the systems studied.

2. Adhesion Fundamentals

Adhesion is a complex phenomenon relating to the physical effects and chemical reactions at the interface. According to Adamson's evaluation "the term adhesion has been used in a restricted and ideal sense, as in the work of adhesion concept. It also has the broader and more practical meaning of being simply the failing load, in some specified test, of a particular joint." Kinloch [24] states, "the term adhesion is used when referring to the attraction between the substances". Mittal [25] defines adhesion in three different forms: (i) Fundamental adhesion, (ii) Thermodynamic adhesion, and (iii) Practical adhesion. "Fundamental adhesion is defined as the summation of all interfacial intermolecular interactions between the contacting materials. The thermodynamic adhesion signifies the change in free energy when an interface is formed (or separated). The practical adhesion signifies the force or the work required to remove or detach a film or coating from the substrate irrespective of the locus of failure." The ASTM definition of adhesion is that it is the state in which two surfaces are held together by interfacial forces that may consist of valence forces or interlocking action, or both. However, all the above definitions would probably be unsatisfactory for one or more fundamental reasons.

As stated earlier, the adhesion between metals and polymers plays a decisive role in the reliability and performance of electronics and, in particular, of future high-density electronic assemblies. Adhesion, therefore, will be considered in more detail in this chapter. First, adhesion is discussed thermodynamically, then the basics of intermolecular forces, adhesion mechanisms and techniques of measuring adhesion are reviewed.

2.1 Thermodynamics of adhesion

The thermodynamic systems to be considered will be regarded as consisting of two bulk phases α and β and their mutual interface, and it will be assumed throughout that the α, β and the interface are in equilibrium with each other. The boundary region between two adjacent bulk phases is known as an interface, although, when one of the phases is gas or vapor, the term surface is commonly used [26].

The Gibbs free energy (G) change for an open system is

$$dG = -SdT + Vdp + \sum_i \mu_i \; dn_i \tag{2.1}$$

where μ_i is the chemical potential of component i, n_i the number of moles of components i in the system, p pressure, V volume, T absolute temperature and S the entropy of the system.

If the system contains an interface, the Gibbs free energy change for the whole system is then

$$dG = -SdT + Vdp + \gamma dA + \sum_i \mu_i \; dn_i \tag{2.2}$$

where γ is the free energy and A the area of the interface.

The definition of surface or interfacial free energy in terms of G is therefore

$$\gamma = (\frac{\partial G}{\partial A})_{T,p,n_i} \tag{2.3}$$

It is observed that in most instances a liquid placed on a solid will not wet it but remain as a drop having a definite angle of contact between the liquid and solid phases.

The change in surface free energy, ΔG^s, accompanying a small displacement of the liquid such that the change in area of solid covered, ΔA, is

$$\Delta G^s = \Delta A \; (\gamma_{SL} - \gamma_{SV^0}) + \Delta A \, \gamma_{LV} \cos{(\theta - \Delta\theta)} \tag{2.4}$$

where γ_{SV^0} is the surface free energy of the solid surface in equilibrium with the saturated vapor of the wetting liquid, γ_{LV} the surface tension of the liquid, and γ_{SL} the interfacial surface free energy between the solid and the liquid [27].

At equilibrium,

$$\lim_{\Delta A \to 0} \frac{\Delta G^{s}}{\Delta A} = 0$$

and

$$\gamma_{SL} - \gamma_{SV}^{0} + \gamma_{LV}\cos\theta = 0^{\dagger} \qquad [2.5]$$

†It can be shown that, regardless of the microscopic geometry of the system, $\Delta\theta/\Delta A$ behaves as a second-order differential and drops out in taking the limit of $\Delta A \longrightarrow 0$ [27].

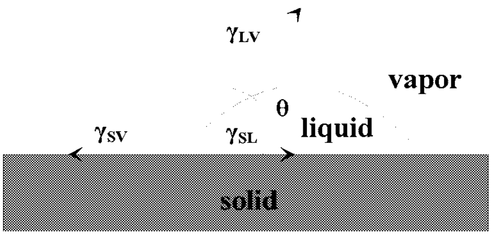


Figure 2.1 Balance of surface energies in the contact angle experiment.

This equation is commonly known as the Young equation. In this, it is assumed that $\gamma_{SV^0} = \gamma_S$, i.e. that vapors from the liquid do not adsorb at the solid-gas interface. The presence of adsorbed vapors of the liquid in equilibrium-contact with the solid cause a reduction of the surface free energy of the solid, known as the equilibrium spreading pressure, $\pi_S = \gamma_S - \gamma_{SV}$. However, for hydrophobic low-energy solid surfaces, there is only a small difference between the observed contact angles (less than the detection limit of the goniometry) measured in air or under vacuum for high-boiling-point liquids. The spreading pressure is considered to be negligible.

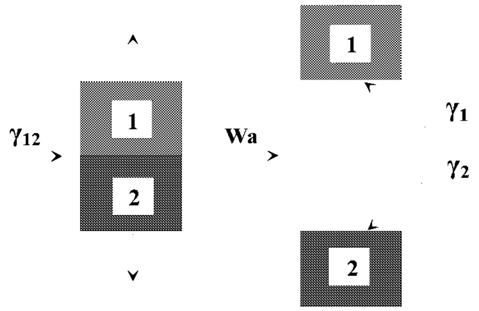


Figure 2.2 Work of adhesion

The work of adhesion is defined as the reversible free energy change for separating two phases that originally have a common interface (Fig. 2.2). Thus, the work of adhesion is given in terms of the surface free energies as

$$Wa = \gamma_1 + \gamma_2 - \gamma_{12} \qquad [2.6]$$

where γ_1 and γ_2 refer to phase 1 and phase 2 in vacuum [28, 29], respectively. Combining the above with the Young equation leads to the Young-Dupré equation:

$$Wa = \gamma_{12}(1+\cos\theta) \qquad [2.7]$$

The ability of a liquid to wet and spread on a solid is often described by the spreading coefficient S_{SL}, which is related to the surface free energy:

$$S_{SL} = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \qquad [2.8]$$

or

$$S_{SL} = Wa - 2\gamma_{LV} \qquad [2.9]$$

This equation defines the spreading coefficient for a liquid on a solid surface, S_{SL}, where γ_{LV} is the surface tension of the liquid. γ_{SV} the surface free energy of the solid and γ_{SL} the interfacial free energy between the solid and liquid. S_{SL} is positive if spreading is accompanied by a decrease in surface free energy. A large positive implies that a liquid will spontaneously wet and spread on the solid. A negative implies a lack of wetting and spreading by the liquid and the existence of a finite contact angle. When the work of adhesion is twice the surface tension of the liquid, the spreading coefficient will be equal to zero and the liquid will wet the substrate.

2.2 Basics of intermolecular forces

There are several forces between molecules that contribute to the adhesion at the intimate molecular contact surfaces of two materials. The typical intermolecular forces are summarized in Table 1 [30-32]. The forces are repulsive at short distances and attractive at large distances. The covalent forces, which exist within the molecule, are of short range, and therefore very strong among the intermolecular forces. The force between the charged ions is the ion-ion force, obeying the coulomb law. A charged ion will also exert a force on a neutral molecule, which is called the ion-dipole force. The force will be much weaker than an ionic bond. Similarly, the dipole-dipole force is the force between a pair of molecules each with a dipole moment, which are weaker than that between an ion and a polar molecule. With increasing distances, the strength of the force between a pair of polar molecules also decreases more rapidly than the force between a pair of ions. Hydrogen bonding is responsible for both hydrophobic and hydrophilic interactions. Hydrophobic interaction drives non-polar groups to form clusters in order to minimize their surface area in the polar medium. They are linked intimately to processes such as the folding of proteins and the binding of enzymes to substrates. Hydrophilic interaction occurs between polar/ionic molecules and the polar liquid. Dispersion forces arise from the temporary variations in electron density around atoms/molecules and exist in all molecules. It should be noted that, for a given pair of molecules, there may be several types of intermolecular force at work.

Type of intermolecular forces	Typical energy (kcal.mol^{-1})	Range (nm)	Molecules involved
Covalent	Complicated	Short range	Carbon-carbon bond
Ion-ion	Proportional to $1/r$ (Coulomb energy)	Short range	2 ions
Hydrogen bond	Complicated Roughly proportional to $1/r^2$	Short range	A-H and B where A, B = F, O, N
Ion-dipole	Proportional to $-1/r^2$ or $-1/r^4$	Variable, long	An ion and a polar molecule
Dipole-dipole	Proportional to $-1/r^3$ or $-1/r^6$	Variable, long	Stationary polar molecules
Induced dipole-ion	Proportional to $-1/r^4$	Variable, long	An ion and a non-polar molecule
Dipole-induced dipole	Proportional to $-1/r^6$	Variable, long	Polar and non-polar molecules
Induced dipole-induced dipole	Proportional to $-1/r^6$	Variable, long	Non-polar molecules

Table1 Type of intermolecular forces. r is distance between interacting atoms or molecules (m).

2.3 Mechanical interlocking

The mechanical theory of adhesion is associated with adhesion to rough surfaces and postulates that the adhesion is achieved as a consequence of coating penetration into surface irregularities resulting in 'interlocking' [33-38], as shown in Fig. 2.3. In the metal/polymer systems, polymer surfaces are treated with etchants, which serve to create microcavities. Anchoring takes place during the plating of electroless metal on the roughened polymer surface. Strong adhesion of the electroless metal plating to the plastics is obtained only when the plastics have been pretreated to produce sufficient interlocking sites. The mechanical effect of surface roughness might then contribute more to parallel shear force than to the tensile forces.

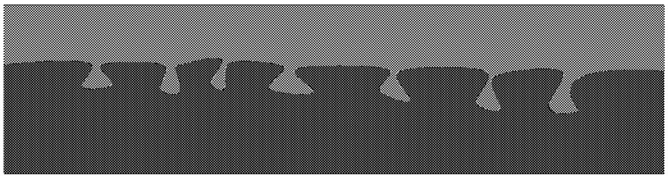


Figure 2.3 Schematic presentation of mechanical interlocking at the metal-polymer interface

Although mechanical interlocking arises solely from the topography of the substrate surface, it should be noted that the treatments for altering surface topography may induce additional chemical changes, such as forming functional groups on the polymer surface so as to render it hydrophilic. Surface roughness is attributed to adhesion and may be due to mechanical interlocking or to its increasing the contact area for chemical interaction, depending, in some cases, on the degree and shape of the roughness.

It should be emphasized that mechanical interlocking is not an adhesion mechanism at molecular level. It is merely a technical means of increasing the adsorption of the coating on the substrate [39, 40]. The roughness of substrates is generally a contributing factor only if the coating penetrates completely into all the irregularities of the surface and wet surface. Failure to completely penetrate can lead to less coating-to-interface contact than the corresponding geometric area and will leave voids between the coating and the substrate. The increased roughness can lead to decreased adhesion, since trapped air bubbles in these voids will allow an accumulation of moisture.

2.4 Chemical bonding

According to this theory, a chemical reaction between two materials coming into contact is responsible for adhesion [41, 42]. The adhering phases undergo chemical reaction with each other to form covalent bonds at the surface. In order to form sufficient chemical bonds, intimate contact between two materials must be achieved. The adhesion due to the formation of chemical bonds at the interface will obviously be strong. This can be achieved by employing proper surface treatments or by using various coupling agents. It does, however, require that there be mutually reactive chemical groups tightly bound at the substrate and coating surfaces. Obviously, coatings containing reactive functional groups such as hydroxyl or carboxyl moieties tend to adhere more tenaciously to substrates containing similar groups. Some polymer surfaces, such as wood, composites and some plastics, contain various chemical functional groups that, under appropriate conditions, can produce chemical bonds with the coating material. For example, the epoxy groups of an epoxy resin can react with the hydroxyl groups of cellulose at the interface (Fig. 2.4).

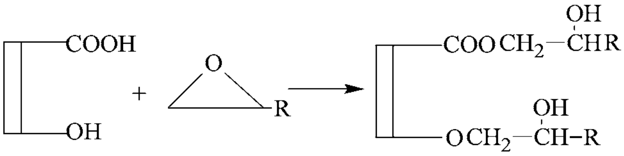
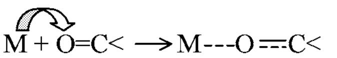


Figure 2.4 Reaction schemes in the polymer/polymer system

Organosilanes are widely used as primers on glass fibers to promote the adhesion between the resin and the glass. Essentially, during application, silanol groups are produced, which then react with the silanol groups on the glass surface, or possibly with other metal oxide groups, to form strong ether linkages. Another example is hybrid inorganic-organic material being synthesized with the sol-gel technology. The reaction of Si-OH groups of the sol with surface hydroxyl groups of the substrates leads to a covalent bond to the surface.

Adhesion frequently takes place through chemical bonding in metal/polymer systems. Chemical bonds are formed at the interface, usually as a result of a charge transfer from the metal to the polymer. In the case of sputter-deposition, which has the energetic nature of the deposition method, some metals (Ti, Cr, Zr, Al) can strongly bond to oxidized polymer surfaces [43, 44]. Copper forms rather less stable bonds, but still gives considerable adhesion improvement. It is expected that, when the hydrophilic groups on the polymer surface make contact with the metal layer, electrons are transferred from the metal to hydrophilic groups, resulting in the formation of a charge transfer complex, which enhances the adhesion between the metal and polymer (Fig. 2.5).



$$M + O{=}C< \longrightarrow M{-}{-}{-}O{=\!=}C<$$

Formation of M-O-C complex (M=Cr, Cu, etc.)

$2Cr + (O)\text{-polymer} \longrightarrow Cr_2O_3$ + organic fragments

Formation of Cr (III) oxide by a redox reaction between Cr and oxygen-containing functional groups of the polymers

Figure 2.5 Proposed reaction schemes for metal-deposited polymers

2.5 Adsorption

The adsorption mechanism theory suggests that bonding is the process of intermolecular attraction. The interactions, which may occur across an interface, include the following: London dispersion forces, dipole/dipole interactions, dipole/induced dipole forces, hydrogen bonding, acid/base interactions, and covalent bonds [24, 45]. Since these forces are effective over distances in the range of several angstroms, the two surfaces must be in extremely close contact with one another if these types of interactions are to contribute to adhesion. It must therefore be emphasized that, according to this theory, the wetting of a coating onto the substrate is the basic contributory factor in improving adhesion (Fig. 2.6).

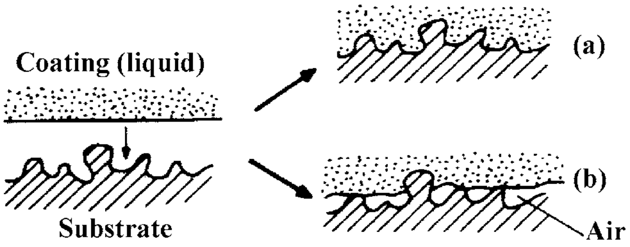


Figure 2.6 (a) good wetting (b) poor wetting

2.6 Weak boundary layer (WBL)

Instead of explaining why two materials adhere together, the weak boundary layer model explains what causes adhesion to fail. The theory suggests that rupture always takes place at the weakest link found at the interface between materials. Upon failure, interfacial bonds break not at the interface, but slightly within the substrate or the coating adjacent to the interface. This suggests that a boundary layer of weak material is formed around the interface between the two materials. The removal of the WBL has been shown to improve interfacial bonding strength [46, 47].

Several classes of weak boundary layers that lead to failure in adhesion are considered. They consist of one of the following four possibilities:

- Air, when the substrate is poorly wetted by the polymer
- Contaminants (impurities, additives, pollutants) or compounds of low molecular weight moving toward the interface, and present in either the coating or the substrate
- Products of reactions between air and substrate or between substrates
- Unfavorable surface topography of the substrate, which acts as a rupture center.

2.7 Diffusion

The interdiffusion or diffusion theory attributes adhesion to intermolecular entanglements across the coating/substrate interface (Fig. 2.7) [48-51]. Bonding is the result of the entanglement of long-chain compounds across the interface after materials have interdiffused into one another. Such interdiffusion occurs only if the polymer chains are mobile (i.e. when the temperature is above the glass transition temperatures) and compatible, as in the case of two thermoplastic materials with some mutual solubility [50, 51]. The thermoplastics diffuse into each other when raised to temperatures above their glass transition point. This interdiffusion causes the strength of the interface to increase with time, until it reaches the cohesive strength of the materials. For example, entanglement of polymer chains is the key contributor to adhesion at the polyimide-to-polyimide interfaces. This interdiffusion has also been found to be maximized with high degrees of monomer flexibility or a coating of a second layer of polyimide film over a partially cured first layer, allowing greater molecular chain entanglement.

Since this model requires that the coating and substrate are mutually soluble and have significant mobility, the mechanism does not directly work in the case of metal/polymer systems. In practice, appreciable diffusion does not take place under normal conditions of temperature. The diffusion model is therefore limited to the autohesion and adhesion of compatible polymers, as well as to the welding of thermoplastics.

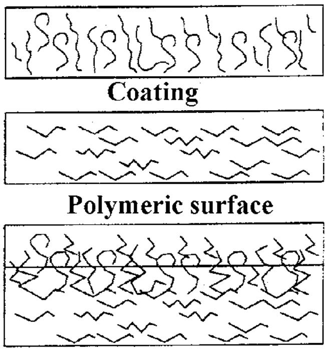


Figure 2.7 Schematics of diffusion of coatings in polymeric surfaces.

2.8. Electrostatic

According to this theory, if two dissimilar materials come in contact, then a charge transfer takes place resulting in the formation of an electrical double layer [52-54]. The attractive forces inherent in the double layer contribute to adhesion. For instance, if two metals are placed in contact, electrons will be transferred from one to the other thus forming an electrical double layer, which produces a force of attraction. Polymers can be negatively or positively charged depending on the contacting metal. A double layer at the polymer-metal interface exists (Fig. 2.8). The electrostatic contribution to adhesion depends on the surface charge density.

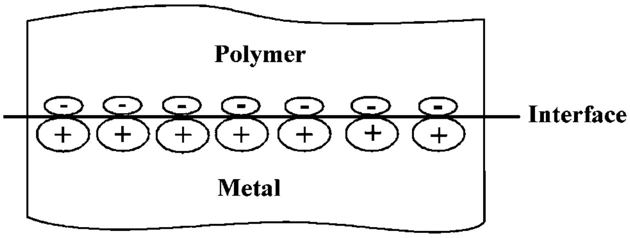


Figure 2.8 Schematic diagram of the electrical double layer at polymer-metal interface

It should be noted that among these theories, the adsorption model is the one concerned with the establishment of intimate molecular contact as a prerequisite for developing strong adhesion. Good adhesion can be established by forming a covalent bond at the interface or by mechanical interlocking. In addition, the diffusion of thermoplastic molecules across the interface, allowing the polymeric chains to entangle, seems to be generally accepted as playing an important role in the polymer-polymer adhesion. However, neither chemical bonding nor interdiffusion can be established in the case of poor wettability, because intermolecular contact cannot be achieved.

Adhesion enhancement of metal/polymer system has been explained by the following mechanisms: (1) interlocking between the metal layer and rough polymer surface, (2) formation of chemical bonding or charge transfer complex between electropositive metal and electronegative hydrophilic groups on the polymer surface (3) removal of a weak boundary layer, etc.

3. Adhesion Measurement Techniques

Techniques to measure the practical adhesion of thin films, thick films, and coatings have been reviewed extensively [25, 55]. These methods can be classified into the following two types: 1) Direct and semi-direct methods (e.g., scratch test, ultrasonic energy); 2) indirect methods (e.g., peel test, pull test, shear test). Test geometries for indirect methods are shown in Figure 3.1. The tape method uses an adhesive tape to lift the film off the substrate. This method gives only qualitative results. The peel test is simple to execute, but peel-strength values are affected by a number of experimental parameters, e.g., angle, rate and width of peel (Fig. 3.2). In a pull test, a stud is attached to the surface to be tested with an adhesive. This technique provides a tensile strength, which involves more quantitative data than the peel test (Fig. 3.3). However, the measured pull strength is limited by the adhesives (used to bond stud). The shear test determines the shear adhesive strength of the forces parallel to the surface that is needed to break the joint. Therefore, the results obtained from the different types of tests are not comparable.

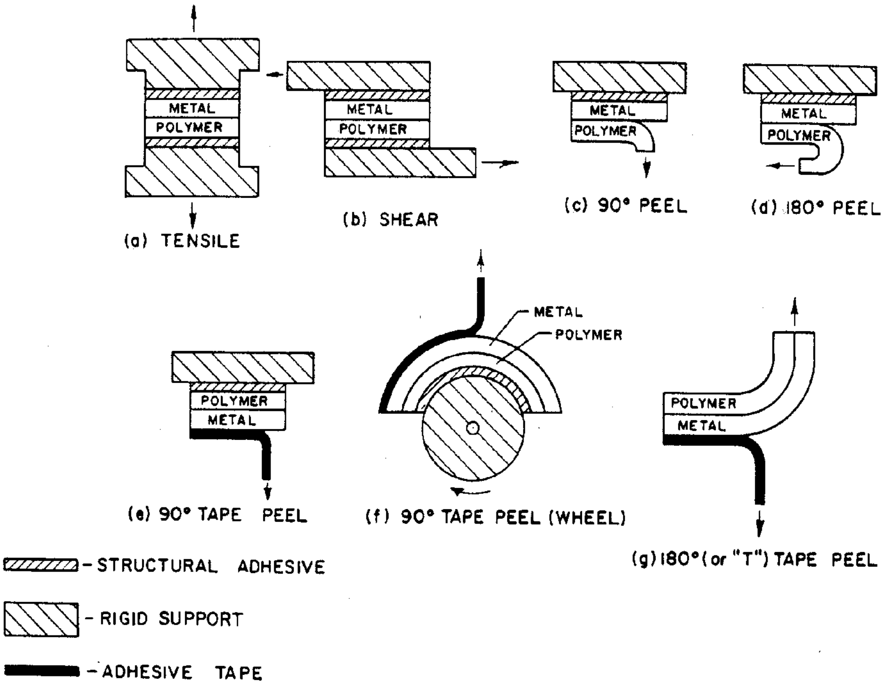


Figure 3.1 Indirect methods: Test geometries

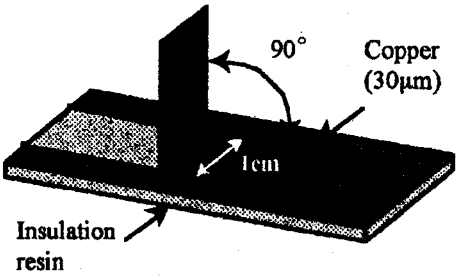


Figure 3.2 90°C peel test

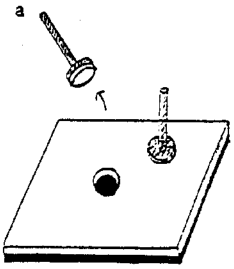


Figure 3.3 Stud pull test

To avoid the problems mentioned, a new pull test method to characterize and evaluate the adhesion of metal/polymer systems has been developed in this work. With this method, it is possible to make a large number of test samples simultaneously with the same semi-additive process. In addition, the data scatter is small; the pull strength values can therefore be obtained with good reproducibility.

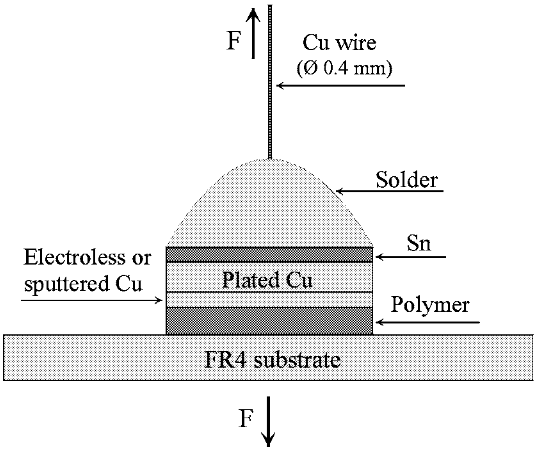


Figure 3.4 Newly developed pull test

In this technique, the tensile test machine (Table Top System 858 from MTS) is used to measure the tensile strength. The test pads are fabricated on the substrate by using a semi-additive plating process. The specimen is then fixed to the test set-up, and a copper wire clamped in the grip and pulled at a constant ramp rate of 0.001 mm/s. The force required to break the weakest interface can be recorded. The test pad area is calculated by assuming that the pad is circular. The pull strength is evaluated as the average tensile strength of the twelve specimens prepared under the same conditions. The schematic representation of the adhesion test configuration is given in Fig. 3.4.

4. Dielectric polymer materials

Dielectric polymer is one of the key materials in electronics. With the development of novel technologies, new and more stringent demands are set for the materials being used. Traditional choices can no longer be relied on; instead, alternatives have to be searched for. Polymer performance is based on the complex interrelationship between such properties as glass transition temperature, moisture absorption, thermal and chemical stability and the inherent electrical and mechanical properties of polymer. Many polymers are nearing the limits of their performance capabilities in many applications, and their final properties depend on changes induced in processing. Careful selection and processing of dielectric material is important to ensure good reliability. Dielectric materials will be selected among commercially available products, taking into account the fabrication process and their impacts on cost, performance and reliability.

The criteria for the selection of high-performance polymers are summarized in Table 2. Dielectric materials that are appropriate in electronic applications include: epoxy, polyimides, benzocyclobutenes, liquid crystalline polymer, inorganic-organic hybrid polymer, cyclo-olefin copolymer, etc.

Table 2. Criteria for the Selection of Materials

- Thermal stability: high glass transition temperature (Tg-value)
- Electrical performance:
  Low dielectric constant, high dielectric strength, stable dielectric property over wide temperature, humidity and frequency ranges
- Low water absorption
- Dimensional stability
- Good planarization
- Processing capability (microvia formation and metallization):
  Compatibility with multilayer processing, good adhesion, good chemical resistance, good mechanical strength, good thermal stability, easy film application
- Availability and cost

Epoxies

The current main dielectric materials are epoxy-based materials, due to their having significantly lower costs than other polymers, e.g., polyimide and benzocyclobutene, etc. Epoxies are usually made photodefinable by mixing the base resin with photosensitizing agents [56-58]. Instead of the radical polymerization of an acrylate and or methacryrate system by using a photo-radical generator, epoxy resins can be cured through etherification of the epoxide rings, which can follow cationic pathways. Cationic photoinitiators are generally onium salts, which, when subjected to UV light, decompose to produce an acid. This acid is a catalyst for the rapid cationic polymerization of epoxides. The acid-catalyzed cationic ring-opening polymerization of epoxy groups is shown in Fig. 4.1.

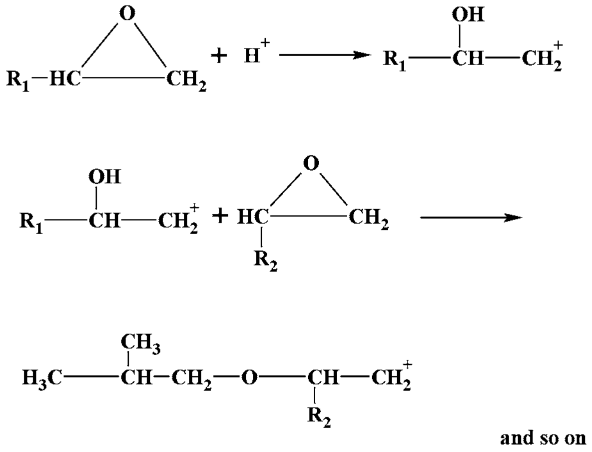


Figure 4.1 Acid-catalyzed cationic ring-opening polymerization of epoxy groups

An advanced epoxy material (SU-8), which is a multifunctional photoresist, has been recently introduced to microelectromechanical (MEMS) applications. Good processibility and high resolution make it exceptionally attractive for the integration active and passive components inside high-density multilayer printed wiring boards; this technology is gaining great importance in the manufacture of the most advanced consumer electronics. The SU-8 provides the highest epoxide functionality commercially available among the epoxies [59]. It therefore results in highly mechanically and thermally stable photoresist. A schematic presentation of the structure of this is given in Fig. 4.2.

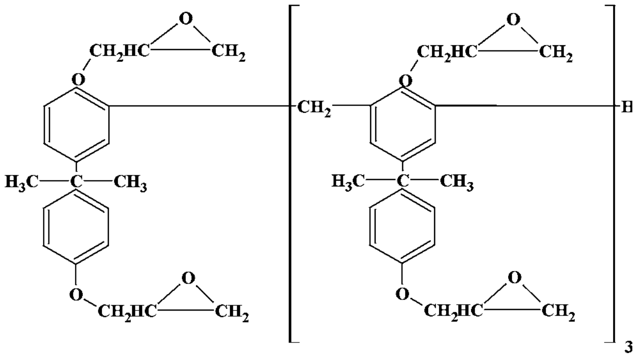


Figure 4.2 Schematic presentation of SU-8 structure

Hybrid inorganic-organic polymers (ORMOCERs)

Inorganic-organic hybrid polymers combine the advantages of polymers, such as flexibility, toughness, and ease of processing, with those of inorganic solids (hardness, chemical resistance and thermal stability), and also with excellent optical properties. They are synthesized with the sol-gel technology [60, 61]. The main advantage of the sol-gel process is that it facilitates molecular-level control with its associated mild conditions to achieve good chemical and physical properties. Such a new approach enables the integration of a variety of different material properties. Figure 4.3 [62] shows the processing of these types of materials. The use of organically functionalized alkoxysilanes enables the permanent incorporation of these groups by crosslinking to the inorganic siloxane network via the Si-O-Si-linkages process.

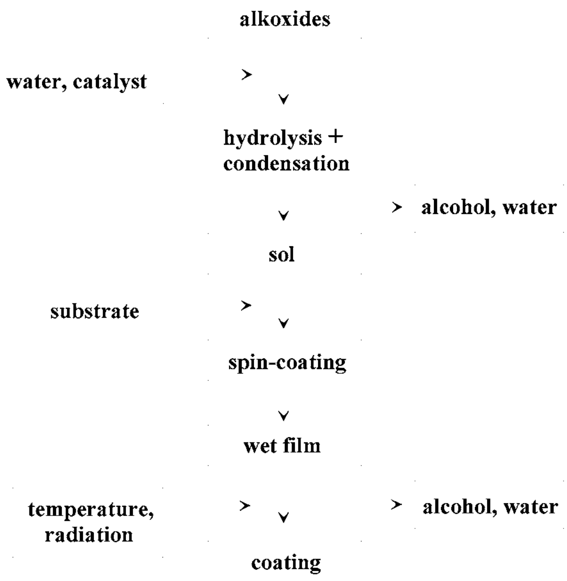


Figure 4.3 Sol-gel materials processing for coatings

During sol-gel processing, the inorganic network is formed first; then, upon UV-exposure, the acrylic C=C double bonds are initiated and start to crosslink the organic part to the inorganic sol-gel network. The sensitivity of the crosslinking process in inorganic-organic sol-gel materials is mainly controlled by photoinitiators. When the photoinitiators are irradiated by UV light it forms an excited state I* by absorption of photons. The excited species undergo homolysis to produce radicals $I^* \rightarrow R\cdot + R'\cdot$ capable of initiating the polymerization of organic sites in the hybrid material. The C=C (carbon-carbon double bonds) open up and react with other double bonds.

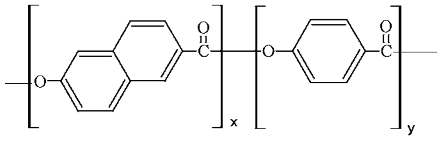
The properties of the material can be adjusted to particular applications. Some features of these materials are:

- High Tg (>300°C)
- Postbaking at moderate temperatures (120-180°C) enables processing on substrates such as FR4 or BT
- Combined use as dielectric and passivation layers in electrical systems and devices as well as core and cladding for optical applications
- Easily adaptable to thin film technology: spin-on with planarization > 90%, via diameters down to even 20 µm, has been achieved.

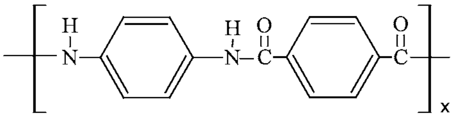
In additional, the sol-gel materials are cost effective, possess good mechanical and chemical stability and high transmission characteristics over a broad wavelength range.

Liquid crystalline polymers

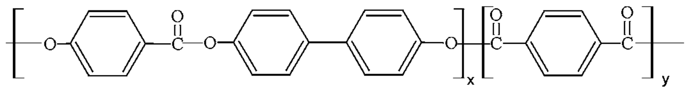
Liquid crystal polymers (LCPs) are thermoplastic. To form a polymeric liquid crystalline phase, the most important molecular feature needed is a rigid anisotropic unit called a mesogen [63-65]. Mesogenic units are important because they create rodlike molecules (main-chain LCPs) or branches (side-chain LCPs), which can organize to form liquid crystalline order. Mesogens are usually based on stiff, aromatic units with bridging groups linking the individual aromatic units. There is a large number of main-chain thermoplastic polymers. They can be classified into two groups. One consists of rod-like moieties along the backbone of the polymer chain, known as wholly aromatic, thermotropic LCPs, and have relatively stiff and extended conformations; the other consists of regularly alternating rod-like mieties and flexible spacers in the main chain, known as semiflexible thermotropic LCPs. As a consequence of chain stiffness and packing density, only the wholly aromatic, thermoplastic polymers exhibit excellent mechanical properties for applications as high-performance materials. The repeating unit structures of the commercial LCP are shown in Fig 4.4.



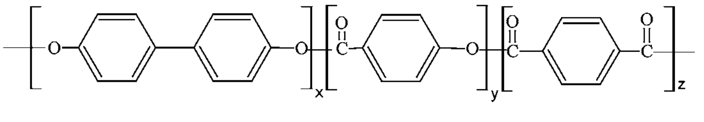
Vectra



Kevlar



Xydar



BIAC

Figure 4.4 Structure of commercially available LCPs

As a result of the unique structure, LCP offers an excellent combination of physical and chemical properties. It was widely used as a high-performance material for high-density printed circuit board (PCB) fabrication and semiconductor packaging. Compared to polyimide, LCP films have about one-tenth of the moisture uptake and both lower dielectric constant and loss (dissipation) factor, which are not significantly affected by physicochemical changes in the operational environment. In addition, it has excellent chemical resistance and is virtually unaffected by most acids, bases and solvents over a considerably long time and through a broad temperature range.

5. Surface Modification and Metallization Techniques

Polymers are inherently hydrophobic, low surface free energy materials, thus their metal/polymer adhesion is generally poor. The approach to enhance the adhesion of metals to polymer has been usually through either a dry process such as plasma, corona discharge, X-ray, laser, ion beam, flame treatments, or wet-chemical treatment. All treatments alter the surface region in one or more ways, by, for example, changing the chemical nature of the surface or the surface topography or by removing a weak boundary layer. Proper surface modifications can offer significant benefits by allowing the surface properties to be tailored to improve adhesion while leaving the bulk polymer unaffected.

5.1 Wet-chemical treatment

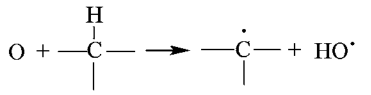
Wet-chemical etching is essentially an isotropic process that produces very roughened polymer surfaces due to polymer heterogeneities, e.g., flexibiliser and silica filler additives. Various types of chemicals such as potassium permanganate and potassium dichromate/sulfuric acid can be used to modify surfaces, depending on the nature of polymers [66, 67]. However, the use of this technique to form a roughened surface layer is not available for all polymers. Often chemicals will work well for one material but will not be effective for another. The wet-chemical etching process with potassium permanganate solution is commonly used to improve the adhesion of electrolessly deposited copper onto polymers in printed circuit boards manufacturing.

The chemical and topographic changes of the polymer surface are dependent on the nature of the polymers and the treatment parameters. During the early stage of etching, polar groups are introduced on the polymer surface. With the longer etching, microcavities, which provide mechanical interlocking sites, can be formed. However, an aggressive treatment can affect the bulk polymer properties and cause fractures at the modified surface/virgin polymer interface, thereby degrading adhesion. The main disadvantage of this method is the need for hazardous chemicals that incur high costs in their safe use and the proper disposal of the waste chemical solutions.

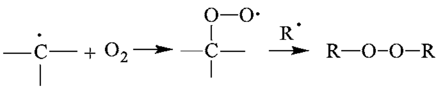
5.2 Plasma treatment

The utilization of plasma typically involves the dry treatment method. During plasma processing, chemically reactive plasmas are formed by introducing gases such as H_2, O_2, CO_2, N_2, and CF_4 etc. The samples are exposed to a complex reactive medium containing energetic species including ions, electrons, radicals etc. Atomic or molecular radicals are often cited as the key species responsible for initiating surface reactions during plasma processing [68-70]. In order to enhance etching of polymers in oxygen plasmas, an efficient way to increase the atomic oxygen concentration in O_2 plasmas is by the addition of fluorine-containing gases. Plasma etching rates can increase after an addition of a small amount of CF_4 to the O_2 gas-feed. Atomic oxygen is mainly produced through electron-induced dissociation processes. Therefore, the enhancement of oxygen atom production upon addition of CF_4 is probably due to increases of the electron density in the plasma. In addition, atomic fluorine can react chemically with a polymer, leading to reactive radical sites. These sites can further react with atomic or molecular oxygen, inducing polymer backbone cleavage by the formed alkoxy radicals. Although fluorine-containing gases like CF_4 can enhance the etching rates of polymers, excess fluorine in the O_2/CF_4 plasma can serve to inhibit etching through fluorination. Unlike polymer-forming plasmas, reactive plasmas do not form solid polymeric deposits but physically and chemically react with the surface of polymeric materials. These reactions can result in crosslinking, oxidation, or etching of the surface macromolecules. The adhesion can therefore be enhanced by several factors: removal of contaminants (weak boundary layers), an increase in the surface energy of the substrate and chemically reactive sites for the coating to chemically bond [71-75].

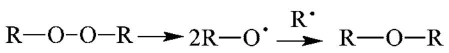
The following oxidation reaction scheme is expected to produce oxygen functional groups on polymeric surfaces. First, hydrogen is abstracted from the polymer backbone, R, by atomic oxygen present in the plasma, leaving the polymer with free radical sites. These species react rapidly with molecular oxygen to produce a peroxyradical whose subsequent chemistry leads to the formation of R-O-R, C=O, and O-C=O functional groups. The alkoxyl radical produced in reaction (6) is the most likely source of cleavage of a polymer chain:



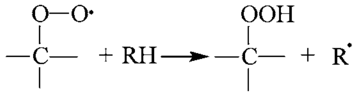
$$\mathrm{O} + -\underset{|}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}- \longrightarrow -\underset{|}{\overset{\bullet}{\mathrm{C}}}- + \mathrm{HO}^{\bullet} \qquad [5.1]$$



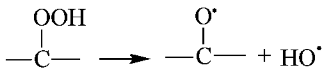
$$-\underset{|}{\overset{\bullet}{\mathrm{C}}}- + \mathrm{O}_2 \longrightarrow -\underset{|}{\overset{\overset{\mathrm{O-O}^{\bullet}}{|}}{\mathrm{C}}}- \xrightarrow{\mathrm{R}^{\bullet}} \mathrm{R{-}O{-}O{-}R} \qquad [5.2]$$



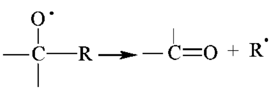
$$\mathrm{R{-}O{-}O{-}R} \longrightarrow 2\mathrm{R{-}O}^{\bullet} \xrightarrow{\mathrm{R}^{\bullet}} \mathrm{R{-}O{-}R} \qquad [5.3]$$



$$-\underset{|}{\overset{\overset{\mathrm{O-O}^{\bullet}}{|}}{\mathrm{C}}}- + \mathrm{RH} \longrightarrow -\underset{|}{\overset{\overset{\mathrm{OOH}}{|}}{\mathrm{C}}}- + \mathrm{R}^{\bullet} \qquad [5.4]$$

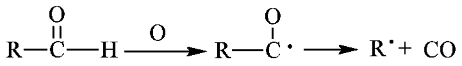


$$-\overset{\overset{\mathrm{OOH}}{|}}{\mathrm{C}}- \longrightarrow -\overset{\overset{\mathrm{O}^{\bullet}}{|}}{\mathrm{C}}- + \mathrm{HO}^{\bullet} \qquad [5.5]$$



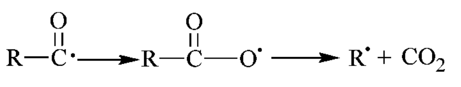
$$-\underset{|}{\overset{\overset{\mathrm{O}^{\bullet}}{|}}{\mathrm{C}}}-\mathrm{R} \longrightarrow -\overset{|}{\mathrm{C}}{=}\mathrm{O} + \mathrm{R}^{\bullet} \qquad [5.6]$$

Reactive plasmas vary in their ability to chemically etch polymers, depending on the volatility of the products they form. The formation of nonvolatile low molecular weight products may dominate etching, depending on the type of substrate, the reactive gas used, and the discharge conditions. The nonvolatile oxidized products resting on a surface provide an extremely unstable state of surface because they are poorly attached to the surfaces, which can be washed away with proper solvents. The formation of volatile CO and CO_2 species results in the removal of carbon from the polymer surface that exits the reactor via the vacuum system through reactions such as:



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}H \xrightarrow{O} R{-}\overset{\overset{O}{|}}{C}{\cdot} \longrightarrow R^{\cdot} + CO}$$

[5.7]



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{\cdot} \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}O^{\bullet} \longrightarrow R^{\bullet} + CO_2}$$

[5.8]

Basically, plasma etching can proceed through two different pathways (Fig. 5.1). Firstly, a polymer substrate is etched by chemical reaction of reactive plasma species (e.g., atomic, molecular and free radicals) with the surface of polymeric materials, referred to as chemical etching. Secondly, ion bombardment onto a polymer surface causes sputtering of the surface, which is a physical process. However, chemical etching is a typically dominant process in the plasma treatment [68-70]. It is an ablative process that causes oxidation and subsequent chain scission of the outermost macromolecules. The formed volatile organic products exit the reactor via the vacuum system. It should be noted that the effects of the plasma reaction depend on a given experiment. For a given substrate, the parameters that play a role in plasma etching can be divided into two categories: apparatus parameters (e.g., reactor type, frequency, electrodes) and discharge parameters (e.g., type of gas (etchant), discharge power, gas flow rate, pressure, treatment time). The reactor used in this work has the barrel plasma-etching configuration (Fig. 5.2); a perforated metal tunnel was added to shield the grounded samples from ion bombardment. The etching is therefore primarily due to the chemical reaction between the etchant gas (oxygen) and the samples, rather than the physical sputtering of the samples. The main disadvantage of plasma treatments is that a vacuum system is required. This demand increases the cost of the operation.

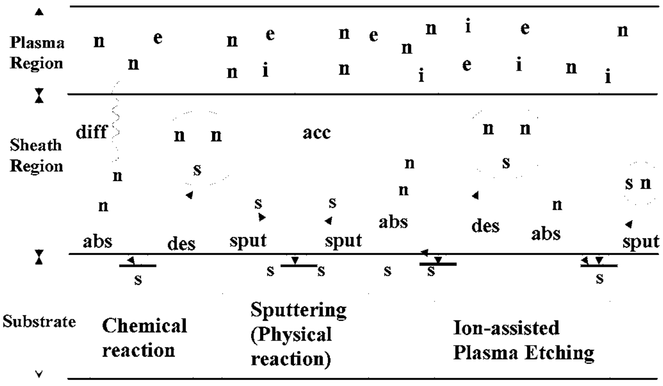


Figure 5.1 Different etch mechanisms. Surface atoms are represented by s, neutral species are represented by n, and ions by i. The abbreviations Diff, abs, des, acc and sput mean diffusion, absorption, desorption, accelerated and sputtering, respectively.

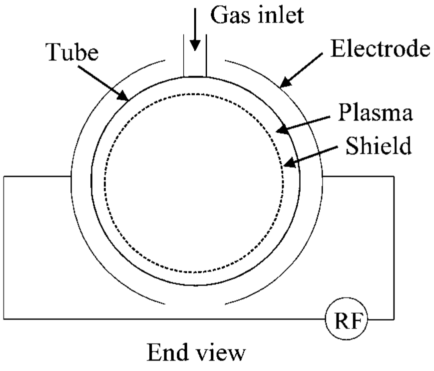


Figure 5.2 A barrel reactor configuration

5.3 Reactive ion etching (RIE)

The combined chemical etching and accelerated ion bombardments result in anisotropical etching of the polymer surface. This combined process is commonly referred to as reactive ion etching (RIE) [76-78]. In this method, a parallel plate reactor is used. The gas pressure is less than 13 Pa, and the samples are biased. The plasma are produced in the region between two electrodes, and the samples are placed directly below the plasma, on a plate shielding the lower electrode, which was powered by a 13.56 MHz radio frequency (RF) generator. The powered electrode has much less area than the grounded one, resulting in a large negative DC voltage on the lower electrode. Physical etching (i.e. ion bombardment) is therefore involved. The general setup is shown in Fig. 5.3 [79].

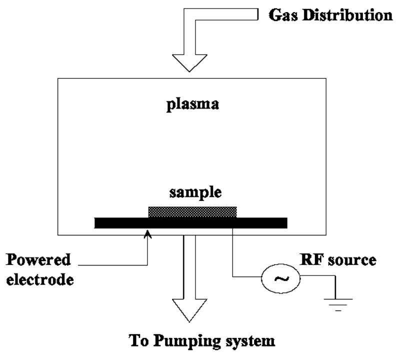


Figure 5.3 A parallel plate reactor configuration in RIE

5.4 Metallization techniques

There are various ways to metallize polymer surfaces. Sputter-deposition and electroless plating are used for relatively thin metal layers. Electroplating, in turn, is used to produce relatively thick metal layers [80-82].

Electroless plating

Electroless plating is a plating process, which involves deposition without any current applied. This process is a wet-chemical deposition process and the copper deposition is the result of redox reaction. Typically, nickel and copper are used in electroless platings. For deposition of electroless copper, several proprietary solutions are available. Basically, a palladium-tin catalyst is used as an activator, while a copper bath contains an alkaline chelated copper reducing solution that deposits a thin layer of copper on the activated surface. The reaction scheme as follows:

$$Pd^{2+} + Sn^{2+} \longrightarrow Pd + Sn^{4+} \qquad [5.9]$$

$$CuSO_4 + 2HCHO + 4NaOH \longrightarrow Cu + 2HCO_2Na + H_2 + 2H_2O + Na_2SO_4 \qquad [5.10]$$

The electroless plating involving a nickel sulfate bath has the following reaction:

$$NiSO_4 + NaH_2PO_2 + H_2O \longrightarrow Ni + NaHPO_3 + H_2SO_4 \qquad [5.11]$$

Sputter deposition

Sputter deposition is a form of physical vapor deposition (PVD). During processing, the substrates are placed in a vacuum chamber with the source material, named a target, while an inert gas (such as argon) is introduced at low pressure. Plasma is struck using an RF power source, causing the gas to become ionized. The ions are accelerated towards the surface of the target, causing atoms of the source material to break off from the target in vapor form and condense on substrate surfaces. It should be noted that sputter-deposition is a high-energy non-equilibrium method.

Electroplating

Electroplating is an electrochemical process by which metal is deposited on a substrate by passing a current through the bath. In Cu electroplating, the plating bath contains sulfuric acid and copper sulfate solution. As the current is applied, positive metal ions from the solution are attracted to the negatively charged cathode and deposit on the cathode. As replenishment for these deposited ions, the metal from the anode is dissolved and goes into the solution where it balances the ionic potential. Cu deposition reaction is composed of the dissociation of Cu sulfate and the reduction of Cu ions:

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-} \qquad [5.12]$$

$$Cu^{2+} + 2e^{-} \longrightarrow Cu \qquad [5.13]$$

Since electrons must be supplied for the cathode reaction, Cu electroplating requires an initial conducting layer.

6. Surface Characterization Methods

6.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is an analysis technique used to obtain information about both composition and the chemical state of material surfaces [83, 84]. The specimens are placed in an ultra-high vacuum < 10^{-6} Pa to prevent contamination of the surfaces and exposed to a monochromatic x-ray source. The incident x-rays cause the ejection of core-level electrons from sample atoms (Fig. 6.1). The emitted electrons, which have mean free path lengths of the order of 1 nm, are detected over the energy range 0 to 1000eV. The mean free path γ is determined by the thickness of matter through which 63% of the traversing electrons will lose energy. As a consequence of this energy loss, only electrons out of the first ten nanometers may leave the surface and be detected as photoelectrons.

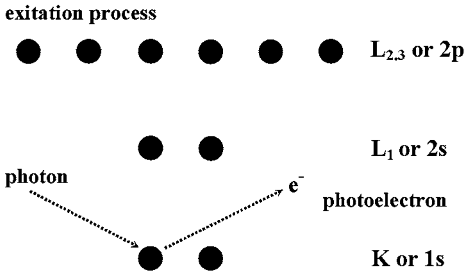


Figure 6.1 Process of photoelectron emission in ESCA

Knowing the binding energy of a particular shell of an atom allows identification of the element. The photoelectron peaks are associated with a particular core level of a particular element. All elements, except hydrogen and helium, are detected. The concentrations of the elements are determined by integrating the area under a characteristic peak for each element taking sensitivity factors into account. The high-resolution spectra allow small shifts in the binding energies to be detected, thus allowing the evaluation of the chemical state(s) of each element through its core electron binding energies. A precise determination of binding energies is made through the use of curvefitting routines applied to the peaks in the multiplex scan. Shifts in the binding energy can result from the oxidation state of the atom, chemical bonds, or crystal structure and provide information about the chemical environment of the atom [85-87].

6.2 Atomic Force Microscopy (AFM)

AFM is a form of scanning probe microscopy (SPM) where a small probe is scanned across the sample to obtain information about the surface of the sample. The information gathered from the interaction of the probe with the surface can be as simple as physical topography or as diverse as measurements of the material properties such as surface chemistry, stiffness, friction and magnetic properties [88-91]. The advantages of AFM as an imaging tool, compared to scanning electron microscopy, is that samples can be imaged under ambient conditions without severe loss in resolution and no surface coating is needed.

Using this method, three-dimensional images of solid surfaces including nonconducting samples such as polymers and ceramics can be produced at very high resolution. However, when AFM is used to obtain topographic information on soft samples such as polymers, the lateral forces exerted by the tip can lead to image artifacts due to disrupture of the surface. Tapping mode is typically used for solving this problem. This tapping mode employs a cantilever oscillating at or near its resonant frequency with high amplitude. The oscillating probe tip is then scanned at a height where it barely touches or 'taps' the sample surface. Since the tip only intermittently 'taps' the surface, the tip-sample interactions (especially shear forces) are greatly reduced, which ensures minimal disturbance of the adsorbed molecules. The vibration is set such that the tip contacts the sample surface once in every vibration period. In this way, the tip sample contact time is limited to a very short period during impact, and, as a result, frictional forces are negligible compared to the normal forces. Because of the reduction of tip-induced damage, the AFM images of the surfaces presented in this work were therefore taken in this mode.

Since the images are collected in digital format, a wide variety of image manipulations are available for AFM data. Quantitative topographical information, such as lateral spacing, step height, and surface roughness are readily obtained. Images can be presented as two-dimensional or three-dimensional representations. Average roughness (Ra) and root mean square roughness (RMS) can be calculated, where

(a) Ra is given by the average deviation of the data referred to the average value.

$$Ra = \frac{\sum_{n=1}^{N} | z_n - \bar{z} |}{N} \qquad [6.1]$$

Where: Z = Average height
Zn = Measured height relative to the minimum value, which is equal to 0
N = number of data points in the area of analysis

(b) RMS is given by the standard deviation of the data.

$$R_{Rms} = \sqrt{\frac{\sum_{n=1}^{N} (z_n - \bar{z})^2}{N-1}} \qquad [6.2]$$

6.3 Contact Angle Measurement

Contact angle measurement is a surface analytical method for the investigation of wetting behavior. The surface free energy of solid material can be estimated from the known surface tensions of probing liquids and the contact angles of the liquids to a given solid material.

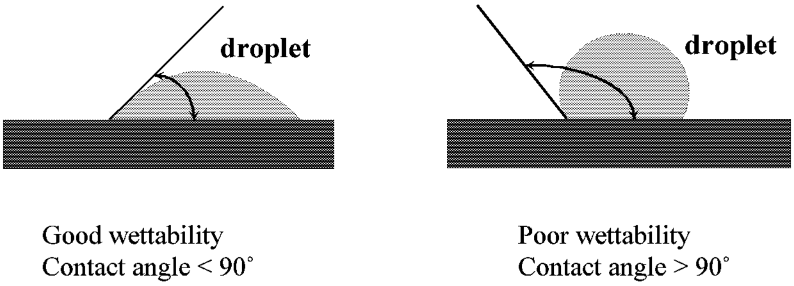


Figure 6.2 The degree to which a liquid coating wets a solid surface is measured by the contact angle θ

The contact angle, θ, is defined geometrically as the angle formed by a liquid at the boundary of the three phases, where the liquid, gas and solid intersect each other (Fig. 6.2). Low values of θ indicate that the liquid spreads, or wets well, while high values indicate poor wetting. If the angle θ is less than 90°, the liquid is said to wet the solid. If it is greater than 90°, it is said to be non-wetting [92]. A zero contact angle represents complete wetting. The difference between the maximum (advanced/advancing) and minimum (receded/receding) contact angle values is called the contact angle hysteresis. It has been used to help characterize surface heterogeneity and roughness. Goniometry is commonly used as a technique to measure contact angles. It involves the observation of a sessile drop of test liquid on a solid substrate. The test is conducted by applying a probing liquid droplet of reproducible size to the test surface. The contact angle can be assessed directly by measuring the angle between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid, at any point along their line of contact.

Contact angle measurement can be used to estimate the magnitude of the surface free energy of solid material. The interfacial free energies are given by: $\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$, where γ_{LV} is the surface tension of the liquid in equilibrium with its saturated vapor, γ_{SV} the surface free energy of the solid in equilibrium with the saturated vapor of the wetting liquid, and γ_{SL} the interfacial free energy between the solid and the liquid. The required assumptions are that the liquid drop rests on an ideally smooth, chemically homogeneous solid surface that is not affected (swollen or partially diluted) by the liquid. The well-known Young's equation is the basis of all the models used to determine the surface free energy of the solid. There are several models in the literature for evaluating the surface free energies from the contact angles [93-96]. These models have been reviewed extensively [97-99].

6.4 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image [100-103]. There are many advantages in using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely-spaced features can be examined at a high magnification. The combination of higher magnification, larger depth of focus, and greater resolution makes the SEM one of the most widely used instruments in research today.

When a focused beam of high-energy electrons is scanned over the surface of a material, the electron beam interacts with the material, causing a variety of signals—secondary electrons, backscattered electrons, X-rays, photons, etc.—each of which may be used to characterize a material with respect to specific properties. SEM imaging is typically obtained using secondary electrons for the best resolution of fine surface topographical features. Samples must be electrically conductive. Nonconductive materials such as polymer can be coated with a thin film of carbon, gold or other conductive material to obtain conductivity without significantly affecting observed surface morphology. Alternatively, imaging with backscattered electrons gives contrast based on an atomic number to resolve microscopic composition variations, as well as topographical information. Surface topography, however, is not resolved as accurately as in secondary electron imaging.

7. Summary of the thesis

The objectives of the thesis were to investigate the effects of various surface modification methods on the adhesion of electroless and sputter-deposited metals to dielectric polymers and to improve the adhesion by using wet-chemical, reactive ion etching and plasma treatments. The adhesion of Cu and Cr/Cu metallizations to the different polymers was measured with the newly developed pull test method. The physicochemical state of the polymer surfaces and the failure modes of the multilayer structures were discovered using conventional microstructural characterization and surface analysis methods. It was demonstrated that, in the case of the electroless deposition, the improved adhesion was mainly attributed to mechanical interlocking rather than to the surface chemical state of the polymers. Sputter-deposited copper, in turn, exhibited good adhesion onto the relatively smooth polymer surfaces. The surface characterizations confirmed the importance of the oxygen-containing polar groups and the enlarged surface contact area on the adhesion.

Finally, the factors controlling interfacial adhesion were found and the adhesion mechanisms in the various metal/polymer systems were shown on both theoretical and experimental grounds. The improved adhesion that can be achieved between the polymer and copper build-up layers is of great importance for the reliability of high-density electronic assemblies.

The thesis consists of five publications. The main results of each publication are summarized as follows:

In publication I entitled, "Adhesion of Electrolessly Deposited Copper to Photosensitive Epoxy", a new pull test method was developed to evaluate the adhesion in copper/polymer systems to avoid the problems associated with conventional peel and stud pull tests. With this method, it is possible to make a large number of test samples simultaneously with the same semi-additive process. In addition, the data scatter is small; therefore the pull strength values can be obtained with good reproducibility. The wet-chemical treatment was employed to roughen the epoxy surface for improving the adhesion of electroless copper to the photoresist epoxy. The results show that the procedure of swelling and etching processes have to be optimized for achieving the desired epoxy surface properties without altering the bulk properties. The mechanical interlocking model was introduced to explain the mechanism behind the measured pull strength values; a good consistency with the literature was obtained.

In publication II entitled, "Effects of Surface Treatments on the Adhesion of Cu and Cr/Cu Metallizations to a Multi-functional Photoresist", the effects of chemical, plasma and reactive ion etching (RIE) treatments on the adhesion of Cu and Cr/Cu to the multifunctional polymer were investigated. The results showed that it was very difficult to roughen the multifunctional photoresist, which has a highly crosslinking nature, by the treatments. However, we demonstrate that, by employing the RIE pretreatment with the gas mixture (O_2+CF_4), a good adhesion of copper to the very smooth surface can be achieved. These findings emphasize the importance of the introduction of CF_4 as a co-reactant to O_2 in determining the amount of generated radical groups for capturing oxygen to form functional groups in the RIE treatment. With the help of XPS, AFM, and SEM as well as the adhesion pull test method, chemical bonding was revealed to be the adhesion mechanism. This publication enables us to develop and refine our understanding of the scientific principles of adhesion through a study of the technologically important example of a Cr/Cu/SU-8 system.

In publication III entitled, "Surface Modification and Characterization of Photodefinable Epoxy/Copper Systems", the adhesion in the various epoxy/copper systems (untreated, chemically or plasma treated epoxy with subsequently deposited electroless and sputter-deposited copper) was investigated. The results showed that the increased surface roughness led to either increased or decreased pull strength values, depending on the metallization techniques in the case of wet-chemical treatment. Combining the information about the physicochemical changes of the epoxy and experimental adhesion results, we demonstrate that, in the case of the electroless deposition, the mechanical interlocking was the main adhesion mechanism. In the case of sputter-deposited copper, the enhancement of the surface polarity of the epoxy and the enlarged surface contact area due to the increased roughness were the most important factors in the adhesion. The surface pretreatments have a strong influence on the adhesion. The importance of the metallization techniques for the adhesion was pointed out by means of a comparison of the electroless and sputter deposition.

In publication IV entitled, “Surface Modification of a Liquid Crystalline Polymer for Copper Metallization”, the effects of the different surface modifications on the adhesion of copper to the liquid crystalline polymer (LCP) were studied. The results show the similarity between the adhesive natures of the various Cu/LCP systems. We demonstrate that the reason behind the similarity was the predominantly cohesive failure mode found in the systems and, hence, that the mechanical strength of the LCP matrix played a dominant role, as there appeared a certain upper limit after which the film was ultimately broken. It was concluded that the adhesion enhancement was attributable to the synergistic effect of the increased surface roughness and the polar component of the surface free energy of the polymer.

In publication V entitled, “Effects of Surface Treatment on the Adhesion of Copper to a Hybrid Polymer Material”, the results obtained from the copper/polymer systems are primarily from the sputter-deposited copper metallization, since the adhesion of electroless copper to the polymer was poor, regardless of the pretreatments. The pretreatments changed the chemical and topographic state of the polymer surface markedly and produced distinctly different adhesion results. The wet-chemical pretreatment induced chemical changes on the polymer surface and removed preferentially the inorganic part of the material. On the other hand, the plasma and RIE pretreatments selectively etched away the organic part of the material, giving rise to a granular surface with markedly increased hydrophilicity. We found that the plasma and RIE pretreatments resulted in the formation of the $[SiO4]_n$ clusters, which highly increased the hydrophilicity. However, the adhesion of sputter-deposited copper to the treated surfaces did not improve appreciably, due to the combination of unfavorable chemical and mechanical changes of polymer surfaces. The experimental results provided evidence that good surface wettability is a necessary but not sufficient condition for good adhesion.

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