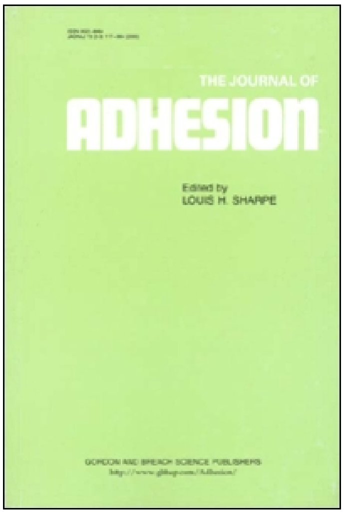

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Atomic Interfacial Mixing to Create Water Insensitive Adhesion

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The concept of Atomic Interfacial Mixing (AIM) is suggested to account for the enhanced water-resistant adhesion of plasma-deposited polymer to various substrate materials. The interfacial interactions were achieved using several techniques involving two basic methods. One method involves using ion implantation to modify the interface. The second method involves manipulation of the plasma discharge conditions to control plasma/substrate interactions. A variety of experimental techniques yields results which provide strong support for the concept of AIM.

INTRODUCTION

Polymer to substrate adhesion is very crucial in successful coating applications. In cases of polymer to metal surface and polymer to glass or ceramic surface, the most serious problem can be recognized as the failure of adhesion due to the action of water molecules which exist in the surrounding media. This problem can be expressed in terms of interactions between molecule–molecule and molecule–atom in the bulk phase of the polymer, at the interface and in the bulk phase of the metal. The intermolecular interaction plays a major role in the mechanical strength of polymers, although covalent bonds exist along the length of a macromolecule. At an interface of a polymer-metal, the interaction of the metal atoms and the polymer largely determines the adhesive strength of the polymer to the metal surface. The highly polar water molecules interact fairly strongly with polymer molecules and very strongly

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with metal atoms at the surface of metal. Consequently, when water molecules reach the polymer-metal interface, the polymer-metal interaction is reduced or destroyed and new water-metal and water-polymer interactions arise.

For good water-resistant adhesion, it is necessary to find methods to provide polymer-metal interaction which will not be affected by the presence of water molecules. In this paper, it is shown that Atomic Interfacial Mixing (AIM), which causes an atomic level interlocking of two phases, provides an alternative physical picture for explaining the improved adhesion of plasma formed polymers to various substrate materials.

FUNDAMENTAL CONSIDERATIONS

A. Adhesion

The strength of adhesion between two surfaces involves many factors. Kaelble[1] lists three criteria of primary importance: wetting, adsorption, and interdiffusion. In principle, all three factors would be optimized to improve adhesion. In practice, polymer/metal adhesion is improved by controlling parameters such as macroroughness and surface contamination, which basically improve wetting and/or adsorption. Thus, wetting is not usually a major problem for conventional polymers or metals, and especially not for vapor-deposited polymers. However, the last two factors are a problem at a polymer/metal interface.

Adsorption can sometimes be improved using conventional surface treatment methods, such as glow discharge or acid etch cleaning. Such treatments can increase both the number and variety of the stronger adsorption sites. But, clearly the predominantly covalent bonding within the bulk polymer and the metallic or other types of bonding in the substrates are often not compatible. As a consequence of this mismatch in structural and electronic properties, considerable thermal and mechanical stresses can arise at the interface. Thus, the formation of primary bonds, *i.e.*, those with a bonding energy >20 kcal/mole, is not likely, and secondary (<20 kcal/mole) bonding mechanisms are usually relied on to provide the adhesion.

Interdiffusion is often a problem. Very little interdiffusion takes place when a polymer is applied in a conventional manner. Heat treatment can improve diffusion, but thermally induced stress often introduces undesired effects such as cracking, spalling, etc.

Although conventional surface treatment methods can improve adhesion in some cases, better methods are needed, especially for water-resistant adhesion of polymers to metals.

Two non-traditional methods to improve both adsorption and interdiffusion which show significant promise are reported here. They involve ion implantation and process control of plasma/substrate to favorably alter *interdiffusion, adsorption, desorption, surface bonding, and other mechanisms* so as to improve adhesion. We refer to the collective effects which alter these mechanisms as Atomic Interfacial Mixing (AIM).

B. Atomic interfacial mixing (AIM)

The purpose of AIM is to improve the interfacial bonding. Basically, this can occur in two ways. One is for the injected atoms to become seed sites for growth of a polymer. In such a case, the atoms would be only slightly embedded and become adsorption sites. Since the site should bond well to the organic plasma, an obvious choice for the injected atom is carbon. However, in some polymer/metal systems, there are other logical choices and several atomic species could be utilized.

Atomic Interfacial Mixing (AIM) is more than interdiffusion over a few monolayers. It also involves modification of surface chemistry. AIM is accomplished by injecting atoms or ions into the substrate surface. As they penetrate the surface, they radically disturb the bonding, perhaps dislodge, or even eject (sputter) atoms and form new compounds or alloys. Thus, AIM significantly alters the surface free energy of the substrate.

The purpose of AIM is to create stronger interfacial bonding. Basically, this can occur in two ways. One is for the injected atoms to become directly involved in forming the stronger bonds or become intermediate bridge bonding species. In such a case, the atoms would be only slightly embedded and become adsorption sites.

Secondly, new interfacial bonding may result from effects which *indirectly* involve the injected atoms. For example, surface structural damage could provide additional types of adsorption sites, such as surface vacancies at sputtered atom sites. Also, as the injected atoms come to rest, they influence and participate in the reformation of the surface bonding which is thus altered. If many atoms are injected, a compound structure might be formed within several monolayers of the surface. For favorable AIM, the polymer bonding at the new interface will be stronger than at the original interface.

Normally, the interface starts developing when the first free or charged radicals (during the process of plasma polymerization) find the lower energy potential wells on the surface and become bound. In this circumstance, only secondary bonds ($\sim$4–8 kcal/mole) are likely to be formed. One major advantage of AIM is that it provides a means for favorably altering bonding mechanisms and introducing new bonding possibilities. Of special importance is the reduction of hydrogen bonding, since water can readily attack such bonds.

It also may be possible to create *primary* bonds with AIM. To do this would require creation of an embedded layer which would allow covalent bonding, or use of an organometal polymer which would allow metallic bonding at its surface or localized bonding through an oxide coupling to a metal surface, *e.g.*, M-O-M'.

The above examples are rather simplistic and clearly do not exhaust all the mechanisms for enhanced bonding by AIM. However, they do indicate the variety of interesting possibilities that can be exploited.

C. Methods and techniques for adhesion enhancement using AIM

1. *Ion implantation method*

a) *Basic information* Ion implantation is a technique in which a target substrate is bombarded by a beam of high energy (accelerated) ions. These ions strike the target surface, become embedded, and often produce major modifications in surface properties.

Only recently has ion implantation been used as a surface treatment technology in non-semiconductor applications. Treatments to improve wear in steel and inhibit corrosion in metals have been studied extensively. Although potential application of ion implantation to alter adhesion has been mentioned in review papers, virtually no publications have appeared in this area. (Reference 2 lists books discussing ion implantation.)

There are three basic parameters which usually have a first order importance on the effects caused by ion implantation. These parameters are ion species, initial ion energy, and ion dose (*i.e.*, number per unit surface area). Ion species is especially important if chemical effects, rather than damage effects, are likely to be important. Initial ion energy basically determines the depth of the implantation since the average depth is approximately proportional to energy. However, the implanted ions do not all stop at the same depth, but are typically spread over a region whose width approximates one-half of the average depth. The ion dose is a measure of the number of implanted ions. A dose of 10^{16} ions/cm^2 can have significant influence. This is because 1000 Å is a typical width of the implanted ion distribution, and hence the atomic concentration of the ions can exceed $(10^{16}$ ions/cm$^2) \times (1/10^{-5}$ cm$)$ $= 10^{21}$ ions/cm^3, *i.e.*, several atomic percent. Thus, the implanted region may resemble more an alloy or compound than a dilute impurity material.

b) *AIM by direct implantation technique* One way to achieve AIM by ion implantation is to implant an atomic species, such as C^+, which should bond well to the polymer. Some fraction of the implanted ions will lie in the near surface region and become adsorption sites for the growing species of the plasma polymer. Thus, the important AIM mechanism for the adhesive improvement involves the chemistry of the implanted species. However, it is also possible that the radiation damage done by the ion may also contribute to the improved adhesion.

c) *AIM by recoil implantation technique* Another method is to use the ion as a projectile which will hit an atom and recoil it into the interface. Thus, when an inert ion, such as Ar^+, is implanted into a thin polymer film which has previously been plasma deposited on the substrate, some of the atoms from the polymer film are driven across the interface. Thus, reactive intermixing of the polymer and substrate atoms occurs and better bonding may result. This atom "drive-in" process has been used to form alloys in some metal-to-metal interface cases.[3] (This "drive-in" method is commonly referred to as *recoil* implantation or ion beam mixing.)

2. *Plasma polymerization method*

a) *Basic information* The polymers used in this study were not made by conventional curing methods. They were made by introducing a monomer gas into a plasma produced in a glow discharge reactor. The substrate within the glow discharge becomes coated with a polymer as reactive plasma species condense on its surface.

Formation of a polymer by plasma polymerization is vastly different from polymerization in the conventional sense.[4] Since the mechanisms of "polymerization" are so different, the use of this word is somewhat misleading, especially since one purpose of AIM is to modify polymer formation mechanisms. A detailed discussion of mechanisms is given in Refs. 4 and 5. Here, only factors relating to AIM are discussed.

The processes in plasma polymerization are schematically shown in Figure 1. Polymers directly formed by plasma-induced polymerization are similar to conventional polymers and it is difficult to control the plasma/substrate bonding using AIM. Such polymerization can be avoided by selecting a "non-polymerizable" monomer for a starting as. For instance, if one chooses CH_4, rather than $CH_2{=}CH_2$ or $CH_2{=}CH{-}Cl$, the lack of double bonds means that the polymer does not form in the conventional manner but forms by reactive processes in the plasma. Such formation is called plasma state polymerization (see Figure 1).

Important to plasma-state polymerization are the many reactive species created by ionization in the plasma. As these species impinge the surface of the substrate, they induce a degree of plasma etching and surface ablation as the "polymer" coating is formed. Since the etching and coating occur simultaneously, there exists the so-called Competitive Ablation and Polymer (CAP)

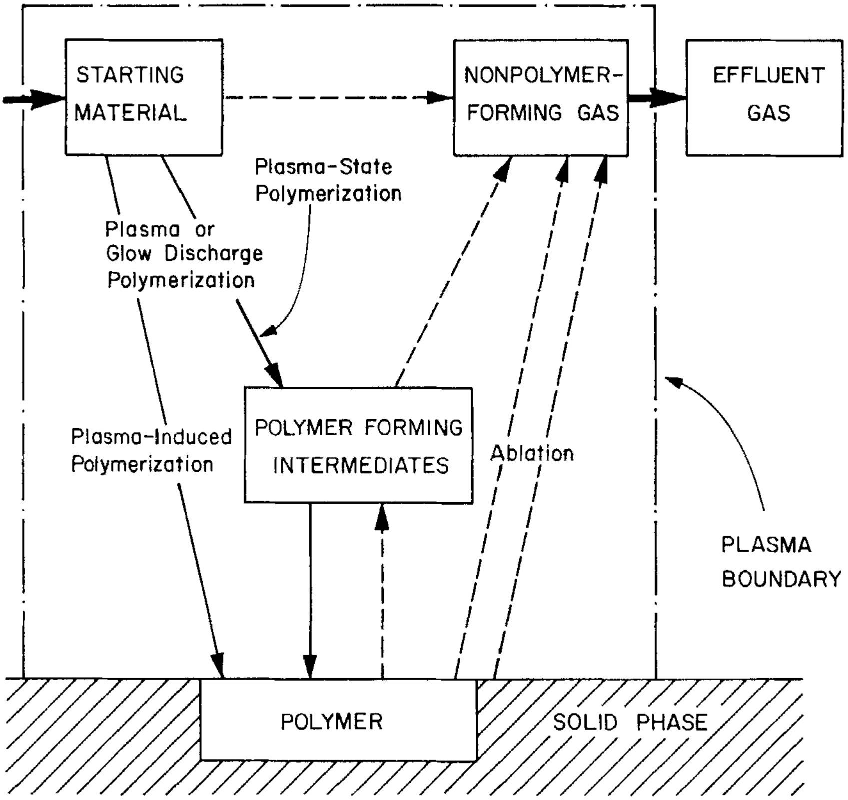

FIGURE 1 Schematic representation of reactions involved in polymer-forming plasma. The polymer can form directly by plasma-induced polymerization or *via* intermediate interactions by plasma-state polymerization. Plasma-state polymerization can be used to modify AIM by either changing the plasma discharge conditions or the starting gases.

formation mechanism. The CAP mechanism means that reactive AIM is continuously occurring at the interface.

In plasma-state polymerization, the plasma reactor conditions can be manipulated using various techniques to alter the degree of AIM.

b) *AIM by energy control technique* Recent studies[7] indicate that adhesion depends on the plasma parameter W/FM, where W is the effective wattage of glow discharge, F is the monomer flow rate, and M is the molecular weight of the monomer. W/FM is a measure of the energy input per unit mass. It was necessary to exceed a certain level of W/FM in order to obtain good adhesion. This dependence on the energy of the impinging active species suggests that an important AIM enhancement mechanism occurs only at high W/FM values.

c) *AIM by choice of gas technique* AIM can also be modified by changing the monomer gas or adding other gases into the plasma reactor. Such changes affect the interactions in the plasma, as well as the etching and ablation processes which occur on the substrate surface. For example, if fluorine is present in the monomer or added to the reactor, considerably more etching occurs.

EXPERIMENTAL

A. Substrate surface preparation

Most of the substrates used in this study were platinum metal in the form of wires or foils. Such substrates were 1) flame reduced, 2) oxidized electrolytically in sulfuric acid, or 3) cleaned in toluene and acetone using an ultrasonic vibrator.

Platinum surfaces used for the measurement of adhesive strength were prepared by electrolytic plating of platinum on polished brass surfaces and cleaned by the solvent rinse mentioned above.

All surfaces were further treated in the reactor using an argon plasma for two minutes at 80 watts discharge power and 30 millitorr pressure under continuous flow conditions. In some cases, this argon plasma cleaning step was omitted intentionally in order to see the effect of the argon plasma pretreatment of the surface and no effect was found.

It is well recognized that the cleaning of surfaces is a very important factor to achieve good adhesion by a polymer coating. However, various methods of precleaning yielded no significant difference when plasma polymers of methane were deposited on various Pt wires in a plasma polymerization process under conditions of good AIM. It appears that effective AIM significantly reduces the problems of surface preparation.

B. Ion implantation

Direct implantation of the Pt wires and foils was carried out using ion beams of C^+, Si^+, Ar^+, or Kr^+. The ion dose was controlled by measuring the beam current with a Faraday cup and choosing an appropriate exposure time to the beam. The beam was rastered in two orthogonal directions such that a uniformly distributed beam was obtained. The ion energy was usually 100 keV.

The wires were continuously rotated at several revolutions a minute in the beam during the implantation so that a uniformly implanted area of the wire was assured. The plasma polymerized methane coating was usually deposited on the implanted sample one or two days after the implantation. Conditions of plasma polymerization were deliberately chosen to decrease AIM so that the polymer/foil adhesion was not originally optimum. Thus, improvement made by the implantation could be easily detected.

Recoil implantations were done on a substrate consisting of a Pt foil which had been pre-coated with a thin (~ 200 Å) plasma polymerized methane film. For testing after implantation, a thicker coat was applied to the implanted thin pre-coat using plasma deposition conditions identical to those of the pre-coat. Ar^+ ions at 100 keV were implanted to a dose of $10^{15}/cm^2$. Some of these ions impact carbon (and also hydrogen) atoms in the methane film and drive them across the interface and into the foil.

C. Plasma polymerization

1. *Capacitive magnetron discharge reactor* A capacitively coupled bell jar reactor equipped with a magnetron electrode system was used for deposition of the polymers (excepting the organo-metallics). This system, which has been described by Morosoff, Newton, and Yasuda[8] has advantages where uniform deposition of polymers at relatively high effective power input levels is essential. Because of the superposed magnetic field, it is possible to create discharge at a much lower pressure (*i.e.*, a lower flow rate, *F*) under contained glow conditions. This prevents polymer deposition at undesired locations.

The substrates were placed on an aluminum disc (12 in. diameter). Wire substrates were attached to the disc by an end with the major portion of the wires extending through an open hole placed on the disc. The disc has four holes symmetrically placed and rotates along the center axis by means of an external motor.

The deposition of the polymers was monitored and controlled using a quartz crystal thickness monitor placed in the plane of the disc, a few millimeters outside its edge. Since the thickness monitor is stationary, it was necessary to determine experimentally the correlation between the thickness recorded by the quartz crystal detector and that deposited on the substrate.

The power input parameter, W/FM, was varied to alter the conditions of plasma polymerization by changing W (wattage), F (flow rate), and M (molecular weight of monomer). The actual glow discharge is controlled by maintaining the discharge current, I, at a constant level. It has been found that control of I at the initial stage of plasma polymerization is extremely important. Because of the change of secondary electron emission caused by polymer deposition onto the electrode surface, I changes significantly at the early stage of polymerization and affects the properties, particularly adhesion, of the polymers. Details of this aspect will be presented elsewhere.

2. *Inductively coupled tubular reactor* Organotin films were prepared in an inductively coupled, glow discharge tubular reactor. In such a system, the

plasma is sustained by an r.f. field. Thus, this plasma system has an electromagnetic field; whereas a capacitively coupled system has a large electrostatic field.

The central part of the reactor is a cylindrical Pyrex glass tube. The system is operated by means of a rotary pump in the millitorr range. The organotin monomer vapors were introduced through a leak valve at one end of the reactor at a controlled flow rate. Pressures were recorded by means of a thermocouple gauge. Further details of reactor construction and design are given in Ref. 9.

Because of the geometry and the flow characteristics of the reactor, the polymers have compositional gradients both laterally and vertically within the tube. Accordingly, it was necessary to determine the deposition rates and product compositions along the axes of the reactor. Ceramic and metal substrates were positioned along the length of the reactor and exposed to an Ar plasma for 30 min. The monomer gases (and when desired, an ablative gas such as oxygen) were then introduced and glow discharge initiated at the optimum reactor parameters.

The deposition rates at the different positions were calculated from thickness measurements *v.* deposition time and the resulting film compositions were determined by monitoring the Sn/C ratios obtained from ESCA-Auger spectral profiles. In general, it was evident that for a fixed value of mass flow rate, higher r.f. powers yielded more metal-rich deposits with better adhesion to the substrate surfaces.

D. Adhesive strength testing

1. *Boiling test* To test the water resistant adhesion, the coated samples were immersed in a 0.9% NaCl solution and boiled at atmospheric pressure. This is an accelerated test of the effects of water on the adhesion. It should be noted that most thin polymer films (< 1000 Å), including plasma polymers which are deposited on platinum surfaces without any attempt to achieve AIM, peel off within a matter of minutes when subjected to the rigors of the boiling saline solution. Any improvement beyond this reference level should be considered as significant improvement in the water resistivity of adhesion.

2. *SEM evaluation* The boiling test was stopped when wrinkles or visible flaws developed in the coating. The surface and interface region was then examined by SEM in order to characterize the adhesive conditions and failure mode.

3. *Pull test evaluation* The direct measurement of adhesive strength was obtained by the "direct pull method"[10] using a rod-shape, adhesive joint

assembly described in the literature.[11] Because of the high cost of platinum, Pt-plated brass was used for the testing. For this and other reasons, the pull test technique using rod shape adhesive joints rather than the lap shear test was chosen. The cross-sectional surfaces could be easily polished and plated in a reproducible manner.

The coated rods were first immersed in the boiling solution. Five samples were used at each particular boiling time interval. These were then cemented to uncoated mild steel rods using an epoxy resin adhesive (Shamrock 304). A uniform and minimum amount of adhesive was used. The rods with the sandwiched substrates were then pressed together in a special alignment tray. After the adhesive was cured (70°C for 3 h), the rods were carefully mounted in the Instron TMSL-180 and standard ASTM procedures were followed at room temperature.

The load which caused failure was recorded and the mode of failure was determined using optical and SEM.

The assembly of the adhesive joints and the pull test are carried out under dry conditions after the boiling of coated samples since no adhesive could withstand the boiling treatment. Thus, the results determine the dry adhesive strength after wet exposure, rather than the wet adhesive strength. However, deterioration of the wet adhesive strength clearly influences the dry adhesive strength.

RESULTS AND DISCUSSION

A. Modifying AIM by ion implantation

1. *Direct implantation techinque* The substrate material was platinum because it has been recognized that it is difficult to adhere polymers (plasma-formed or otherwise) to its surface. A plasma polymer of methane was deposited onto both Pt wires and foils. The reaction parameters of the plasma polymerization were chosen to yield a coating having poor adhesion (*i.e.*, low W/FM parameter) so that any improvement due to ion implantation could be easily recognized.

Figure 2 is an SEM micrograph of a Pt wire which was implanted with 100 keV C^+ to a dose of 10^{15} ions/cm^2 over part of its length and then coated in the capacitive reactor. The sample was immersed in a 0.9% saline solution for 10 h. The significant improvement due to the ion implantation is clearly seen. There is almost a well-defined boundary between the peeling (unimplanted) and non-peeling (implanted) sections. Results on a wire implanted with Ar^+, Kr^+, and Si^+, rather than C^+, did not show significant improvement in adhesion over wires which were not ion implanted. Thus, this example

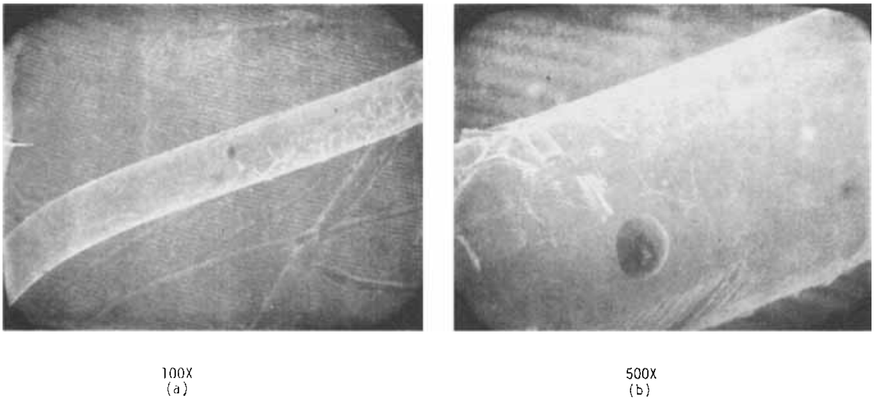

FIGURE 2 Scanning electron micrographs of glow discharge polymer coated platinum wires after soaking in 0.9% saline solution of 10 hours. The left half of the wire in (a) and right half in (b) was ion implanted with C^+ prior to coating. Note the clear difference between each half of the wire.

suggests that the important AIM mechanism here involves implanted atom carbon chemistry.

2. *Recoil implantation technique* Figure 3 shows a second example involving a thin (~200 Å) pre-coated plasma polymerized methane film on a Pt foil implanted with Ar^+ at 100 keV to a dose of 10^{15} ions/cm^2. After implantation, a thicker coating of the same polymer was applied, and boiling testing was done for 4 h. Again, a striking improvement is seen in the effects on adhesion.

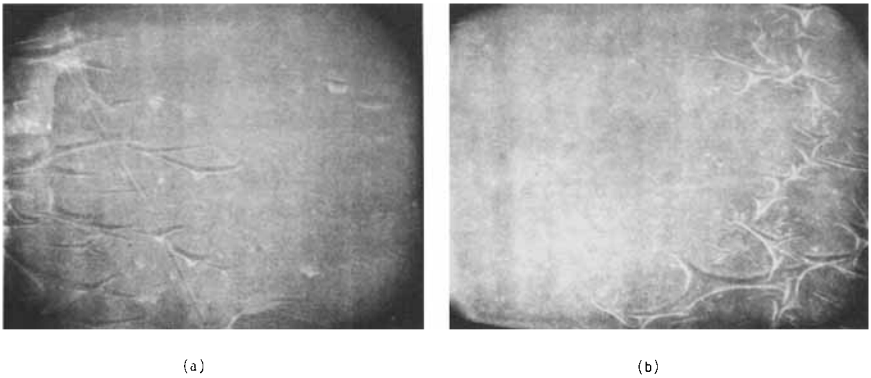

FIGURE 3 Scanning electron micrographs of glow-discharge-polymer-coated platinum foil after 4 h in the boiling test (1500X). In this case, a thin pre-coat was "mixed" into the metal by ion implantation of Ar^+. Then, the thicker coating was applied. Note the change in adhesive properties between the unimplanted region [left side in (a) and right side in (b)] and the implanted region.

These two examples clearly demonstrate that ion implantation can be effectively used to improve adhesion. Furthermore, both results (although limited in scope) appear to support the concept of the AIM process as regards the creation of water insensitive adhesion.

B. Modifying AIM by plasma discharge parameters

1. *Energy control technique* For these experiments, the capacitive reactor was used to deposit both methane and tetrafluoroethylene polymer onto the Pt coated pull test rods. The importance of the plasma parameter, W/FM, has already been reported.[7] When the energy of the active polymer forming specie was increased to the critical level by increasing W/FM, significant improvements in the adhesion of the deposited polymer coating were observed. Good water-resistive adhesion was obtained only when the W/FM value exceeded 10^{10} joule/kg for methane and 2×10^{8} joule/kg for tetrafluoroethylene. The results of the pull testing after boiling for these two polymers are shown in Figure 4. Clearly, the adhesive strength did not significantly deteriorate even

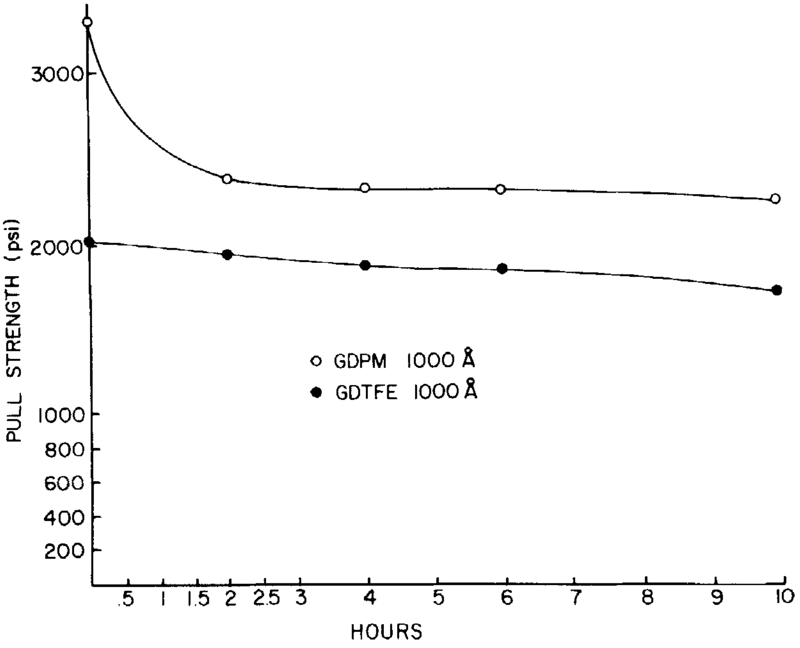

FIGURE 4 Effect of boiling test on the adhesive strength of plasma polymerized polymers of methane (GDPM) and tetrafluoroethylene (GDTFE). Each point is an average of five samples. The x-axis is the exposure time of the sample in the boiling solution.

after ten hours in the boiling solution. (This should be contrasted with conventionally applied polymers or low W/FM applied plasma-deposited polymers which lose much of their adhesion after several minutes in the boiling solution.) It is quite evident that the adhesion of plasma polymers prepared with high energy input provide a high degree of water resistive adhesion.

2. *Choice of gas technique* In this series of experiments, the inductively coupled reactor was used to prepare polymerized tetramethyltin (TMT). The conditions for the glow discharge synthesis are given in Table I. Samples of aluminum and 304 stainless steel were positioned along the length of the reactor. Prior to film deposition, the substrates were exposed to an argon plasma for 30 min.

To control AIM and also the composition of the deposited polymer, oxygen was introduced through a leak valve which was separate from the TMT vapors. The oxygen preferentially reacts with C in the TMT to produce CO and CO_2 which are non-polymerizing gases that are pumped out of the reactor. This removal of C means there is an increased Sn/C ratio in the deposited polymer. Highly reflective, metallic films developed in a region 8 to 36 cm from the monomer inlet. The highest Sn/C ratios usually occurred within the 20–26 cm range. ESCA-Auger depth profiles showed these films on various metal substrates positioned near the center to contain very little C when O_2 was introduced at a flow rate of 6.8×10^{-4} cm^3 (STP) sec^{-1}.

Pull test results are summarized in Table II. Examination of the data reveals that the pull strengths are highest for the higher Sn/C ratios with the maximum pull values ranging from about 4800 psi on stainless steel to about 3750 psi on aluminum. The latter value, however, is a lower limit because the failure mode was determined to be cohesive, *i.e.*, in the polymer, and not at the polymer/metal interface. (ESCA examination of the pull test area indicated a residual film of about 200–300 Å still present on the aluminum substrate indicating the adhesive strength to be higher than the reported value.) Much

TABLE I

Conditions for plasma polymerization of TMT

Ar-ion cleansing	30 min, 40 mμ pressure, r.f. power 35W
Flow rate of TMT (STP)	2.8×10^{-3} cm^3 sec^{-1}
Flow rate of O_2 (STP)	2.5×10^{-4} cm^3 sec^{-1}
System pressure prior to application of power	50–55 mμ
System pressure after application of power	36–38 mμ
Radiofrequency	3.9 MHz at 31W
Max. deposition rate	0.30 Å/sec

TABLE II

Pull tests on polymerized TMT deposited on various substrates

Sample position from monomer inlet (cm)	Aluminum		Stainless steel (304)	
	Failure mode	Pull strength (psi)	Failure mode	Pull strength (psi)
20.5	Adhesive failed on steel rod	>3340±325	Chemlok[a] adhesive-film interface, cohesive failure	>3390±400
26.5	Film–Al interface, cohesive failure	>3740±225	As above	>4840±465
33.0	Chemlok[a] adhesive-film interface, cohesive failure	>2550±300	As above	>3390±130

[a] Hughson Chemicals, Lord Corporation, Erie, Pennsylvania.

lower pull strengths have been reported by Kny *et al.* for organotin films formed on stainless steel.[12] The same authors report values of up to 2840 psi for organotin films on Al where the failure mode is cohesive. These films, however, contained more C and were not prepared in the presence of oxygen.

The above results are consistent with the concept of AIM. However, Kny *et al.*[13] have also shown that ESCA and Auger analyses indicate some primary bonds of Sn—O—Al and Sn—O—Si to be involved on Al and glass substrates. One might argue therefore that the enhanced adhesion observed for organotin films formed in the presence of O_2 is attributable solely to the increased Sn content. However, plasma polymerized organotin films of the same or slightly less Sn content, formed on glass in the presence of small amounts of O_2, have been shown to exhibit consistently higher values of pull strength[14] thus suggesting the enhancement of AIM upon introduction of an ablative gas such as O_2. Further experiments are in progress to ascertain if similar results occur for other substrate surfaces.

SUMMARY

The foregoing experimental results, although limited in extent and scope, provide strong support for the concept of AIM. The results of both the direct and recoil implantation of Pt clearly evidence the improved water resistant adhesion of plasma polymerized methane in boiling saline solutions; see SEM micrographs, Figures 2 and 3.

The manipulation of the plasma polymerization parameter W/FM so as to exceed 10^{10} joule/kg for improved adhesion of "polymethane" to Pt is significant in that lower values are ineffective in promoting adhesion. The pull tests after boiling in saline solution also reinforce the conclusions that improved adhesion results from the manipulation of W/FM.

The pull tests applied to plasma polymerized organotin films on different substrates in the presence or absence of an ablating gas, O_2, also support the concept of AIM as perceived by the CAP mechanism[6] where in this instance the process of plasma etching is enhanced by chemical ablation produced by simultaneous introduction of an ablative gas with the monomer species.

Extensive and systematic studies of the adhesion of plasma polymers carried out under conditions to delineate processes considered important to AIM are in progress.

Acknowledgements

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