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## ADHESION

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### INTRODUCTION

Adhesion refers to the bond (chemical or physical) between two adjacent materials, and is related to the force required to effect their complete separation. Cohesive forces are involved when the separation occurs within one of them rather than between the two (1). The ASTM defines adhesion as the "condition in which two surfaces are held together by either valence forces or by mechanical anchoring or by both together" (2). Adhesion is a macroscopic property which depends on three factors: 1) bonding across the interfacial region, 2) type of interfacial region (including amount and distribution of intrinsic stresses) and 3) the fracture mechanism which results in failure (3-5). Equating adhesion, which is a gross effect, to bonding or cleanliness may be very misleading. Failure of adhesion may be more related to fracture mechanisms than to bonding. In thin films, the intrinsic stress may result in adhesive failure even though chemical bonding may be high. Also, the interfacial morphology may lead to easy fracture though bonding is strong. With copper, if an acid dip prior to plating is too strong so that the etching results in the development of large areas with {111} planes constituting the surface, the subsequently deposited films may not only grow non-epitaxially, but also lose adhesion to the substrate forming an interfacial crack because of the voids (6). Good adhesion is promoted by: 1) strong bonding across the interfacial region, 2) low stress gradients, either from intrinsic or applied stress, 3) absence of easy fracture modes, and 4) no long term degradation modes (3-5).

Adhesion of a coating to its substrate is critical to its function. Mechanical, chemical, and metallurgical factors may contribute to such

adhesion. For a coating to be retained and to perform its function, its adhesion to the substrate must tolerate mechanical stresses and elastoplastic distortions, thermal stress, and environment or process fluid displacement. Good adhesion performance of a coating depends on a variety of the attributes of the interface region, including its atomic bonding structure, its elastic moduli and state of stress, its thickness, purity and fracture toughness (7).

The durability of coatings is of prime importance in many applications and one of the main factors that govern this durability is adhesion. This is particularly true if the coating or substrate, is subject to corrosion or to a humid atmosphere, as under these circumstances any tendency for the film to peel from the substrate may well be aggravated. When adhesion is poor, rubbing action can cause localized rupture at the coating/substrate interface, leading to blistering or even complete spalling off of the coating. For example, material loss in wear tests was minimum with Pb/Sn films deposited by ion plating which results in very good adherence. By comparison, heavy material loss was obtained with Pb/Sn films deposited by evaporation which provides considerably less adherence. With the less adherent films deposited by evaporation, several failure mechanisms such as plucking, peeling, film displacement, etc., were observed (8).

In general, adhesion can be broken down into the following categories (9):

1. *Interfacial adhesion*: the adhesive forces are centered around a narrow well defined interface, with minimal atomic mixing, such as gold on silica.
2. *Interdiffusion adhesion*: the film and substrate diffuse into one another, over a wider interfacial region. For example, gold, evaporated onto freshly etched silicon (removing the surface oxide layer) at 50°C produces a diffuse interface extending many atomic layers.
3. *Intermediate layer adhesion*: in many cases the film and substrate are separated by one or more layers of material of different chemical composition, as in the case of films deposited on unetched silicon whose surface is covered with several nanometers of oxide.
4. *Mechanical interlocking*: this will occur to some degree wherever the substrate surface is not atomically flat and will account for some degree of random fluctuation of adhesive forces.

## TESTING

Adhesion tests can be broken down into two categories, qualitative and quantitative. They vary from the simple scotch tape test to complicated flyer plate tests which require precision machined specimens and a very expensive testing facility. It is not the intent to provide a complete review of all adhesion tests in this chapter but rather provide some coverage of those that were used to generate the data that is presented later. For those interested in more detail, references 1 and 10-14 are recommended.

Table 1 gives a general breakdown of adhesion tests, classifying them into qualitative and quantitative. In many cases, the qualitative tests are quite adequate and are certainly easier and cheaper to perform. As with all tests, thickness of the coating can noticeably influence the results. This is shown in Figure 1 for the scotch tape test. Aluminum panels were not given any special activation treatment prior to plating with varying thicknesses of palladium so it was known that adhesion would be poor. The panel coated with only  $1.25\ \mu\text{m}$  (0.05 mil) of Pd indicates fairly good adhesion; only a small amount of coating was removed by the tape test. As the thickness of Pd was increased increasing amounts of coating were removed by the tape. Although not shown, if the coating were increased to around  $25\ \mu\text{m}$  (1 mil) no coating would be removed since the coating would be stronger than the tape even though the deposit would still be non-adherent. Likewise, with a very thin coating, e.g., around  $0.5\ \mu\text{m}$  (0.02 mil), no failure would be noticed with the scotch tape test. This strongly shows that with a qualitative test, a variety of results can be obtained and they can be quite misleading.

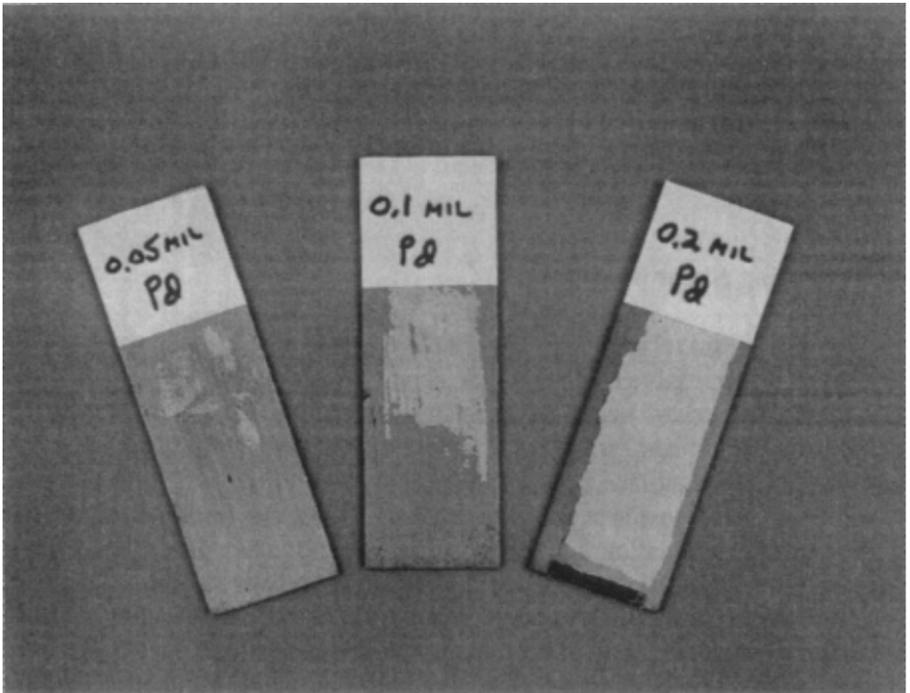
In cases where coatings are required for engineering applications, qualitative tests are often inadequate and must be replaced with tests that provide quantitative data. Of those listed in Table 1, four that were used to generate data that will subsequently be discussed include tensile, shear, peel and flyer plate so some details will be given for these tests.

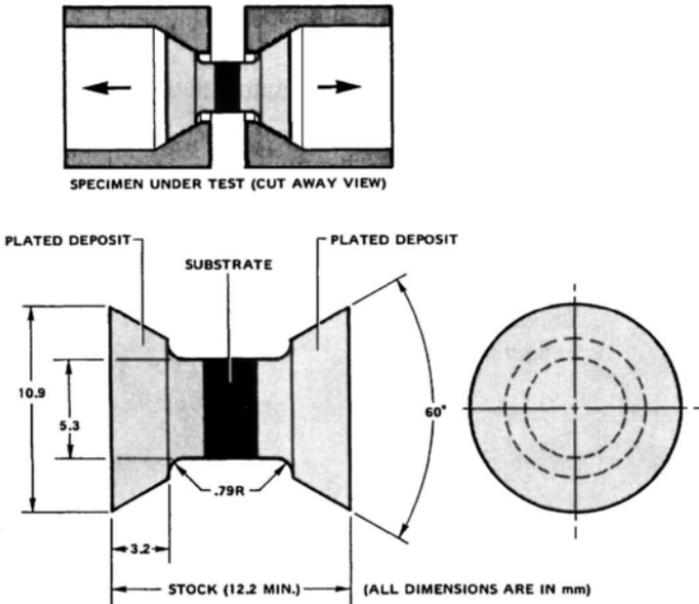
### A. Conical Head Tensile Test

With this test, the electrodeposit, the substrate and the bond between the two are tested in a tensile fashion, the bond being normal to the loading direction. Flat panels are plated on both sides with thick electrodeposit (e.g., around 3 mm) and then conical head specimens are machined and tested using standard tension testing procedures. Figure 2 is a schematic of conical head tension specimens. More detail on this test can be found in references 15-17.

**Table 1 - Adhesion Tests**

<u>Qualitative</u>	<u>Quantitative</u>
Scotch tape	Tensile
Bending	Shear
Abrasion	Peel
Heating	Ultrasonics
Scribing	Centrifuge
Grinding	Flyer Plate
Impacting	

**Figure 1:** Scotch tape test for palladium plated on aluminum.

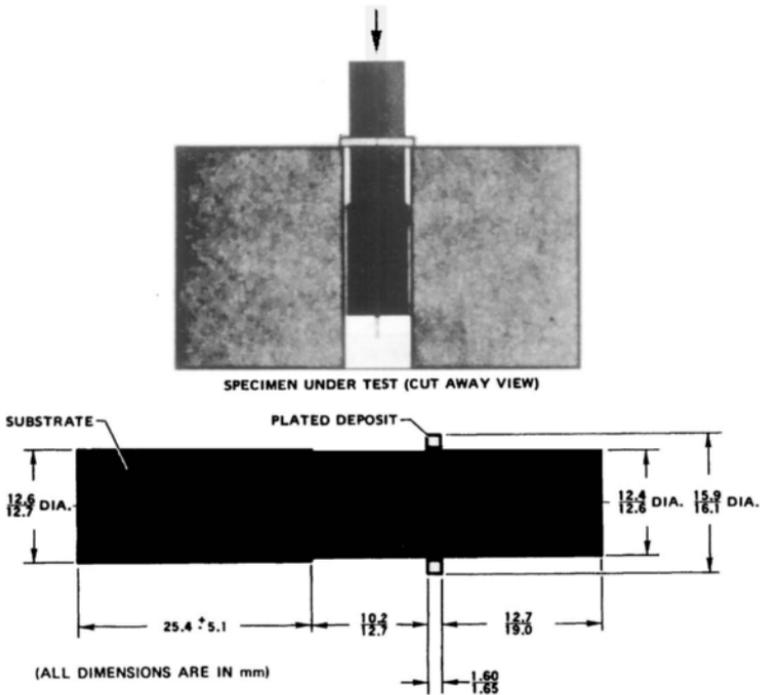


**Figure 2:** Conical head tensile specimen.

## B. Ring Shear Test

Ring shear tests are an effective, relatively simple method for obtaining quantitative data on the bond between coatings and their substrates. An added benefit with this type of test is that substrate material is easier to obtain and specimens cost less to fabricate and evaluate than for other types of quantitative tests (17).

A typical test is accomplished by preparing a cylindrical rod via the process under evaluation and then plating to a thickness of about 1.5 mm. The rod is machined in a manner that removes all of the plated deposit except for small rings of plating of predetermined width (generally 1.5 mm wide, spaced approximately 2.5 cm apart). The rod is then cut between the plated rings. These sections of the rod with the plated rings are tested by forcing the rod through a hardened steel die having a hole whose diameter is greater than that of the rod but less than that of the rod and the coating. The bond strength can be calculated by using the load to cause failure and the area of the coating. Figure 3 shows a ring shear test specimen and die. References 16-18 provide more detail on ring shear testing.



**Figure 3:** Ring shear test specimen and die.

### C. Flyer Plate Tests

Flyer plate tests are used for quantitatively measuring the adhesion of plated coatings under dynamic loading conditions. The principle of this kind of test is to create a compressive shock wave in a sample in such a way that the wave travels from the substrate to the coating perpendicularly to the outer surface. This wave is then reflected at the surface as a tensile shock wave propagating from the coating to the substrate. This tensile wave produces detachment of the coating if the peak stress value exceeds the adhesion of the coating (19). The test consists of utilizing magnetic repulsion to accelerate thin, flat metal flyer plates against the substrates under test in a vacuum. The flyer plate test apparatus, originally developed for shock wave testing of materials, consists of two conductors, a ground plate, and a flyer plate, separated by a thin insulation film of plastic. The conductors are connected so that the current flowing through them produces a magnetic repulsive force that drives the thin flyer (0.2 to 1.02 mm) away

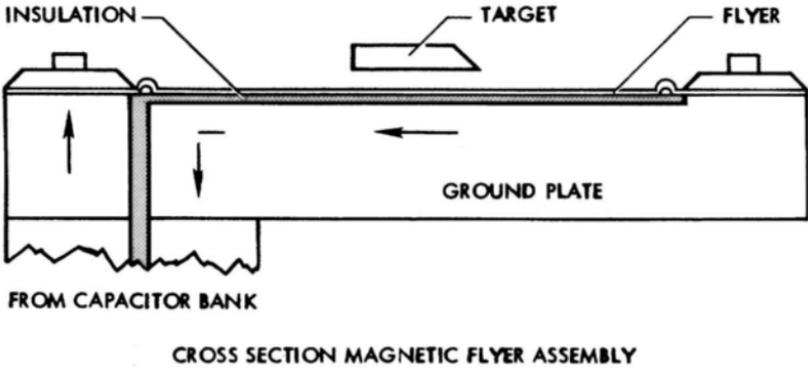
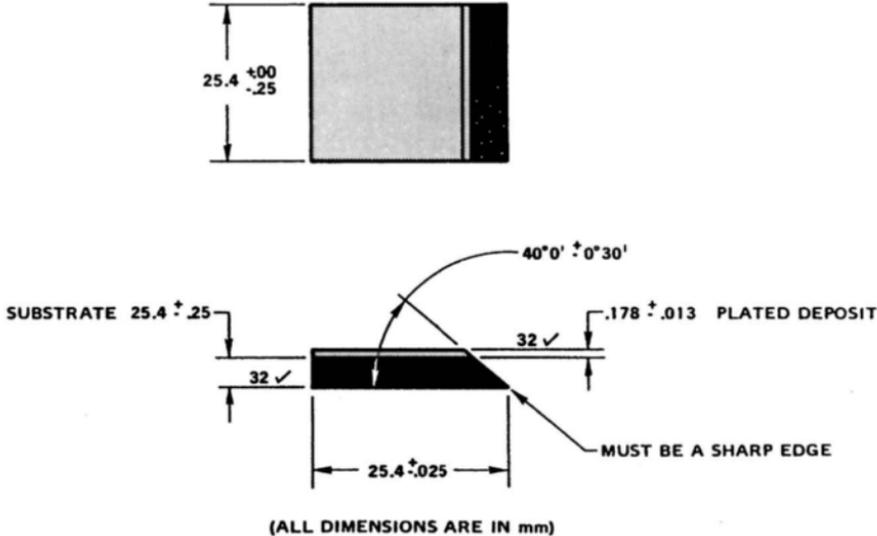
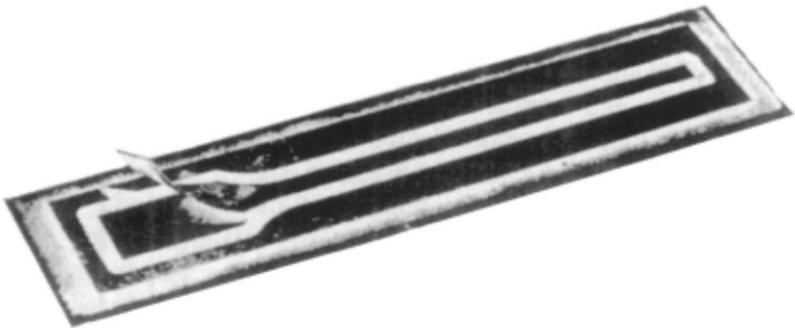


Figure 4: Flyer plate test specimen (top) and test apparatus (bottom).

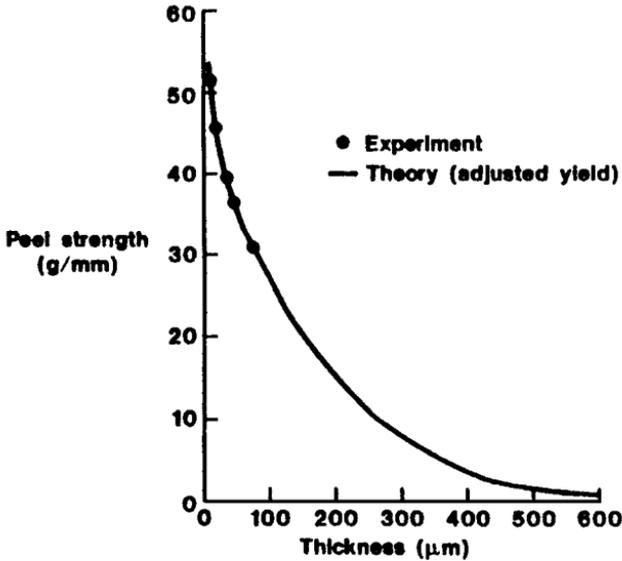
from the relatively heavy ground plate and into the target specimen suspended above the flyer. The output of the flyer plate is determined by measuring the flyer velocity with a streaking camera. This velocity, coupled with metallographic cross sections of the specimens, provides the information needed to quantitatively compare different samples. Dynamic forces with amplitudes up to 100 kilobars and durations ranging from 100 to 500 ns have been obtained with a 14 kJ capacitor bank. A test specimen schematic is shown in Figure 4 and additional details on the test can be found in references 20 and 21.

#### D. Peel Test

The peel test shown in Figure 5, was one of the early quantitative tests proposed for determining adhesion. Jacquet first used this method in 1934 to measure the adhesion of copper on nickel (22). A Jacquet type peel test has been used extensively since 1965 to determine the peel strength of plated plastics (23). For this test, an overlay of copper around 50  $\mu\text{m}$  thick, is deposited on the plated plastic strip. Strips of metal, 25 mm (1 inch) wide, are then peeled normal to the surface. Peel strengths around 26 N/cm (15 lb/in) are commonly obtained. Klingenmaier and Dobrash have developed procedures for testing of various plated coatings on metallic substrates, and have used the peel test on production parts (24).



**Figure 5:** Peel test.



**Figure 6:** Comparison of the theoretical and experimental peel strengths as a function of Cr film thickness on a Si substrate. Adapted from reference 25.

Kim, et al. studied mechanical effects in the peel strength of a thin film both experimentally and theoretically (25). They reported that the adhesion strength measured by the peel test provides a practical adhesion value but did not represent the true interface adhesion strength. Factors which are of major importance in peel testing include: thickness, Young's modulus, yield strength, strain hardening coefficient of the film, compliance of the substrate and interface adhesion strength. A higher peel strength is obtained with thinner or more ductile films even though the true interface adhesion strength is the same. Figure 6 shows the comparison of the experimental peel strength for chromium films on a silicon substrate and theoretical values predicted by taking the strain-hardening factor and Young's modulus of the substrate into account. The theoretical model appears to be an excellent fit to experimental results and clearly indicates that most of the measured peel strength does not come from the true interface adhesion but from the plastic deformation of the film (25).

## COMPARING ADHESION TEST RESULTS

Adhesion testing methods must duplicate the stresses to which the components are subjected in assembly and service. Very good adhesion in

one test, does not necessarily mean that good adhesion will be obtained in another test because the failure mode could change drastically. This is shown in Table 2 which compares peel strength and ring shear data for nickel plated 6061 aluminum. With the peel test, the phosphoric acid anodizing activation process provided better adhesion than the double zincate process. However, in the ring shear test, the double zincate process provided greater than an order of magnitude higher adhesion. This shows that equating adhesion, which is a gross effect, to bonding or cleanliness may be very misleading. Failure of adhesion may be more related to fracture mechanisms than to bonding as mentioned earlier.

**Table 2 - Peel Strength and Ring Shear Data for Nickel Plated 6061 Aluminum**

<u>Preplate Treatment</u>	<u>Peel Strength N/cm(lb/in)</u>	<u>Ring Shear Strength MPa (psi)</u>
Double zincate	107 (61), ref 24	200 (29,000), ref 26
Phosphoric acid, 40 V	140 (80), ref 24	17 (2,500), ref 27

## TECHNIQUES FOR OBTAINING GOOD ADHESION

The purpose of this section is to provide a methodology for use with those substrates that are difficult to coat with an adherent electrodeposit. Table 3 lists a number of materials and classifies them according to ease of coating with adherent electrodeposits. The discussion that follows will be directed at those that require special treatment beyond routine cleaning and acid pickling to ensure adherence of the subsequent deposit.

The reason that some substrates are difficult to coat with adherent deposits is that they have a thin naturally protective oxide film which reforms quite quickly when exposed to air. Therefore, even though a pickling operation might remove the oxide layer, it reforms before the part is immersed in the plating solution. One can remove such surface layers by sputter etching in vacuum but upon removal from the vacuum chamber the film reforms. For that matter, a gas monolayer can even form in one second at  $10^{-5}$  Torr (9). Table 4 lists oxide thickness of some metals revealing the thinness of these troublesome layers.

A variety of techniques have been used to prepare difficult-to-plate

**Table 3- Different Substrates Require Different Treatments to Provide Adherent Coatings**

<u>Easy to Plate</u>	<u>Special treatment</u>	<u>Very difficult</u>
steel	stainless steels	titanium
copper	aluminum	molybdenum
brass	beryllium	tungsten
	magnesium	niobium
	plastics	tantalum
		glass

**Table 4- Thickness of Oxide Films**

<u>Oxide</u>	<u>Thickness (Å)</u>	<u>Reference</u>
Al <sub>2</sub> O <sub>3</sub>	18	28
Fe <sub>2</sub> O <sub>3</sub>	40	28
NiO	6,10	28,29
Ta <sub>2</sub> O <sub>5</sub>	16	30,31
300 Series StainlessSteel	20-100	30,31

substrates for coating. They include pickling in concentrated acids, mechanical roughening, intermediate strike coatings, displacement films, anodic oxidation, heating after plating, plasma/gas etching and physical vapor deposition using augmented energy (ion plating). Examples of each technique, itemized in Table 5, will be presented in the following sections.

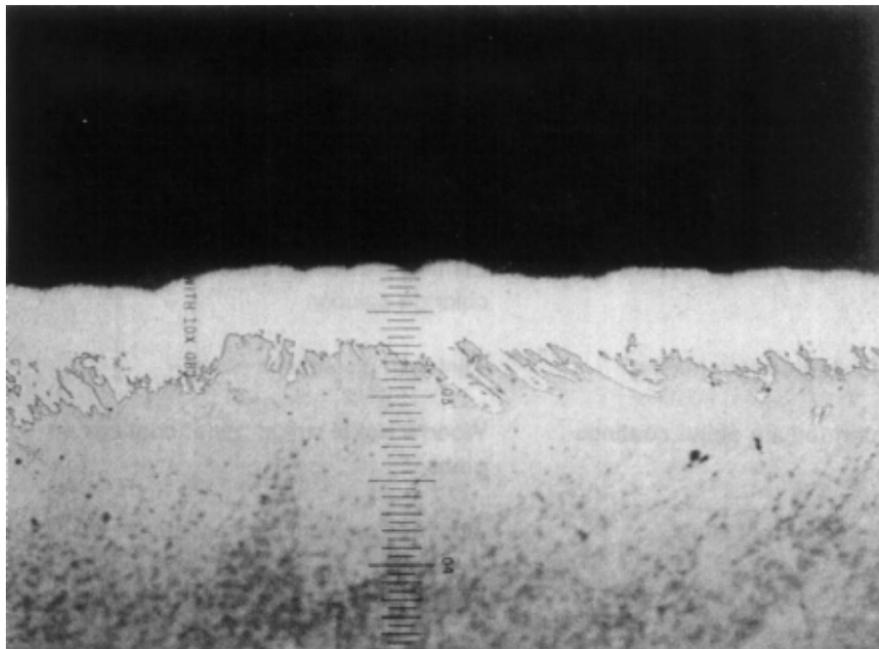
#### A. Pickling in Concentrated Acids

Uranium is a good example to use to demonstrate how pickling in concentrated acids can help provide adhesion in some cases. If proper procedures are used, it is possible to obtain suitable mechanical adhesion between uranium and electrodeposited coatings. The most, successful techniques involve chemical pickling of the uranium in concentrated acid solution containing chloride ions (e.g., 500 g/l nickel chloride plus 340 ml/l nitric acid), followed by removal of the chloride reaction products in nitric acid before plating. This treatment does nothing more than provide a much

**Table 5- A Variety of Techniques are Available for Preparing Difficult-to-Plate Substrates for Coating**

<u>Technique</u>	<u>Examples(discussed in text)</u>
Pickling in concentrated acids	Etching uranium in nitric acid/nickel chloride solution
Mechanical roughening	Tantalum plated with nickel
Intermediate strike coatings	Wood's nickel strike; "glue" coatings on glass
Displacement films	Zinc films on aluminum and beryllium
Anodic oxidation	Phosphoric acid anodizing of aluminum
Heating after plating	Electroless nickel on aluminum; nickel on Zircaloy-2
Plasma/gas etching	Plating on plastics
Physical vapor deposition (ion plating)	Coatings on tungsten, molybdenum and titanium
Miscellaneous	Interface tailoring, oxide formation, partial pressure of gases, reactive ion mixing, phase-in deposition

increased surface area with many sites for mechanical interlocking or "interfingering" of the deposit. However, extremely good adherence can be obtained. Figure 7 shows the roughening and tunneling sites in etched uranium that provide the mechanical interlocking. Ring shear tests on parts receiving this type of treatment show failure in the coating rather than at the interface between the substrate and coating (32).



**Figure 7:** "Interfingering" developed in uranium as a result of etching in nickel chloride/nitric acid solution prior to nickel plating. Magnification is 300  $\times$ .

## B. Mechanical Roughening

Tantalum is one of the most difficult metals to coat with an adherent electrodeposit. Results that have been reported previously are qualitative in nature, probably because quantitative data simply couldn't be obtained. Recent data show that by using mechanical roughening followed by anodic etching, reasonably good adhesion can be obtained. Adherent deposits of nickel, copper, and silver were obtained on tantalum when the tantalum was sandblasted and then anodically etched for 20 minutes at 200 A/m<sup>2</sup> in a methanol solution containing 2.5 v/o HCl and 2.5 v/o HF operated at 45°C. Depth of pitting as a result of the sandblasting/etching process was approximately 50-75  $\mu\text{m}$  (2-3 mils). Peel strength data in Table 6 clearly show the importance of the mechanical roughening (sandblasting) part of the process. Without the mechanical roughening step, the subsequent anodic etch was extremely non-uniform and adhesion was considerably reduced.

**Table 6-Peel Strength Data for Tantalum Electroplated With Nickel\***

Preplating cycle	Current density in etch solution ( $A/m^2$ )	Average peel strength (lb/in) (N/cm)	
Sandblast, etch at 45 C for 20 min.	200	8.8	15.4
Sandblast, etch at 45 C for 20 min.	400	6.0	10.5
Scrub, etch at 45 C for 20 min.	400	3.8	6.7

\*For comparison purposes. peel strength adhesion of nickel plated on aluminum is 100-200 N/cm (57-114 lb/in), reference 24.

### C. Intermediate Strike Coatings

The Wood's nickel strike (33) is an excellent example of use of an intermediate strike coating to improve adhesion. Typically used on stainless steels and nickel based alloys, a Wood's strike produced in a solution containing 240 g/l nickel chloride and 125 ml/l hydrochloric acid produces a thin, adherent deposit of nickel which serves as a base for subsequent coatings. Ring shear test results showing the value of using a Wood's nickel strike with 410 stainless are shown in Table 7. The only process that resulted in failure within the subsequent gold electrodeposit was that which included the Wood's nickel strike. Activation of stainless steel by immersion or cathodic activation in hydrochloric acid provided considerably inferior adhesion.

**Table 7. Influence of Various Activation Treatments on Ring Shear Adhesion of Gold Plated 410 Stainless Steel (A)**

<u>Treatment</u>	<u>Shear Strength</u>		<u>Location of Failure</u>
	<u>MPa</u>	<u>psi</u>	
Immersion in 6 percent (by weight) HCl	5	700	Gold-Stainless Steel Interface
Cathodic Treatment in 6 percent (by weight) HCl at 968A/m <sup>2</sup> for 2 min.	15	2,200	Gold-Stainless Steel Interface
Cathodic Treatment in 37 percent (by weight) HCl at 968A/m <sup>2</sup> for 2 min.	66	9,600	Gold-Stainless Steel Interface
Cathodic Treatment in Wood's Nickel Strike <sup>(B)</sup> at 108A/m <sup>2</sup> for 2 min.	152	22,000	Within Gold Deposit

(A) The gold was plated in a citrate solution at 32A/m<sup>2</sup>. Stainless steel 410 contains 11.5 - 13.5 Cr and no Ni. From reference 34.

(B) The Wood's nickel strike solution contained 240 g/l nickel chloride and 120 ml/l HCl.

Table 8 shows the influence of current density used with the Wood's nickel strike on subsequent adhesion of gold or nickel deposits on stainless steel. When no nickel strike was used, failure occurred at the electrodeposit/substrate interface at very low strengths (5 MPa). When the nickel strike was used and overplated with gold, optimum adhesion was obtained when the current density in the Wood's solution was 108 A/m<sup>2</sup>, or higher.

Prior to overplating with thick nickel in sulfamate solution, higher Wood's strike current densities were needed. Fairly strong bonds were obtained at current densities of 291 and 538 A/m<sup>2</sup>, but maximum bond strength was not obtained unless the current density in the Wood's strike was 1080 A/m<sup>2</sup>, or higher. The fact that a higher current density was

**Table 8 - Influence of Wood's Nickel Strike Current Density on Ring Shear Adhesion of Gold or Nickel Plated AM363<sup>(A)</sup>**

<u>Wood's Nickel Strike Current Density</u>		<u>Ring Shear Bond Strength</u>			
		<u>Gold</u>		<u>Nickel</u>	
<u>A/m<sup>2</sup></u>	<u>ASF</u>	<u>MPa</u>	<u>psi</u>	<u>MPa</u>	<u>psi</u>
0	0	5	700	5	700
54	5	54	7,800	48	6,900
108	10	152	22,000	48	7,000
161	15	152	22,000	54	7,800
291	27	152	22,000	318	46,100
538	50	152	22,000	337	48,900
1080	100	152	22,000	488	70,700

(A) The cleaning/plating cycle consisted of anodic treatment at 323 A/m<sup>2</sup> in hot alkaline cleaner, rinsing, immersion in 18% (wgt) HCl for 2 minutes, rinsing, Wood's nickel striking (240 g/l nickel chloride, 120 ml/l HCl) for 2 minutes, rinsing, and plating in either citrate gold solution at 32 A/m<sup>2</sup> or nickel sulfamate solution at 269 A/m<sup>2</sup>. AM363 stainless steel contains 11.5 Cr, 4.5 Ni, 0.50 Ti, 0.04 C, 0.50 Mn, 1.0 Si and balance Fe. From reference 35.

required prior to nickel plating than prior to deposition of gold is attributed to the difference in shear strengths of the two electrodeposits, with nickel being much stronger.

With some stainless steels or nickel based alloys, a combination of anodic treatment in sulfuric acid followed by cathodic treatment in a Wood's strike may be necessary to insure a high degree of adhesion. Table 9 shows the benefit of using an anodic treatment in sulfuric acid solution prior to striking at 268 A/m<sup>2</sup> in a Wood's nickel solution when preparing 17-4 PH stainless steel for plating. The ring shear strength of parts given only a Wood's nickel strike was 195 MPa, whereas a combination of anodic treatment in sulfuric acid followed by the strike provided strengths of 472 MPa.

**Table 9 - Ring Shear Data for Nickel Plated  
17-4 PH Stainless Steel (A)**

Cleaning/Activating Cycle	Ring Shear (MPa)	Strength (psi)
Clean (B), HCl Pickle, Wood's Nickel Strike at 268 A/m <sup>2</sup> for 5 min., Sulfamate Nickel Plate	195	28,200
Clean, HCL Pickle, Anodic Treat in 70 wt.% H <sub>2</sub> SO <sub>4</sub> at 1070 A/m <sup>2</sup> for 3 min., Wood's Nickel Strike at 268 A/m <sup>2</sup> for 5 min., Sulfamate Nickel Plate	472	68,300

- (A) The composition (in wt.%) of 17-4 PH stainless steel is 0.04 Carbon, 0.40 Manganese, 0.50 Silicon, 16.5 Chromium, 4.25 Nickel, 0.25 Iridium, 3.6 Copper and the remainder is Iron. From Reference 35.
- (B) In all cases, the cleaning step included degreasing, then anodic and cathodic treatment in hot alkaline cleaner. The HCL pickle was 30 wt.%.

This is an unusual result since for most stainless steels, the ring shear test does not provide discrimination between Wood's nickel and anodic sulfuric acid treatment since failure typically occurs in the nickel deposit regardless of which procedure is used. For example, when AM363 stainless steel is plated with either nickel or nickel-cobalt, ring shear adhesion tests show no difference between Wood's strike activation and activation in anodic sulfuric acid followed by Wood's strike since all failures occur within the electrodeposited coatings (Table 10). By contrast, flyer plate tests which measure adhesion under highly dynamic conditions, show approximately a 50% improvement in bond strength when sulfuric acid treatment is used prior to Wood's striking (Table 10). This indicates that if electroplated stainless steel parts are to be used under conditions subjecting them to dynamic loading, use of anodic treatment in sulfuric acid prior to Wood's nickel striking is important.

**Table 10 - Influence on Static and Dynamic Adhesion of Anodic Treatment in Sulfuric Acid Prior to Wood's Nickel Striking of AM363 Stainless Steel (A)**

Activation Treatment	Electro-Deposit	Dynamic Adhesion		Static Adhesion	
		Flyer Plate Spall (B)		Ring Shear Strength	
		Threshold Velocity			
		MPa	psi	MPa	psi
Wood's Strike	Nickel	4000	579,000	455	66,000
Anodic Sulfuric Plus Wood's Strike	Nickel	6000	868,000	455	66,000
Wood's Strike	Nickel-Cobalt	4480	648,000	559	81,000
Anodic Sulfuric Plus Wood's Strike	Nickel-Cobalt	6700	969,000	559	81,000

- A. The complete preparation cycle included anodic cleaning in hot alkaline solution, rinsing, immersing in 18% (wgt) HCl at room temperature for one minute, rinsing, anodic treating in 70% (wgt) sulfuric acid at 1080 A/m<sup>2</sup> (100A/ft<sup>2</sup>) for 3 minutes, rinsing, and then Wood's striking at 270 A/m<sup>2</sup> (25 A/ft<sup>2</sup>) for 5 minutes prior to nickel or nickel-cobalt plating in sulfamate solution. In some cases, the anodic treatment in sulfuric acid was omitted as indicated above. From reference 35.
- B. Spall is the separation of the plated deposit from the substrate due to the interaction of two rarefraction waves.

Some practitioners prefer to use the Wood's strike anodically and then cathodically to help promote adhesion. It's important to note that if this is done, a risk that is taken is that the Wood's solution can become contaminated during the anodic portion of the cycle. The best approach to use if one prefers to use the Wood's strike in this manner is two have two solutions, one for the anodic cycle and the other for the cathodic cycle. This way, all contamination that is introduced during the anodic cycle will not be re-plated out during the cathodic cycle, and interfere with adhesion.

Glass is another example of material which requires an intermediate coating to promote adhesion of any subsequent coating. The conventional technology used by platers for metallizing nonconductors with stannous

chloride/palladium chloride activation followed by electroless deposition prior to final electroplating is not acceptable for glass when thick coatings are required. With this approach, deposits thicker than around 12.5  $\mu\text{m}$  (0.5 mil) easily separate from a glass substrate.

The generally accepted criterion for adhesion between an oxide substrate such as glass and a metal film is that the metal must be oxygen active to react chemically with the oxide surface, forming an interfacial reaction zone (4). Intermediate oxide layers can be achieved by depositing an oxygen active metal (A) onto an oxide surface (BO), promoting the reaction  $A + BO \rightarrow AO + B$  at the interface (9). Materials with large heats of oxide formation such as niobium, vanadium, chromium, and titanium are effective (Table 11). The higher the negative heat of formation, the higher the affinity for oxygen. Deposition of a thin layer (1000-2000 Å) of one of these metals on glass via vacuum evaporation can then be followed by a further metal layer, adherent to the intermediate layer. This is the basis of several multilayer systems such as Ti-Au, Ti-Pd-Au, and Ti-Pt-Au which are used commercially (4,36). Deposition of one of these "glue" or "binder" layers by evaporation followed by a thin layer of copper without breaking vacuum produces an adherent base for thick electroplating. Using this approach, glass parts have been coated with adherent copper as thick as 1 mm (37).

With glass, the interfacial region can change with time. For example, the adhesion of silver films on glass measured 75 days after

**Table 11 - Heat of Formation of Various Metal Oxides\***

Oxide	Heat of formation, kcal/mol
Nb <sub>2</sub> O <sub>5</sub>	-463
V <sub>2</sub> O <sub>3</sub>	-290
Cr <sub>2</sub> O <sub>3</sub>	-270
TiO <sub>2</sub>	-218
WO <sub>3</sub>	-200
MoO <sub>3</sub>	-180
Cu <sub>2</sub> O	-40
Ag <sub>2</sub> O	-7
Au <sub>2</sub> O <sub>3</sub>	+19

\* Values taken from Handbook of Chemistry and Physics, Chemical Rubber Co., Cleveland, OH (1971).

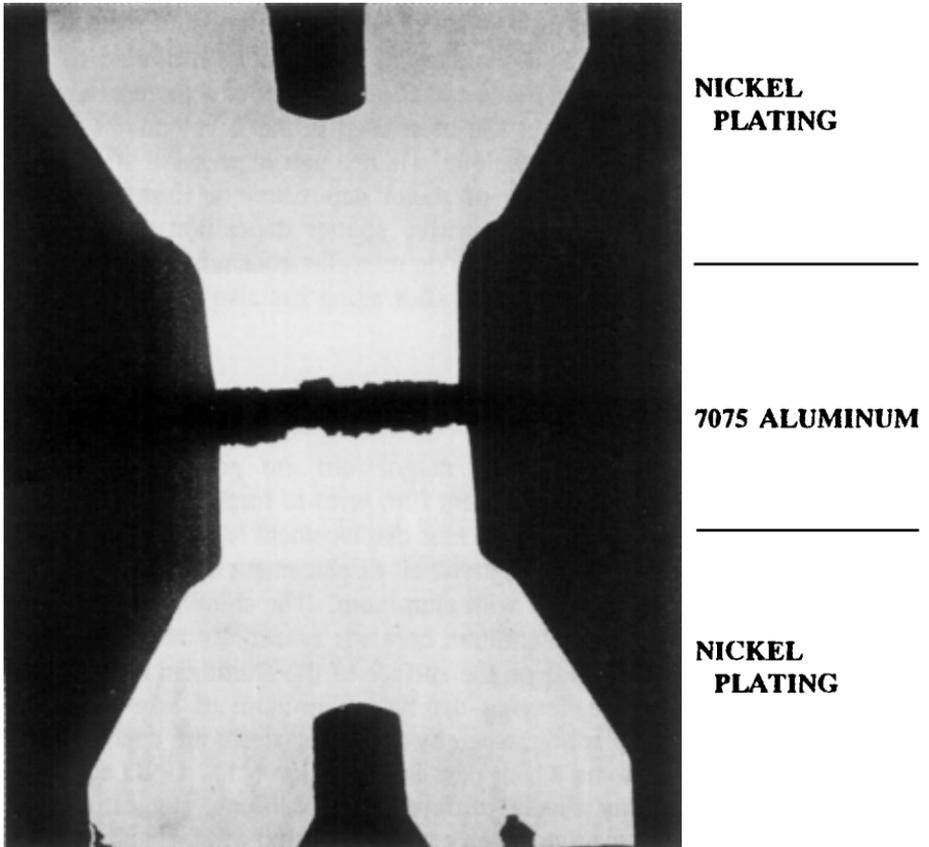
deposition increased by a factor of 2.5 compared with the initial adhesion values (38). Similar results have been obtained with vacuum evaporated aluminum on glass (39). This increase in adhesion is attributed to the migration of oxygen to the interface and the formation of a more extensive reaction zone (3). This concept has been used in the development of the "composite film" metallizing technique, where a partial pressure of reactive gas is used in the initial stages of metal deposition to form a graded composition interfacial zone by reactive sputter deposition (40) and is discussed in more detail in the section on miscellaneous adhesion enhancement techniques. Improved adhesion after aging has also been noted with plated plastics (23).

#### D. Displacement Films

Aluminum, beryllium and magnesium are good examples of substrates where use of a displacement film prior to final electrodeposition can provide excellent adherence. A zinc displacement films works well on all three of these metals although other displacement coatings such as stannates have proven effective with aluminum. The solution used for the zinc immersion process for aluminum contains essentially zinc oxide and sodium hydroxide. The oxide on the surface of the aluminum is dissolved by the sodium hydroxide, leaving the bare aluminum to take part in a chemical displacement reaction, whereby three zinc atoms are deposited for every two aluminum atoms which pass into solution (41). Good adhesion has been obtained using several different compositions, suggesting that adhesion may not be sensitive to the exact proportion of ZnO and NaOH.

Conical head tensile tests with 2024 and 7075 aluminum given a double zincate treatment prior to plating with nickel showed failure in the aluminum. Figure 8 is a cross section showing a 7075 aluminum sample after testing. The failure in the aluminum is clearly evident; no damage is seen in the nickel plating or at the interface between the nickel and the aluminum.

Often a copper cyanide strike is used directly after the zinc immersion step to protect the zinc film and provide a base for subsequent deposition. Table 12 compares use of such a strike on a number of aluminum alloys prior to electroless nickel deposition. Ring shear tests were run with a number of different alloys--1100, 2024, 5083, 6061 and 7075. Electroless nickel deposits 25  $\mu\text{m}$  thick were overplated with 1.5 mm of copper to provide the necessary thickness needed for the ring shear test specimens. Tests results showed that, in general, bond strengths were higher for the as-deposited specimens when a copper strike was used. One exception was the 2024 alloy, which was not affected by lack of a copper strike. Most seriously affected by lack of the copper strike was the 6061



**Figure 8:** Cross section of nickel plated 7075 aluminum conical head tensile specimen after testing. Magnification is 6 ×.

alloy (31 MPa without the strike versus 184 MPa with the strike). The 1100 and 7075 alloys exhibited lower bond strengths when a copper strike was not used, but upon heating to 149°C strengths were improved to levels comparable to those obtained with the copper strike (42).

With beryllium, very poor adhesion, less than 60 MPa was obtained when no zinc immersion treatment was used and also when the pH of the, zinc immersion solution was 9.3, or higher (Table 13). Specimens given a zincate treatment in solutions ranging in pH from 3.0 to 7.7 exhibited good adhesion; shear strengths ranged from 232 to 281 MPa (43).

**Table 12 - Adhesion of Electroless Nickel Deposited on Various Aluminum Alloys<sup>(A)</sup>**

Alloy	Shear Strength <sup>(B)</sup> (MP <sub>a</sub> )			
	Zincate + Copper Strike + Electroless Nickel <sup>(C)</sup>		Zincate + Electro- Less Nickel	
	As- <u>Deposited</u>	Heat <sup>(D)</sup> <u>Treatment</u>	As- <u>Deposited</u>	Heat <sup>(D)</sup> <u>Treatment</u>
1100	99	90	68	108
2024-T351	221	246	251	204
5083-0	173	144	—	—
6061-T6	184	203	31	46
7075-T651	250	239	107	213

(A) The pre-plating cycle consisted of vapor degreasing, alkaline cleaning, rinsing, nitric acid pickling, rinsing, zincating for 30 sec., rinsing, nitric acid pickling, rinsing, zincating for 30 sec., rinsing, then either copper striking in cyanide solution or electroless nickel plating. The zincate solution contained 525 g/l hydroxide and 97.5 g/l zinc oxide. From reference 42.

(B) Each reported value is the average of five tests from one rod.

(C) All samples prepared with one proprietary electroless nickel solution, except for the 5083 alloy, which was plated using a different proprietary.

(D) Heat treatment was one hour at 149 C. Shear testing was done at room temperature.

**Table 13 - Ring Shear Data for Nickel Plated Beryllium\***

<u>Process</u>	<u>pH</u>	<u>Shear Strength</u>	
		<u>MPa</u>	<u>psi</u>
No zinc immersion treatment		0-51	0-7,400
Zinc immersion treatment	10.7	26	3,700
Zinc immersion treatment	9.3	60	8,700
Zinc immersion treatment	3.0	232	33,700
Zinc immersion treatment	3.2	241	35,000
Zinc immersion treatment	7.7	281	40,800

\*Beryllium was S-200-E, 12.7 mm (0.5 in.) dia rod. The nickel plating solution contained 450 g/l nickel sulfamate, 40 g/l boric acid, <1.0 g/l nickel chloride. Current density was 268 A/m<sup>2</sup> (25 A/ft<sup>2</sup>), pH 3.8-4.0, temperature 49°C, and anodes were SD nickel. From reference 43.

## E. Anodic Oxidation

Aluminum is the only metal that has been commercially prepared for reception of adherent electrodeposits by use of anodic oxidation. Although anodizing has been used as a pretreatment for plating on aluminum for over 50 years, the process isn't nearly as common as the zincate and stannate processes (44,45). The anodizing process, done in phosphoric acid solution, takes advantage of the oxidation characteristics of aluminum, and, in particular, the ability to form a porous anodic film under certain electrochemical conditions. Typical conditions include 15 to 50 volts for 10 minutes in a 36 wt% solution of phosphoric acid solution at 38°C (24).

The influence of varying the voltage during the phosphoric acid preplate treatment on the peel strength of several aluminum alloys is compared with that obtained with a double zincate treatment in Table 14. Different anodizing voltages were required for the three alloys given in Table 14 to obtain satisfactory adhesion. A substantially lower voltage (15 V) which was used to anodize the 3003 alloy produced peel strengths significantly higher than were obtained with the other alloys, 6061 and 7046. Both of these alloys showed increasing peel strengths with increasing voltage during anodizing. Although peel strengths comparable to those reached by zincating were obtained with the 6061 alloy by anodizing at 30 to 40 V, similar results were not obtained with the 7046 alloy even when anodizing as high as 50V. The 7046 alloy has a much higher alloy content which may contribute to the lower adhesion obtained by anodizing (24).

Although the anodizing process isn't nearly as popular as the zincating process for preparing aluminum for plating it has potential for future development. Low cost of chemicals, freedom from the use of cyanides, and lower waste treatment costs are definite advantages (44). The reason for the lack of popularity of this process apparently is due to the low adhesion on certain alloys, the high power required for some alloys and the variability of conditions required for different aluminum alloys.

## F. Heating After Plating

Heating after plating occasionally can improve adhesion. In some cases the heating is done at relatively low temperatures, e.g. 100 to 200°C, and in other cases the temperature can be very high, thus promoting rapid diffusion between the coating and substrate, e.g. electroless nickel on titanium heated at 850°C (46). Table 12, discussed earlier, provides data for various aluminum alloys coated with electroless nickel. Heating for one hour at 149°C was particularly effective in improving the bond strengths for 1100 and 7075 alloys which had been zincated and then directly plated with

**Table 14 - Influence of Voltage During Phosphoric Acid Anodizing of Aluminum on Peel Strength of Subsequent Nickel Electrodeposits\***

		<u>Peel Strength, N/cm (lb/in.)</u>	
<u>Alloy</u>	<u>Preplate Treatment</u>	<u>Range</u>	<u>Average Mean</u>
3003	double zincate	173 to 245	196 (112)
	phosphoric acid anodize, 15V	183 to 227	198 (113)
6061	double zincate	70 to 210	107 (61)
	phosphoric acid anodize, 15 V	44 to 61	51 (30)
	phosphoric acid anodize 20V	70 to 88	79 (45)
	phosphoric acid anodize, 30 V	96 to 130	105 (60)
	phosphoric acid anodize, 40 V	131 to 149	140 (80)
7046	double zincate	96 to 210	156 (89)
	phosphoric acid anodize, 20 V		no adhesion
	phosphoric acid anodize 30 V	17 to 35	26 (15)
	phosphoric acid anodize, 40 V	70 to 87	79 (45)
	phosphoric acid anodize, 50 V	70 to 123	96 (57)

\*Peel test width was 25 mm. Thickness of nickel deposited in sulfamate solution was 160  $\mu\text{m}$ . From reference 24.

electroless nickel (no intermediate copper strike). Ring shear bond strength of 1100 improved from 68 to 108 MPa as a result of heating and that of 7075 improved from 107 to 213 MPa.

Ring shear data for nickel plated Zircaloy-2 are shown in Table 15. The treatment cycle used to prepare the rods for plating consisted of etching in ammonium bifluoride solution. Neither this step nor any other chemical etching or other activation steps provided much higher adhesion in the as-deposited condition (47). To determine the influence of heating on adhesion, some rods were heated in vacuum at 700°C in both constrained and unconstrained conditions. The constraining was done by placing the specimens in a TZM molybdenum die with a 25 µm or less clearance and then heating. Since the coefficient of thermal expansion for the molybde-

**Table 15 - Influence of heating on the ring shear strength of nickel-plated Zircaloy-2.<sup>a</sup>**

Activation Treatment	Ring Shear Strength, MPa		
	As-deposited	700°C, 1h (unconstrained)	700°C, 1 h (constrained) <sup>b</sup>
Vapor degrease Cathodic alkaline clean Immersion in 15 g. NH <sub>4</sub> FHF, 0.5 mL H <sub>2</sub> SO <sub>4</sub> per litre, for 1 min at 22°C Ni plate	16,25,15 ... ...	38 ... ...	140,292,224 ... ...
Vapor degrease Cathodic alkaline clean Immersion in 45 g NH <sub>4</sub> FHF per litre for 3 min at 22°C Ni plate	31, 6 ... ...	38, 12 ... ...	235,234 ... ...

<sup>a</sup> Each reported value is the average of at least two tests. From references 47 and 48.

<sup>b</sup> A TZM molybdenum ring was used to constrain the specimens during heating. Clearance between the specimens and the ring was 25 µm or less on the diameter.

num is lower than that of zirconium or nickel, it provided a stress calculated to be greater than 69 MPa on the electrodeposit as the assemblies were heated (48). The data in Table 15 clearly show a noticeable improvement as a result of heating for specimens which were constrained during heating. Bond strengths around 230 MPa were obtained for a number of specimens. By comparison, bond strengths in the as-deposited condition averaged 19 MPa. Heating in the unconstrained condition improved this to 29 MPa, still very low compared to the data obtained when constraint was used during heating.

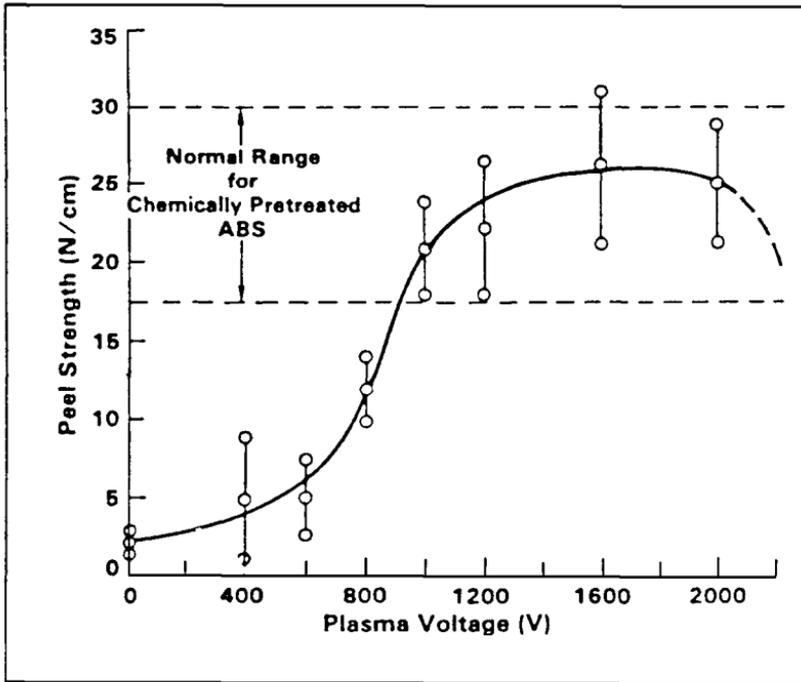
### G. Plasma/Gas Etching

Chemical processes for plating on plastics are expensive, require rigorous chemical control, and present effluent treatment problems. Alternate processes that work well in preparing a variety of plastics for reception of adherent electrodeposits involve plasma or gas etching. Use of an oxygen, radio frequency (RF) glow discharge plasma treatment to condition ABS (acrylonitrile butadiene styrene) plastic followed by thin (1000 Å) layers of nickel and copper applied by sputtering or electron beam evaporation provides a base for subsequent thick electrodeposition (49). The nickel layer helps establish a metal-plastic bond and the copper provides enhanced electrical conductivity for electroplating. With the proper plasma voltage during the first step, adherence equal to that obtained by conventional chemical preplating (17.5 N/cm, and above) is obtained (Figure 9).

Figure 10 shows that the adhesion strength of vacuum deposited silver on modified polyethylene (PE) increases in the following order: untreated < argon plasma < oxygen plasma < nitrogen plasma treated PE (50). Argon plasma treatment of PE has little or no effect on the adhesion of vacuum deposited silver whereas oxygen and nitrogen plasmas improve adhesion of PE five and eightfold, respectively. Changes in the PE core levels after submonolayer deposition of Ag were interpreted as due to the formation of Ag-O-C and Ag-N-C species on oxygen and nitrogen plasma treated PE (50).

Another process that works well on ABS and ABS alloys including polycarbonate varieties involves ozone etching followed by alkali conditioning (51). The ozone gas "sees" and reacts uniformly with all exposed surfaces producing a very uniform etch. A significant advantage of the ozone process is that the reaction is diffusion controlled and, therefore, self-terminating. By contrast, chromic acid, used for aqueous etching, never stops reacting.

Vapor etching of plastics using sulfur trioxide is also gaining favor as a replacement for chromic acid etching prior to plating (52). During this



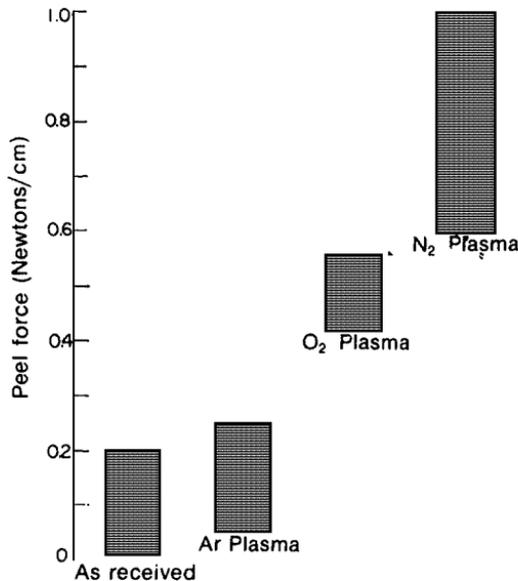
**Figure 9:** Peel strength vs. dc plasma voltage for ABS plastic. From reference 49. Reprinted with permission of The American Electroplaters & Surface Finishers Soc.

process, liquid sulfur trioxide is used and gasified on-site using a special generator system. At the end of the etch cycle, the gas is neutralized with ammonia before it is expelled from the chamber. The economics of this process are highly favorable when compared with chromic acid etching (53).

## H. Physical Vapor Deposition (Ion Plating)

A relatively new approach to providing adherence of electroplated coatings on difficult-to-plate substrates is that of utilizing augmented energy physical vapor deposition techniques such as ion plating to provide an initial layer which can be used as a base for subsequent, adherent electrodeposition.

Physical vapor deposition (PVD) is a process whereby a material in bulk form is atomistically converted to a vapor phase in a vacuum and condensed on a substrate to form a deposit. PVD techniques fall into three



**Figure 10:** Comparison of adhesion strength of vacuum deposited silver on untreated and plasma treated polyethylene. From reference 50.

broad categories: evaporation, sputtering, and augmented energy. In evaporation, vapors are produced from a material located in a source which is heated by radiation, eddy currents, electron beam bombardment, etc. The process is usually carried out in vacuum (typically  $10^{-5}$  to  $10^{-6}$  Torr) so that evaporated atoms undergo an essentially collision-less line of sight transport prior to condensation on the substrate which is usually at ground potential (not biased). Sputtering involves positive gas ions (usually argon) produced in a glow discharge which bombard the target material thereby dislodging groups of atoms or single atoms which then pass into the vapor phase and deposit on the substrate. Augmented energy techniques have been employed recently to improve the energy of the deposition process. These include ion plating, thermionic plasma and formation of plasmas using hollow cathode discharge sources. Ion plating is a generic term applied to atomistic deposition processes in which the substrate is subjected to a flux of high energy ions sufficient to cause appreciable sputtering before and during film deposition. The ion bombardment is usually done in an inert gas discharge system similar to that used in sputter deposition, except that in ion plating the substrate is made a sputtering cathode. The substrate is subjected to ion bombardment for a time sufficient to remove surface

contaminants and barrier layers (sputter cleaning) before deposition of the film material. After the substrate surface is sputter cleaned, the film deposition is begun without interrupting the ion bombardment. Variations in the ion plating technique have given rise to terms such as vacuum ion plating, chemical ion plating, bias sputtering, and others which refer to specific environment, sources or techniques.

With PVD films, adhesion varies from poor to excellent (54-56). Sputtering provides much better adhesion than the generally weak adhesion obtained with evaporation. This is due to the higher energy of the deposition species in sputter deposition as compared to that of evaporated atoms (1 to 10 eV vs. 0.1 to 0.2 eV) (13,57). By comparison, electroplating usually develops only a few tenths of an electron volt (58). With ion plating, adhesion is excellent and better than with sputtering. Again, this is attributed to the highly energetic deposition ions (>100 eV) as well as to the in-situ substrate precleaning and the simultaneous deposition and substrate sputtering due to the continuous bombardment of the substrate during deposition (54). Another factor that should be considered is the temperature at which sputtering or ion plating is done. Typically, use of higher temperature during either of these processes can lead to improved adhesion. Industrial applications where the technologies of ion plating and electroplating have been combined to provide adherence on difficult-to-plate metals can be found in references 59-63.

As mentioned in Table 3, the refractory metals such as tungsten, molybdenum and titanium are among the most difficult to electroplate with adherent, functionally thick acceptable deposits. All of the techniques discussed in sections A through G have been tried with these metals with less than optimal results. Recent efforts have shown that use of augmented energy physical vapor deposition to provide an initial adherent coating and then electroplating over this to final thickness provides excellent adhesion.

Ring shear data for tungsten, molybdenum and titanium are presented in Table 16. The results clearly show that use of an augmented energy PVD process for the initial stage of the coating cycle provided extremely good adherence. In all cases, the adherence was considerably improved over that obtained without use of the initial PVD layer. For example, the wet chemical process for tungsten consisted of etching parts in a HF/HNO<sub>3</sub> concentrated solution, followed by anodic treatment in 300 g/l KOH. Adhesion with this process was only 48 MPa, whereas, with ion plating as the initial step, adhesion was 173 MPa. With molybdenum, the plating process included two firing operations at 1000°C in dry hydrogen and the resulting adhesion of the gold electrodeposit was strong enough to cause failure in the gold at 125 MPa. By comparison, use of magnetron ion plating to provide the initial coating (60,000 Å of copper) followed by thick electroplated copper resulted in a bond that failed in the copper deposit at

**Table 16– Ring Shear Data Show the Value of Combining PVD with Electroplating for Coating Difficult-to-Plate Metals**

Metal	Ring Shear Adhesion (MPa)	
	Electroplating	PVD & Electroplating
Tungsten	48 <sup>a</sup> (Cu) <sup>b</sup>	173 <sup>c</sup> (Cu)
Molybdenum	125 <sup>d</sup> (Au)	216 <sup>e</sup> (Cu)
Titanium	145 <sup>f</sup> (Ni)	252 <sup>g</sup> (Cu)

- a) This process included etching in 3 parts HF, 1 part HNO<sub>3</sub>, and 4 parts H<sub>2</sub>O for 5 min. at 22°C followed by anodic treatment (1076 A/m<sup>2</sup>) in 300 g/l KOH at 50°C for 5 min. prior to plating.
- b) Metal in parenthesis was that used for building up the thick ring (1.5mm) required for ring shear testing.
- c) The magnetron ion plating process included sputter etching in vacuum, magnetron ion plating with 6µm of copper and then electroplating to final thickness. Base pressure of the system was  $5 \times 10^{-6}$  Pa ( $10^{-8}$  Torr), etch power was 0.5 watts/cm<sup>2</sup>, and bias power was 0.078 watts/cm<sup>2</sup> (but tapered to zero after deposition of about 20,000Å of copper).
- d) This process included degreasing in perchlorethylene, firing in dry hydrogen (<2ppm H<sub>2</sub>O) for 10 min., immersing in a solution containing four parts NH<sub>4</sub>OH (28%) and one part H<sub>2</sub>O<sub>2</sub> (30%) for 8 to 10 seconds at room temperature, rinsing in distilled water, gold striking to deposit 0.15 to 0.63 mg/cm<sup>2</sup> (0.08 to 0.32 µm), rinsing in distilled water, firing in dry hydrogen at 1000°C for 10 min., and then electroplating to final thickness.
- e) The magnetron ion plating process included sputter etching in vacuum, magnetron ion plating with 6µ of copper and then electroplating to final thickness. Base pressure of the system was  $5 \times 10^{-6}$  Pa ( $10^{-8}$  Torr), etch power was 0.5 watts/cm<sup>2</sup> and bias power was 0.078 watts/cm<sup>2</sup> throughout the coating run.
- f) This process included abrasive blasting, cleaning in hot alkaline solution, pickling in HCl, bright dipping in a solution containing 10% by vol. of HF (70%), 1% HNO<sub>3</sub> and balance water, followed by anodic etching for 6 min. at 162A/m<sup>2</sup> in a 40°C solution containing 13% by vol HF (70%), 83% acetic acid and 4% water. Then 25 µm of Ni was plated in a sulfamate solution at 48°C. Specimens were heated at 480°C for 2 hours and then plated with approximately 1.5 mm of nickel.
- g) This process included coating with 10 µm of copper by hot hollow cathode deposition and then electroplating to final thickness. Conditions for the etch cycle included a source power/rate of 10Å/sec, substrate voltage of 2 KV and pressure of  $3 \times 10^{-4}$  Torr. Conditions for the coating cycle were a source power/rate of 100 Å/sec, and a pressure of  $3 \times 10^{-4}$  Torr.

216 MPa. Lastly, the same type of result was obtained with titanium. The wet chemical process included an anodic etch in HF/acetic acid and a heating step at 480°C for 2 hours and this provided a bond with a shear strength of 145 MPa. Use of ion plating provided a bond with a shear strength of 252 MPa. Clearly, coupling augmented energy PVD processes with electroplating provides better adhesion than obtained with the wet processes and also eliminates : 1) the need for roughening the surface chemically or mechanically and 2) heating after coating.

## I. Other Adhesion Enhancement Techniques

This section is intended to be futuristic in nature, and will build on the previous discussion of combining PVD techniques and electroplating since this approach represents new technology. A wide variety of methods have been used to improve the adhesion of vapor deposited films on solid substrates with which they have no chemical affinity in the bulk (7). Since the value of using PVD techniques to provide an intermediary coating has already been demonstrated, some discussion on techniques for improving adhesion of these films on difficult-to-plate substrates could be of future value. Techniques to be discussed include interface tailoring, alloying surface layers with metals exhibiting a high negative free energy of oxide formation, use of partial pressure of various gases during deposition, reactive ion mixing and phase-in deposition.

*a. Interface Tailoring:* The most direct techniques employ elevated substrate temperatures to increase the mobility of atoms arriving on the substrate and thereby improving the quality of the surface coverage (7). Recently developed beam processing techniques, however, offer fresh possibilities of interface "tailoring" which provides a powerful means of manipulating interface atomic structure in order to benefit adhesion. Providing interface irradiation by utilizing energetic ions (100 keV to several megaelectron volts) has been used to penetrate through metal films on various substrates to produce "stitching" at the interface. Modest doses ( $10^{15}$  -  $10^{16}$  ions  $\text{cm}^{-2}$ ) have been shown to improve adhesion dramatically in systems such as Cu/ $\text{Al}_2\text{O}_3$  or Au/Teflon in which no bonding could initially be found (7).

In terms of tailoring the interface layers to optimize their performance in bonding, the standard ultrahigh vacuum methods of molecular beam epitaxy would often work. However, it has recently been shown that non-ultrahigh vacuum techniques, including use of large area, low energy (500eV) beams of ions before or during deposition, can offer valuable interface control and produce adhesion superior to that obtained by other methods. Strong bonds which were thermally stable have been produced by this manner with copper on alumina and Teflon (7,64,65).

**b. Free Energy of Oxide Formation:** The adherence of amorphous chemically vapor deposited (CVD) alumina on pure copper was considerably enhanced by alloying a thin surface layer with preevaporated Zr, Al, or Mn; i.e., with metals exhibiting a high negative free energy of formation of the oxide similar to the situation with glass discussed earlier in this chapter. Table 17 compares the free energies of formation of oxides of the alloying elements with adhesion of subsequently applied alumina films. This clearly shows that the oxygen affinity of the metal, expressed by the negative free energy of formation of the oxide matches the predicted behavior (66).

However, these results are not valid for a non-oxidizing process such as sputtering at low temperatures. During the first step of chemical vapor deposition of alumina, the intermediate layer is partially or totally

**Table 17- Adherence of Chemically Vapor Deposited Alumina Coatings on Copper Pre-Coated With Various Films by Vacuum Evaporation (1.2)**

<u>Metal</u>	<u>Free Energy of Formation of Oxide (kcal/gram-atom of oxygen)</u>	<u>Thickness of Metal (A)</u>	<u>Adherence(3) (kg/mm<sup>2</sup>)</u>
Ag	+ 5	200	Very weak
Ni	- 43	20,200,1000	Very weak
Sn	- 51	200	Very weak
Mn	- 78	200	Strong (2.8)
Al	- 114	50,100,200,1000	Strong (1.6-2.3)
Zr	- 114	200	Strong

1. From reference 66.

2. During vacuum evaporation the copper substrate was heated to 250C, and during subsequent CVD treatment the temperature reached 500C.

3. Determined by bonding a 0.6 cm diameter pin to the substrate and pulling in tension.

oxidized, which is not the case during sputtering (67). Adherence of sputtered alumina to copper is poor, however, use of a titanium intermediate layer enhances adhesion significantly. Also, use of an intermediate nickel layer (which has a lower thermal expansion coefficient than copper) prior to titanium deposition further enhances adhesion (67).

In a somewhat similar manner, the existing technology for deposition of adherent films of copper onto alumina utilizes an initial layer of chromium to provide an adherent metal/oxide film. Since this technology results in a number of difficulties when these films are used for transmission lines or are etched for clearance for via-holes, an alternate process which eliminated the chromium interface was developed for providing good adhesion. It was shown that formation of a copper aluminate spinel ( $\text{CuAl}_2\text{O}_4$ ) as an intermediate layer between the copper film and an aluminum oxide substrate worked quite well (68). Adhesion, measured by a pull test, showed a 50% improvement with the spinel interface as compared with the chromium interface as shown in Table 18.

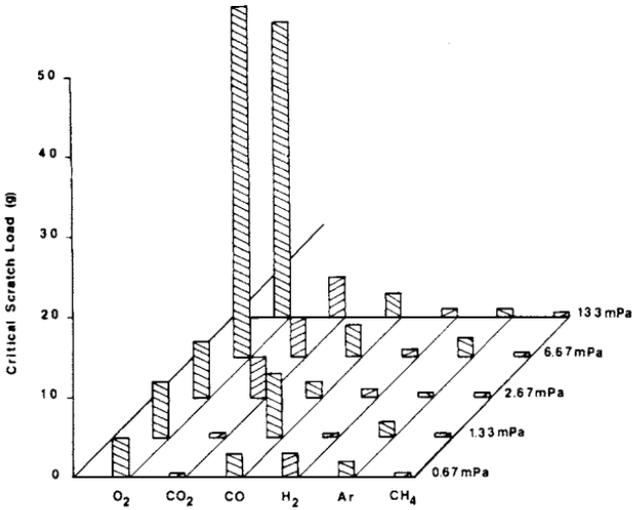
*c. Partial Pressure of Various Gases:* As shown in Table 11, chromium is one of the "glue" or "binder" layers that works well in providing adhesion on glass due to the fact that chromium is oxygen active and reacts chemically with the oxide surface. An adhesion-pressure dependency has been shown to exist with results strongly influenced by oxygen in the system. Figure 11 shows that backfilling the deposition chamber with oxygen at pressures greater than 6.67 MPa produced superior adhesion as measured by a scratch test. Adhesion for oxygen backfill pressures less than 6.67 MPa was considerably reduced as was influence of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{Ar}$  and  $\text{CH}_4$  regardless of backfill pressure. The adhesion

**Table 18- Adhesion of Copper Films on Alumina and Sapphire(1)**

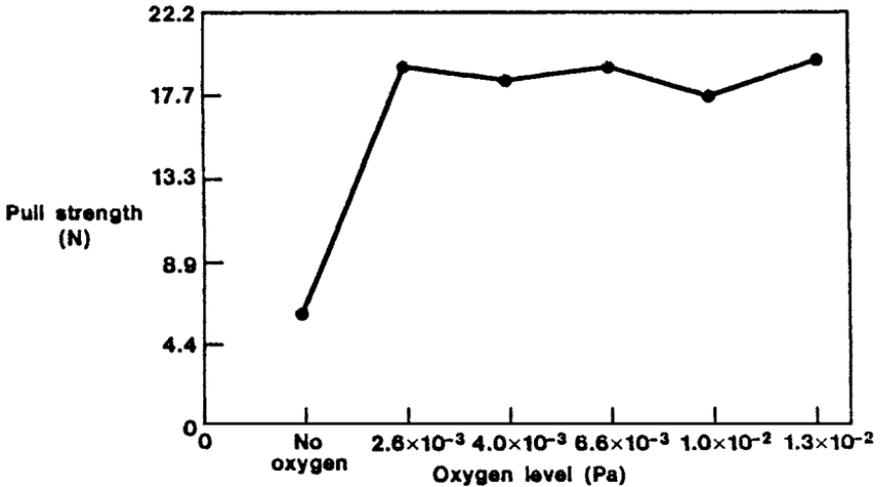
System (2)	Pull Strength	
	MPa	psi
Cu/alumina	0.6	93
Cu/Cr/alumina	3.1	>454
Cu/Cr/sapphire	4.6	667
Cu/spinel/sapphire	6.3	>907
Cu/spinel/alumina	6.9	1005

1. From reference 68.

2. The copper films were deposited by vacuum evaporation; the spinel films were formed by heating after copper deposition.



**Figure 11:** Initial adhesion scratch loads of chromium on glass for hydrogen, argon, methane, oxygen, carbon monoxide, and carbon dioxide at various backfill system pressures. From reference 69.



**Figure 12:** Lead frame adhesion strengths and failure modes for various oxygen levels. Adapted from reference 70.

dependence of chromium corresponds to an oxygen/chromium impingement ratio of approximately 3, and it has been suggested that this ratio corresponds to the condition of critical condensation for a coherent chromium oxide adhesion layer (69). It was also noted that the critical scratch loads for all films tested were observed to increase with increasing time. This is attributed to the formation of an interfacial oxide layer of gradually increasing dimensions.

In a similar fashion, the influence of oxygen introduced into the evaporation system during the initial phase of chromium deposition on alumina substrates of hybrid microcircuits was shown to have a noticeable effect on adhesion. Figure 12 shows results from 90 degree pull tests of thermocompression bonded lead frames. With no oxygen in the system, very low pull strengths were obtained. The results for system pressure levels  $2.67 \times 10^{-3}$  through  $1.33 \times 10^{-2}$  Pa were excellent. Production yields of HMC's which had been as low as 45% exceeded 98% upon incorporation of oxygen backfill during chromium deposition (70). Another example is the sputter deposition of gold films on silica in a partial pressure of oxygen, which yield very adherent films without the use of an intermediate metal layer (71).

*d. Reactive Ion Mixing:* Metal/polymer adhesion is becoming increasingly important to a variety of modern technologies such as the microelectronics industry where the development of flexible circuit boards, multilevel very large scale integrated (VLSI) interconnections, and advanced microelectronics packages are largely dependent on the integrity of the metal/polymer interface (72). Considerable attention has been devoted to polyimides (PIs) because of their excellent thermal, dielectric, and planarization properties. Recent work utilizing the unique capabilities of reactive ion mixing to modify the interfacial chemistry and adhesion of low reactivity metal/polyimide specimens has shown promising results. Implantation of  $^{28}\text{Si}^+$  enhanced adhesion of Ni/PI specimens by a factor of 20 or greater (measured by the scratch test), such that the films were only removed as a result of failure in the PI substrates (Table 19). This adhesion increase was attributed to a combination of the substrate hardening, interfacial mixing (mechanical interlocking), interfacial grading and new chemical bonding characteristics (72).

Use of  $^{84}\text{Kr}^+$  implantation was also examined in order to isolate and evaluate the interfacial mixing (mechanical interlocking) and substrate hardening observed under  $^{28}\text{Si}^+$  implantation without participating in any chemical bonding. The mechanical interlocking and substrate hardening induced by  $^{84}\text{Kr}^+$  resulted in an adhesion increase of a factor of only 3, which was considerably smaller than that observed following  $^{28}\text{Si}^+$  implantation (Table 19), indicating that the substrate hardening and mechanical interlocking had only a very small influence on the adhesion

**Table 19 - Influence of  $^{28}\text{Si}^+$  and  $^{84}\text{Kr}^+$  Implantation on Nickel/Polyimide Film Removal (a)**

<u>Processing</u>	<u>Critical Force (N)</u>	
	<u>Ni/PI (adhesion)</u>	<u>PI substrate (toughness)</u>
As-deposited	< 1(b)	10
$1 \times 10^{16} \text{ Si/cm}^2$	4	12
$5 \times 10^{16} \text{ Si/cm}^2$	8	15
$1 \times 10^{17} \text{ Si/cm}^2$	20 (c)	20
$5 \times 10^{15} \text{ Kr/cm}^2$	3	11
$1 \times 10^{16} \text{ Kr/cm}^2$	3	13
$5 \times 10^{16} \text{ Kr/cm}^2$	Ni film destroyed	22

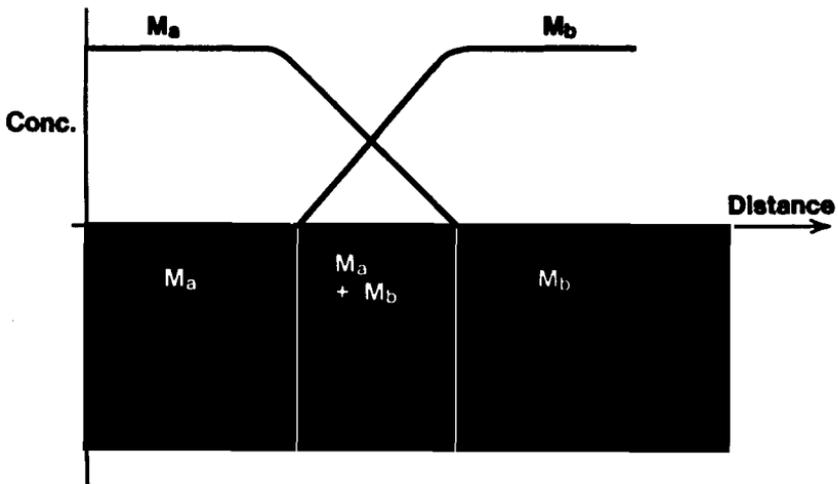
a- The nickel film was 300 angstroms thick and deposited using electron beam evaporation. For details see references 72 and 73.

b- Evaluated by scratch test measurement. The lower limit with the test apparatus used was 1 N.

c- This measurement was limited by catastrophic substrate failure.

enhancement induced by  $^{84}\text{Kr}^+$  implantation, and that the chemical bonding and interfacial grading produced by the  $^{28}\text{Si}^+$  were primarily responsible for the large adhesion increases observed (73).

*e. Phase-in Deposition:* Phase-in deposition is a method widely employed in the electronic industry to provide improved adhesion for physically vapor deposited (PVD) films (74). As illustrated in Figure 13, this technique results in a physically intermixed layer in between two dissimilar metal layers. This intermixed layer consists of regions of different composition from 0% to 100% and often plays an important role in determining adhesion and overall physical and electrical properties of thin-film devices. For example, co-evaporation of Cr and Cu has been found to form a fine mix of Cr and Cu grains along the interface and this results in a very high adhesion strength which is superior to that obtained with Cr alone (74).



**Figure 13:** Schematic diagram of an electron beam evaporation system and the structure expected by phase-in deposition. Adapted from reference 74.

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