SVC
SOCIETY of VACUUM COATERS

Educational Guide to Vacuum Coating Processing

Surface and Film Characterization:

Film Adhesion and "Deadhesion"

Adhesion is the mechanical strength joining two different objects or materials and is a fundamental requirement of most deposited film systems. The "apparent adhesion" is determined by applying an external mechanical stress, and failure may occur in the interfacial region or nearby material. Failure of adhesion (or "deadhesion") can be due to mechanical failure by fracture or deformation, chemical causes such as corrosion or dissolution, or diffusion processes such as the diffusion of material to or away from the film-substrate interface. Poor adhesion may be localized so as to give local failure and form pinholes in the film or coating. In PVD processing, film adhesion is intimately connected with the nucleation, interface formation, film growth, and surface coverage, as well as the properties of the materials in contact and the environmental stresses (mechanical, chemical, thermal, fatigue) to which the system is exposed.

Good adhesion is promoted by a high fracture toughness of the interface and nearby materials, the absence of fracture-initiating features, the presence of fracture blunting and deflecting features, low residual film stress, and no operational adhesion-degradation mechanisms (such as diffusion or corrosion). Poor adhesion can be attributable to a low degree of chemical bonding, poor interfacial contact, low fracture toughness of the interfacial (or nearby) material, high residual film stresses, fracture-initiating features, and/or operational adhesion-degradation mechanisms. In many systems where film adhesion is difficult to attain, an intermediate material is introduced into the interfacial region to bond to both the substrate and the film material. For example, in the gold metallization of oxides, a layer of oxygen-active material—such as titanium, which chemically reacts with the oxides and has solid solubility with gold—is used in the interfacial region to provide a "glue layer."

The nucleation density of the deposited film atoms is an early indication of good or poor adhesion. A high nucleation density indicates strong chemical interaction of the deposited atoms with the substrate surface and is desirable for good adhesion. A low nucleation density indicates poor interaction, the development of poor interfacial contact, and the formation of interfacial flaws, which will lead to poor adhesion.

The nature of the interfacial region is important to developing a fracture-resistant interfacial material. A diffusion-type or compound-type interfacial region is good for adhesion, provided excessive diffusion and reaction do not introduce voids, stresses, and fractures in the interfacial region. Roughening the substrate surface can improve or degrade the adhesion, depending on the ability of the deposition technique to fill in the surface roughness and on the film morphology generated.

An important factor in the apparent adhesion is the residual film stress. Invariably, PVD films have a residual stress that can be either tensile or compressive and can approach the yield or fracture strength of the materials involved. These stresses arise from differences in the thermal coefficient of expansion between the film and the substrate in high-temperature depositions, thermal gradients formed in the depositing film, and/or stresses due to the growth of the film. In many cases the stress level will change with film thickness. The total stress that appears at the interface from residual film stress will depend on the film thickness and the film material. High-modulus materials such as chromium, tungsten, and compound materials can generate the highest stresses. These stresses will be added to any applied stress, but can be capable of causing spontaneous deadhesion of the film with no externally applied stress.

High residual film stress can cause blistering of the film from the surface in the case of compressive stress or by microcracking and flaking in the case of high tensile stresses. If the compressive stresses are isotropic, the blistering will be in the form of "wormtracks." If the tensile stresses are isotropic, the microcracking will be in the form of a "dried-mudflat" cracking pattern, often with the edges curled away from the substrate. If the film adhesion is high or the fracture strength of the surface is low, the actual fracture path may be in the substrate and not at the interface. Localized regions of high intrinsic stress may be found in films due to growth discontinuities. These stressed areas can lead to localized adhesion failure, giving pinholes. If the film has a high residual stress, "static fatigue" can allow the propagation of a fracture with time, resulting in long-term failure with no externally applied stress.

If high residual film stresses are generated they can often be limited by restricting the film thickness, changing the film materials, changing the film structure, or changing the deposition technique or deposition parameters. Another commonly encountered problem is the high compressive stresses that can be developed in low-pressure sputter deposition where high-energy reflected neutrals from the sputtering target bombard the growing film. The compressive stresses can be lowered by increasing the deposition pressure so as to "thermalize" the high-energy reflected neutrals before they reach the growing film surface.

Film composition and growth morphology can also be important to adhesion. Generally, a dense film is desirable; however, such a film will transmit stresses more easily than a less dense or porous film. In some cases a porous film formed by columnar growth morphology can be used as a "compliant" film or layer in the film structure. In cases where there is a large difference in the physical and mechanical properties of the film and the substrate, it may be advantageous to grade the properties through an interfacial region rather

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than have a sharp discontinuity in properties. This can be done by controlling the nitrogen availability in the plasma during reactive deposition of nitride films.

Surface preparation and modification processes can be important to adhesion. Of course, contaminant layers that prevent chemical interaction of the depositing material and the surface should be eliminated. When depositing hard coatings or wear-resistant coatings it is important that the underlying material does not deform or fracture under the load, causing coating fracture. This may mean that some type of surface-hardening process should be used, such as plasma nitriding or shot peening. When coating polymers, the chemical reactivity of the surface is often increased by "functionalizing" the surface. This is done by using an oxygen or nitrogen plasma that creates radical groups on the surface, which will react with the depositing film atoms. This plasma treatment can also cause crosslinking of low-molecular-weight polymers in the near-surface region, which increases the strength of the material in this region.

Adhesion can decrease with time if there are operational degradation processes. For example, in chromium-gold metallization, if the system is exposed to a temperature of greater than 200°C in air, the chromium will diffuse through the gold and react with oxygen to form an oxide on the surface. In the extreme, all of the chromium will diffuse away from the interface, giving deadhesion. In titanium-gold metallization, the Ti-Au forms a galvanic corrosion couple and the interface will corrode if an electrolyte is present. To prevent this corrosion, a layer of palladium is added to give a corrosion-resistant Ti-Pd-Au film structure.

There are many film-adhesion tests. Some of the most common are the tape-peel test, the stud-pull test, the scratch test, and the indentation test, as shown in Figure 1. The tape test is commonly used for films such as mirror coatings and may be non-destructive (except for contaminants that may be left on the surface). In the tape test it is important that the tape be pulled across a scratch, which provides the failure initiation. The stud-pull test is more stringent than the tape test. The wire-pull tests are often used in microelectronics and may be used as a non-destructive test. The shear test is also used in microelectronics. The scratch test is used in many areas. The acoustic emission sensor allows detection of the initiation of fracture, and the scratch pattern gives an indication of the type of failure. For example, the fracture may be acceptable but the spalling may not be acceptable. The indentation test is used with hard coatings, and again the failure pattern is used to indicate acceptable behavior. Often the acceptable adhesion is correlated with service performance, and failure behavior is used to determine whether the processing is reproducible or not.

In general, adhesion tests are used as comparative tests and not to give absolute values of adhesion strength. Film adhesion is generally tested immediately after deposition. If there is the possibility of time/environment adhesion degradation, however, an adhesion testing program should be designed to expose the film system to the subsequent fabrication, storage and service conditions, and exposure times that it will see after fabrication. For example, in the Au-Al metallization system, prolonged exposure to a temperature above 200°C in service will cause progressive interfacial diffusion and the formation of pores, fractures, and the Al-Au intermetallic phase in the interfacial region. The degraded interfacial region will easily fracture and exhibit the purple color of the intermetallic phase ($AuAl_2$); this failure is called the "purple plague."

If film adhesion is a problem, consideration must be given to these questions:

- Are the materials in contact chemically reactive so as to form strong chemical bonds?
- Are there contaminant layers that prevent intimate contact?
- Is the substrate surface mechanically strong and defect-free so that fracture does not occur in a weak substrate surface region?
- Is there a high nucleation density of the adatoms on the substrate surface?
- Do the interfacial region and the interfacial material have high fracture toughness?
- Are there high residual film stresses?
- Are there operational degradation mechanisms?

In many cases adhesion problems that occur in production can be traced to variable substrate surfaces, poor surface preparation, or uncontrolled deposition parameters.

Reference:

"Adhesion and Deadhesion" Chapter 11 in Handbook of Physical Vapor Deposition (PVD) Processing, Donald M. Mattox, William Andrew Publishing/ Noyes Publications, 1998

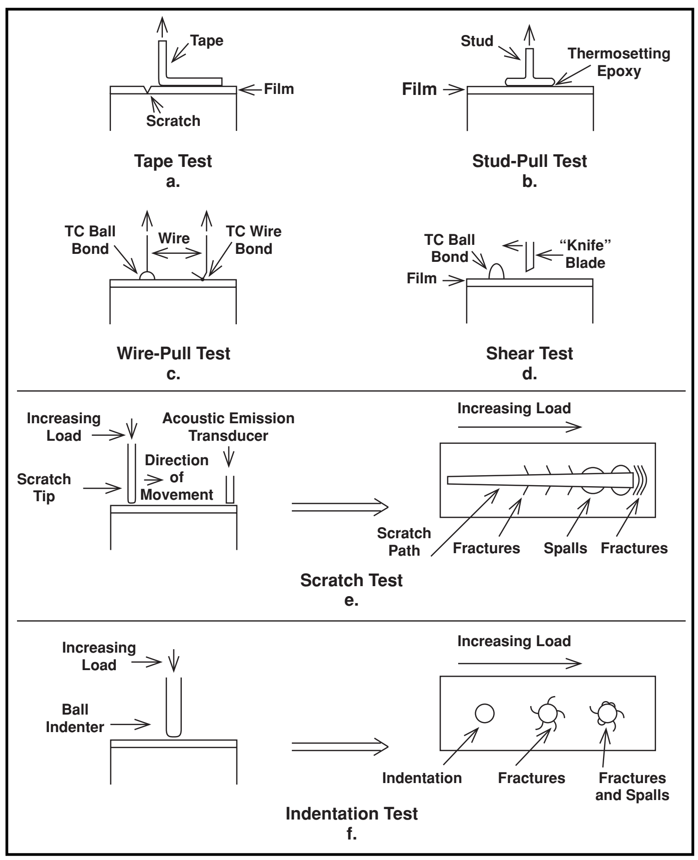

Figure 1: Adhesion tests. a) Tape test; b) Stud-pull test; c) Wire-bond and ball-bond pull test; d) Shear or topple test; e) Scratch test and scratch pattern; and f) Indentation test and indentation patterns.