

THIN FILM METALLIZATION OF OXIDES IN MICROELECTRONICS*

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The factors affecting adhesion are reviewed, and it is shown that the structure of the interfacial region is probably a controlling factor in film adhesion. Nucleation, film growth and surface effects control the structure of the interfacial region and may determine the adhesion obtained. The adhesion stability of a metallization system may be determined by processing and service requirements. Specific metallization systems in common use in the microelectronics industry are discussed together with their applications and limitations.

INTRODUCTION

In microelectronics, thin film metallization is deposited on three types of oxide surfaces. First, conductors, resistors, electrodes or bonding pads may be deposited on bulk oxides, which may be smooth or rough compared with the film thickness. Second, the metallization may be deposited on thick oxide insulating films. These metal films may be used as electrodes, interconnects or to make contact to devices or circuits through "windows" etched in the oxide. Third, the metallization may be deposited on thin naturally occurring oxide layers on circuits and devices. In this case the metallization is usually expected to react sufficiently with the oxide layer to provide good electrical contact. Metallization patterns are usually formed by photolithography and etching procedures. One of the prime concerns is the adhesion of the metallization to the oxide surface.

Adhesion is a macroscopic property of a two-component system and involves both the chemical bonding in the interfacial region and the fracture mechanism¹. Adhesion in a thin film system differs from that between bulk materials by how the materials are brought into contact (nucleation and growth *versus* deformation and bulk contact) and how they are made to react (interface formation). In addition, thin films of materials often have very different properties from the bulk form, and these may affect the fracture properties. To understand thin film adhesion, all these parameters need to be considered.

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NUCLEATION

When atoms impinge on a surface, they lose energy to the surface and finally condense by forming stable nuclei. Before condensing, the atoms have a degree of mobility over the surface which is determined by their energy and the strength of the interaction between the atom and the surface. For instance, aluminum atoms react strongly with an oxide surface and thus the surface mobility is low and the nucleation density high. As the aluminum deposition proceeds, the nuclei grow laterally and form a continuous film at low film thickness, giving a high interfacial contact area. This type of nucleation and growth might be termed "wetting growth".

In the case of non-reacting systems, such as gold on carbon, the surface mobility is high and films are nucleated on charge sites, defects or impurities, or by atom-atom collisions of depositing atoms on the surface, giving nucleation by forming isolated "critical nuclei"². This gives a low nucleation density, and as the gold deposition proceeds the nuclei grow vertically as well as laterally, forming the often-studied island-channel-film stages of film growth³. These widely separated nuclei require an appreciable thickness before the film becomes continuous, and the nucleation and growth might be termed "non-wetting growth". For the reactive system of aluminum on glass it has been found that the film becomes electrically continuous at 9 Å thickness, while for the non-reactive system of silver on glass the film must be 50 Å thick before the film is continuous⁴. In some cases, particularly at elevated temperatures, the nuclei may tend to "de-wet" from the surface, giving a low interfacial contact area^{5, 6}. Figure 1 shows such a growth mode, which might be termed "de-wetting growth".

Figure 2 depicts the de-wetting, non-wetting and wetting type of nuclei growth. Although individual non-wetting nuclei may have high adhesion⁷, the lack of over-all contact area and the presence of voids at the interface as the film becomes continuous may lead to low film adhesion because of easy fracture propagation in the interfacial region. The nuclei density can be increased by increasing the deposition rate so as to increase the atom-atom collision probability of the film atoms on the surface. Thus rapid initial deposition may be used to enhance adhesion in some cases.

As the nuclei form on non-reactive surfaces, they have some ability to move and coalesce, forming larger nuclei. The small nuclei may rotate during coalescence, giving a preferred orientation to the larger nuclei. At high temperatures on suitable substrates the resulting film may have a highly preferred orientation



Fig. 1. "De-wetting growth" of gold nuclei on carbon⁵.

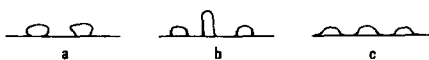


Fig. 2. Nuclei shape: (a) "de-wetting", (b) "non-wetting" and (c) "wetting".

(epitaxial growth). Low temperatures can inhibit coalescence, and at very low substrate temperatures amorphous films may be formed. Charge effects can inhibit nuclei coalescence by electrostatic repulsion⁸, while an electric field in the plane of the film can enhance coalescence⁹.

Nucleation density, and thus adhesion, can also be affected by surface impurity atoms. For instance, a very thin nucleating layer of non-stoichiometric bismuth trioxide can be used to give thin adherent gold films on glass with good electrical conductivity¹⁰. Surface impurity atoms which are conducive to good adhesion may arise from mechanical polishing of the surface, diffusion from the bulk or as a residue from chemical etching¹¹. Sometimes small amounts of impurity can have a significant effect on adhesion¹².

Nucleation in the non-reacting system can also be affected by the atmosphere present before and during deposition. For example, exposure of glass surfaces to oxygen after glow discharge cleaning reduces the agglomeration tendencies of gold nuclei¹³, giving a higher nucleation density. Another example is the sputter deposition of gold films on silica in a partial pressure of oxygen, which yields very adherent films without the use of an intermediate reactive metal layer¹⁴. This adhesion is probably due to changes in the nucleation stage of film growth. The nucleation and structure of silver films deposited on glass have been shown to be very sensitive to the vacuum during vacuum deposition¹⁵.

INTERFACE FORMATION

The generally accepted criterion for adhesion between a metal film and an oxide substrate is that the metal must be oxygen active so as to react chemically with the oxide surface, forming an interfacial reaction zone¹⁶⁻¹⁹, although electrostatic effects may have some affect on adhesion²⁰. Table I gives the heat of formation of the oxides of a number of metals often used in the thin film metallization of oxide surfaces. In multilayer metallization, materials having a high heat of oxide formation are used to provide direct contact to the oxide, while materials

TABLE I*

Oxide	Heat of formation (kcal/mol)
Ta ₂ O ₅	-500
Al ₂ O ₃	-399
V ₂ O ₃	-290
Cr ₂ O ₃	-270
TiO ₂	-218
WO ₃	-200
MoO ₃	-180
Cu ₂ O	-40
Ag ₂ O	-7
Au ₂ O ₃	+19

* Values taken from *Handbook of Chemistry and Physics*, 52nd edn., Chemical Rubber Co., Cleveland, Ohio, 1971.

having other desirable properties are used as surface layers. An example is the titanium-gold metallization where the titanium is used as a "bonding layer" between the oxide and gold, which has good joining properties.

In addition to the metallurgical system used for thin film metallization, we also have the option of deposition technique, the most common ones being vacuum evaporation and sputter deposition. In vacuum evaporation the material to be deposited is vaporized and condensed on the substrate surface in a vacuum sufficient to prevent collision between the film-forming atoms and residual gas atoms as they traverse the distance between source and substrate²¹. Thus the vacuum deposition process involves atoms having thermal energies (0.1–0.5 eV) and line-of-sight deposition. Resistively heated vaporization sources are normally used for low temperature materials, and electron-beam heated sources are used to vaporize refractory materials.

Sputter-deposited films are formed by the condensation of atoms formed by sputtering²². Sputtering is a process in which high energy particles striking a surface cause the ejection of a surface atom by momentum transfer²³. These ejected atoms may have energies (1–100 eV) much greater than thermal. Generally it is found that sputter-deposited films have better adhesion than vacuum-deposited films. This is in part due to the high energy of the sputtered atoms, which have²⁴ (1) a high condensation energy, (2) the ability to clean the substrate surface, and (3) the ability to create local defects in the substrate surface. The incident particle energy may affect nucleation, with the higher energy particles giving a higher nuclei density²⁵. This may be due to the generation of defects and charge sites on the surface which influence nucleation⁸.

In an atomistic film deposition process such as vacuum evaporation or sputtering, the energy released during condensation causes heating. This heating along with heating due to the processing (radiation, electron bombardment, ion bombardment etc.) may cause appreciable surface temperature rises in both vacuum evaporation²⁶ and sputter deposition²⁷.

A high surface temperature promotes the development of an interfacial reaction zone, if the materials are reactive and there are no barrier layers present. It is usually found that deposited refractory metals have better adhesion than metals with a low vaporization temperature, even if the heat of oxide formation is the same²⁸. This may be attributed to the greater energy available during the condensation of the refractory materials. The formation of an interfacial reaction zone can also be promoted by heating the substrate during deposition. For metal-to-metal systems a negative heat of reaction (miscibility) is often taken as the necessary criterion for adhesion²⁹, although it has been shown that clean metal surfaces of systems which are non-miscible in the bulk (positive heat of reaction) can give good adhesion^{1, 30, 31}. This may mean that bulk values of thermodynamic properties have limitations when applied to surfaces.

Typically, in reactive metal-oxide systems the reaction zone will consist of complex oxide phases involving both the metal and the substrate materials; these have been termed "adherence oxides" by ceramists who study the bonding between metals and glasses^{32, 33}. For thin film metallization, this interaction zone is typically 10–100 Å in extent^{34–36}. Very thick interaction zones may

create problems by introducing high stress gradients between phases which may cause fracture in the substrate material or fracture at low externally applied stress levels, or even without an applied stress. Extensive interfacial reaction zones may also present problems in complete removal of the film material during etching. For these reasons the extent of interaction in the interfacial region must often be limited. For non-reacting systems there is no interaction zone and there is an abrupt change from one material to another¹. This type of interface may be necessary, as in tunnel junction devices where a very thin insulating layer ($\sim 10 \text{ \AA}$) is used and the metallization is used as an electrode.

Good adhesion can also be obtained by having the film material soluble in the substrate material, thus forming an interfacial diffusion zone. For instance, gold adheres quite well to high lead glasses because of solubility and reaction with the large lead cations, but it generally has poor adhesion to other glasses because of the lack of solubility and the lack of chemical reaction between gold and the oxygen anions which form the surface layer of many oxide materials³⁷. The solubility of gold in glass can be increased by the addition of small quantities of tin oxide, bismuth oxide or cerium oxide¹¹.

The interfacial region can change with time. For example, in vacuum-evaporated aluminum on glass it has been found that the adhesion increases with time^{38, 39}. This increase in adhesion is attributed to the migration of oxygen to the interface and the formation of a more extensive reaction zone. This concept was used in the development of the "composite film" metallizing technique⁴⁰, 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. If reactive gases are excluded from the interface during the initial stages of film formation, the adhesion may be decreased⁴¹. This means that in some cases a partial pressure of reactive gas in the system during the interface formation may be conducive to good adhesion. Ion bombardment during and after film formation has been used to enhance adhesion by altering the nucleation mode^{42, 43} and by promoting interfacial reaction after deposition⁴⁴.

The structure and properties of the interfacial region are important in interfacial fracture. Stresses due to differing properties of the film, interfacial material and substrate should be "graded" or distributed over appreciable thicknesses so that there are no sharp discontinuities in stress. The interfacial region should not contain voids or defects which act as stress concentrators⁴⁵. Such voids may be formed in non-wetting interfaces, on rough surfaces, or by Kirkendall diffusion, where material diffuses faster in one direction than in the other⁴⁶. Thus the type of interface most conducive to good adhesion from a fracture standpoint is a diffusion interface with no sharp discontinuities in physical properties, no porosity and low intrinsic stress. The type of interface least conducive to adhesion is a porous interface with high stresses and a sharp discontinuity in stress and material properties.

FILM PROPERTIES

Film properties are also important to adhesion. High intrinsic film stresses

can allow failure at low externally applied stresses. It has been shown that interfacial shear stresses are more important to failure than are pure tensile stresses⁴⁷. In an extreme case, high film stress can cause failure in the substrate material. The failure may occur some time after deposition by static fatigue enhanced by exposure to moisture⁴⁸.

In any system which uses a high strength film material, such as tungsten or chromium, care must be taken not to introduce too much stress in the system. For example, when using chromium on smooth surfaces, the film thickness should be kept less than 500 Å to ensure a low intrinsic stress. A number of techniques have been developed to measure film stress⁴⁹, including the use of quartz-crystal resonators⁵⁰ and bending beams⁵¹. Film deposition techniques and parameters can radically affect stress levels, with high substrate temperatures and low deposition rates usually giving lower film stress. Vacuum-deposited metal films usually have tensile stresses, while sputter-deposited metal films usually have compressive stresses. Films having high tensile stresses fail by cracking, while high compressive stresses cause buckling. Generally it is a good policy to limit the thickness of "bonding" metals noted for high intrinsic stresses and build up the metallization thickness using low yield materials such as gold or silver. Very thin "bonding" layers (10–50 Å) can provide good adhesion¹⁸, but some authors report a thickness dependence on adhesion which may be related to interfacial porosity⁵². Typical bonding layer thicknesses are 100–300 Å.

SURFACE EFFECTS

An important aspect in interface formation during deposition is the presence of surface contaminants which prevent reaction and/or diffusion. In the case of oxides, probably the most noxious contaminants are the hydrocarbons. Carbon and carbides form very effective barrier layers for diffusion and reaction. Hydrocarbons are adsorbed from the air and are often introduced by improper storage and/or handling. The most effective means of removing hydrocarbons is by the use of solvent cleaning followed by oxidizing treatments, such as potassium dichromate⁵², hydrogen peroxide⁵², air firing at high temperatures⁵² or exposure to an oxygen plasma^{53, 54}. Ultraviolet radiation has been used to remove photoresist polymers from surfaces, probably by a depolymerization/oxidation mechanism⁵⁵. Glow discharge cleaning using low energy (~10 eV) ions has also been shown to be an effective cleaning procedure⁵⁶. Care must be used in sputter cleaning, where high energy ions (>100 eV) are used, as gas incorporated into the surface during cleaning may be subsequently desorbed in the interfacial region, causing a loss of adhesion⁵⁷. In all cases, cleaning should be done just prior to insertion into the deposition system and substrates should be handled in an ultra-clean manner. If storage must be done prior to deposition, organic-free containers should be used. Freshly oxidized aluminum containers are very good since they preferentially adsorb and retain organics quite well⁵⁸. The normal "oxygen" surface found on many fresh oxide surfaces is highly polarizable and capable of adsorbing hydroxyl radicals^{17, 37}. This type of surface contaminant may also be removed by the oxidation-type cleaning procedures.

In some cases, pinholes and film porosity can be of concern in thin film metallization. For very smooth surfaces, dust is the primary source of pinholes⁵⁹. Surface defects in smooth surfaces can cause pinholes and cone-shaped defects in the deposited films⁶⁰, while if steps are present on the smooth surface, as is the case when circuit patterns are defined, pinholes can form due to geometrical shadowing of the base of the step^{61, 62}. These pinholes can be eliminated by tailoring the shape of the step⁶³. Geometrical shadowing is also the cause of pinholes and porosity in films deposited on rough surfaces⁶⁴. Ion plating⁶⁵ and sputtering, particularly bias sputtering⁴¹, are more effective in covering severe surface roughness than is vacuum evaporation^{63, 65, 66}.

Geometrical shadowing is also one cause of the columnar structure often found in thick deposits. Ion bombardment during ion plating or bias sputtering causes sputtering of the growing film, eroding the peaks and filling the valleys, giving a less columnar structure in thick deposits⁶⁷. Sputtering of depositing atoms probably occurs at a higher rate than sputtering of a bulk surface. Film deposition at an oblique angle to the surface aggravates the porosity problem, particularly on a rough surface⁶⁸. Thus porous films can result from deposition conditions or from an extensive number of pinholes, such as occur in thin deposits on rough surfaces. Pinholes and porosity in soft materials such as gold can sometimes be sealed by burnishing the deposit⁶⁹. Heating, either during deposition or subsequently, may decrease the pinhole density by causing lateral surface diffusion of the depositing particles and reaction and diffusion with the underlying material in the pinhole region^{70, 71}.

Coverage and sealing of a porous surface is very difficult since there is no "bridging" mechanism with sputter deposition and vacuum deposition. A random deposition leaves a "pipe" of unfilled pore because of geometrical shadowing. Sputtering of the depositing film will aid in filling the pore, but the film thickness must be greater than the pore diameter before sealing is accomplished⁷².

Fracturing of an interface on a rough surface can be quite different from that on a smooth surface. For a fracture to propagate along a plane of weakness in a rough interface it must change direction often or it must pass through stronger regions. This means that the direction and magnitude of the local applied stress is variable and makes fracture propagation more difficult than on a planar surface where the applied stress is more uniform. There is also some degree of mechanical interlocking between film and substrate on a rough surface.

A problem which is sometimes encountered with vacuum-deposited films is the deposition of "nodules", particularly when high rate evaporation is used. The nodules form bumps on the metallization surfaces and can cause problems in subsequent photolithography and joining. The nodules originate from exploding gas pockets in the melt and can be minimized by vacuum pre-melting the evaporant charge and using an evaporation source designed to give multiple vaporization or surface wetting before the atoms escape the vapor source^{21, 73}.

JOINING

In microelectronics applications the metallized surface is usually bonded to another surface by a variety of techniques⁷⁴. One of the most commonly used is thermocompression bonding. In this technique, heat and pressure are applied simultaneously to the joining surfaces. The pressure tends to deform the surfaces, exposing virgin material, and brings the materials into intimate contact. The heat promotes solution of interfacial contaminants and diffusion and reaction between the joining surfaces. If there is little deformation and a barrier layer is present, joining may be poor^{75, 76}. However, a barrier layer can be useful in some cases to limit diffusion⁷⁷. For gold thermocompression bonding, rather thick layers ($> 10\,000\text{ \AA}$) of gold are used to allow deformation and limit shear stress at the interface. Interestingly, gold is often a bad actor in joining⁷⁸. Gold surfaces chemisorb hydrocarbons from the air with great affinity⁷⁹. These are not desorbed or dissolved on heating, thus forming barrier layers to joining. A porous film may adsorb contaminants which are very difficult to remove. Plasma oxidation has been used to good advantage in cleaning photoresist and hydrocarbons from the surfaces of microelectronics circuits⁸⁰.

Other properties such as hardness, grain size, impurity concentration etc. may effect thermocompression bonding⁷⁶, and these film properties, which are determined by the deposition technique and parameters, may be quite variable. Joining may also be improved by introducing a shearing motion during the joining operation to improve contact and aid in disruption of contaminant layers.

When joining is achieved by soldering or extensive diffusion, such as in solid-liquid interdiffusion (SLID) joining⁸¹, some component of the metallization may be preferentially dissolved or "scavenged". In these cases, alloys⁸² or surface layers⁸³ may be used to limit the interactions.

STABILITY

Properties of the metallization may be affected by subsequent processing. Often during subsequent processing the metallization is subjected to heating. In some cases this heating can cause diffusion, further reaction, stress relief, grain growth or other property changes. Diffusion in multilayer metallization can be very dependent on film morphology. If the film is dense the primary diffusion mechanism will probably be by grain boundary diffusion. If the film is porous, surface diffusion will probably predominate since it is much more rapid than either grain boundary or bulk diffusion^{84, 85}. Extensive diffusion in multilayer metallization may occur during deposition if the substrate temperature is high⁸⁶. Excessive diffusion may cause a depletion of the interfacial bonding metal, causing loss of adhesion. In some cases, interfacial reaction can create a diffusion barrier which reduces the diffusion rate⁸⁵.

The metallization may also be exposed to chemical treatments, such as cleaning or etching. If there are pinholes or porosity in the metallization, etchants may reach the interfacial region, causing loss of adhesion^{69, 70}. In photolitho-

graphy, pinholes or nodules in the metallization may cause pinholes in the photoresist which allow etchants to attack the metallization in undesirable places.

The long-term stability of thin film metallization can be affected by the properties of the film. Stress relief and structural changes in films may occur at very low temperatures^{87, 88}, especially in films deposited at high rates and low substrate temperatures. This may be true even for gold films^{89, 90}. Apparently a combination of high intrinsic stress and high defect concentrations can lead to a metastable metallurgical system, where changes can occur at low temperatures compared with the temperatures necessary to cause changes in the bulk.

Corrosion can also affect the long-term stability of thin film metallization. Chemical corrosion can occur if a reactive film is exposed to a corrosive environment. For instance, grain boundary oxidation can occur in tantalum films at 300 °C⁹¹ and titanium bonding layers are corroded by an air/HCl environment⁹². If extensive corrosion takes place, adhesion may be destroyed. Corrosion can be minimized by packaging in a hermetically sealed container or by covering the metallization with a "passivating" dielectric layer⁹³.

Electrochemical corrosion can occur where two metals are exposed, such as at edges and pinholes, when there is an electrolyte present, and this may be aggravated by a continuously applied voltage⁹⁴. Failure may be in the form of dissolution of the material or by the formation of whiskers by electrodeposition, causing shorts between conductors.

Mass transfer of material in conductor metallization by momentum transfer from the conduction electrons to film atoms at high current densities and elevated temperatures is called electromigration. This process can cause failure in some metallizations, particularly aluminum^{95, 96}.

Progressive reactions under service conditions can cause changes in the metallization. The aluminum-gold system is a classic example. At rather low temperatures (~200 °C) an aluminum-gold reaction proceeds at the interface, forming various intermetallics and finally a loss of adhesion⁹⁷. Apparently the cause of failure is the formation of Kirkendall porosity and brittle intermetallic phases in the interfacial region.

Certain long-term stability problems with film properties may be due to gas incorporation during deposition. In sputter deposition it has been shown that up to several atomic percent of atoms of the sputtering gas can be incorporated into the deposited film^{98, 99}. This gas can precipitate into bubbles¹⁰⁰ or be released by heating¹⁰¹, and may affect the film properties. The incorporated gas can increase the stress and raise the annealing temperature of sputter-deposited gold films^{99, 102}. The same effect is found in electron-beam evaporated films where residual gases, often released by heating during evaporation, are incorporated into the deposit and may cause property changes¹⁰³.

METALLIZATION SYSTEMS

Table II gives some of the most common single and multilayer metallization systems used in microelectronics.

The most widely used single-metal metallization system is evaporated

TABLE II

THIN FILM METALLIZATION SYSTEMS

<i>One-component</i>	<i>Two-component</i>	<i>Three-component</i>
Al	Ti-Au	Ti-Pd-Au
Cr	NiCr-Au	Ti-Pt-Au
Nichrome ^R (NiCr)	Cr-Au	NiCr-Cu-Pd
W	Mo-Au	Ti-Cu-Pd
Mo	Nb-Au	
Au	Cr-AuPd	

aluminum¹⁰⁴. This metal presents bonding problems when attached to gold unless careful control of processing and service environments is maintained⁹⁷. Aluminum metallization may also fail by electromigration at high current densities⁹⁶ and is susceptible to corrosion by halogen vapors.

Tungsten and molybdenum deposited by sputtering or electron-beam evaporation hold some interest for single-component metallization because of their high temperature capabilities, which are sometimes needed in service and in subsequent processing. The properties of these refractory materials are very process sensitive, which makes process development and control very important¹⁰⁵. Thin films of chromium or Nichrome^R are sometimes used for thin film resistors¹⁰⁶, but care must be taken to ensure that the stress levels are kept low.

As has been previously pointed out, gold has been used to metallize oxide substrates without the use of an intermediate bonding layer¹⁴. Table III shows some of the pull strengths obtained on gold films sputter deposited onto alumina substrates in oxygen and in pure argon. This technique has not been widely used in microelectronics technology but represents an interesting system which apparently does not follow the commonly accepted rules for adhesion.

TABLE III

SPUTTERED GOLD ON Al₂O₃

<i>Gas</i>	<i>R.f. bias</i>	<i>Pull strength* as deposited</i>	<i>Pull strength* 500 °C in air/1 h</i>
Argon	0 V	0	-
Argon	-100 V	$\frac{1}{4}$ lb (max)	-
100% O ₂ graded to 100% argon	-500 V graded to -100 V	2-2 $\frac{1}{4}$ lb	3-4 lb

* Pull tests on 0.002 in. × 0.015 in. gold ribbons thermocompression bonded to gold metallization.

Two-component (two-layer) metallization systems have been developed to improve properties and stability over one-component systems. The systems generally consist of an intermediate bonding layer followed by a surface layer (usually gold) which is easily joinable. The reactivity of the bonding metal may determine which system is used in microelectronics technology. For instance,

titanium is more reactive than Nichrome^R (NiCr) and makes good ohmic contact to Ta₂N resistor circuits by reacting with the 20–50 Å of oxide normally found on the surface¹⁰⁷. This same reactivity makes the titanium unacceptable as a material for use as electrodes on tantalum/Ta₂O₅ capacitors where NiCr/Au or Cr/Au metallization is necessary¹⁰⁷. The amount of reaction that may be tolerated may dictate the deposition technique and parameters. For instance, in the sputter deposition of conductor materials the deposition parameters must often be controlled to prevent over-heating of the substrate¹⁰⁸. The system Cr–AuPd is used for soldering, where the AuPd alloy limits scavenging⁸².

The Ti/Au, Cr/Au and NiCr/Au two-component systems have the limitation that at elevated process or service temperatures there is interdiffusion that can change the film properties, cause loss of adhesion or degrade electrode joinability¹⁰⁹. For instance, in the Cr/Au system, chromium diffusion can occur at temperatures as low as 220 °C^{110, 111}. The chromium causes an increase in electrical resistivity and segregates on the surface, where it oxidizes, causing joining problems. In order to alleviate this problem, refractory metal bonding layers of molybdenum¹¹² or niobium⁴⁰ may be used in place of chromium or NiCr^R. This leads to some production complexities since molybdenum and niobium must be sputter deposited or electron-beam evaporated, whereas the other materials may be resistively evaporated, which is a somewhat easier process. A potential problem in the Mo/Au system is that the composite structure is difficult to etch if there is extensive intermixing (> 50 Å) in the interface region. In addition to diffusion, electrochemical corrosion may be a problem in the two-component metallization.

In an effort to develop high temperature, corrosion resistant metallizations which are easily etched, the three-component systems were developed using platinum or palladium as a diffusion barrier/electrochemical potential modifier^{107, 108, 113}. In this system the cathodic properties of the platinum or palladium alter the corrosion behavior of the anodic titanium^{114, 115}. Reaction between the titanium and palladium may also form an intermetallic layer (Ti₃Pd) which then limits diffusion⁸⁵. Typical film thicknesses in the Ti/Pd/Au metallization system are 500 Å, 1000 Å and 10 000 Å, respectively.

A three-component system used for solder joining is evaporated NiCr/Cu/Pd⁸³. This system was developed in order to limit the amount of diffusion and scavenging during soldering. Titanium may be used instead of Nichrome^R to alleviate the problem of whisker growth during soldering⁸³.

Multilayer metallization may be fabricated by sequential deposition or by “grading” the components by beginning the second deposition before stopping the first. If sequential deposition is used, care must be taken to ensure that the surface is not contaminated between depositions since small amounts of contaminants may affect interface formation. For instance, oxygen layers of less than a monolayer have been shown to affect nucleation in a metal-to-metal system drastically¹¹⁶ and small amounts of material may act as diffusion barriers. Extensive “grading” or reaction in the interfacial region between metallization layers may present problems in subsequent etching since the etchants for each of the layers may not be suitable for etching the interfacial material.

CONCLUSIONS

These are by no means the only metallization systems possible, but they are the ones most widely used. The generally accepted criterion of "reaction for adhesion" seems to be good, with notable exceptions. Development of a new metallization system or use of a standard metallization with new requirements should be undertaken with great care. Often, new materials or requirements give rise to processing or stability problems, and comprehensive testing should be done to reveal any such weaknesses. The difficulty in chemically etching some systems may be overcome by using sputter etching¹¹⁷, which will probably become more widely used in the years to come.

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