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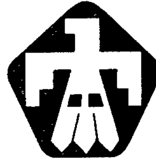

Sandia Corporation

MONOGRAPH

INTERFACE FORMATION AND THE ADHESION OF DEPOSITED THIN FILMS

by

D M Mattox

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INTERFACE FORMATION AND THE ADHESION OF DEPOSITED THIN FILMS

by

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ABSTRACT

A discussion is given of the types of interfacial regions which may be formed between a film and a substrate. Various deposition techniques are compared as to their ability to form the various types of interfacial regions. The mechanism of failure of the bond between film and substrate is discussed in terms of the type and structure of the interfacial region. The reasons for poor adhesion are discussed and approaches for overcoming adhesion problems are presented. The deposition process of "ion plating" is presented as one technique for overcoming many adhesion problems.

SUMMARY

It is shown that by recognizing the causes of poor adhesion between a deposited film and a substrate, it is possible to modify existing deposition techniques or devise new ones which will circumvent the causes of poor adhesion. The ion plating process is used as an example of how a new deposition technique can be developed using the properties of an ideal deposition process as a guide. The ion plating process allows us to deposit many adherent film-substrate samples which were heretofore difficult or impossible to deposit using conventional techniques and to do the depositions using very simple equipment.

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TABLE OF CONTENTS

	Page
SUMMARY	3
Introduction	5
Deposition Techniques	5
Substrate Surface	6
Interface Formation and Nucleation	7
Film Growth	9
Adhesion as a Macroscopic Observable	9
Reasons for Poor Adhesion	10
Techniques for Overcoming Adhesion Problems	11
The Ideal Deposition Technique for Adhesion	12
Ion Plating Technique	13
Representative Deposition Problems	15
LIST OF REFERENCES	18

LIST OF ILLUSTRATIONS

	Page
Figure 1 -- Ion plating apparatus	13
Figure 2 -- Composition across the interface between the aluminum substrate and the ion plated gold film	16

LIST OF TABLES

	Page
TABLE I	17
TABLE II	17

INTERFACE FORMATION AND THE ADHESION OF DEPOSITED THIN FILMS

Introduction

The adhesion of a deposited metal film to a substrate depends on the type and structure of the interfacial region between the film and substrate, and the nature and extent of bonding across this region. Under usual deposition conditions, the atoms of the film material arrive at the substrate surface one at a time, nucleate, and gradually coalesce to form a film. Since the film is created an atom at a time, it is expected that the adhesion between the film and substrate will be, to some degree, a function of film thickness. The first atoms to reach the surface create new surface electronic states which change the surface electronic configuration that determines the bond energy. As the film becomes thicker, the electronic configuration will change until it reaches some equilibrium value. The film thickness at which this equilibrium value is reached may vary from a few angstroms in the case of metals on metals to many angstroms for metals on dielectrics. The nuclei which are formed by the agglomeration of the atoms will have a surface free energy whose value will depend on the nuclei size. These considerations must be kept in mind when discussing adhesion and interface formation in extremely thin films.

An understanding of the relationship between the interface and adhesion allows the specification of the causes of poor adhesion and the general approach to the solution of adhesion problems. To understand the manner in which an interfacial region forms, requires a knowledge of the behavior of the depositing atoms and how a film is formed. This, in turn, requires a knowledge of deposition techniques and the environment and energy of the depositing atoms.

Deposition Techniques

Electrodeposition[1] is accomplished by the mass transfer of ions in solution. The ions of the film material are made to move toward the substrate, which is the cathode of a low voltage dc supply, by a low field of a few volts per centimeter. Because of the low mean free path of the ion in solution and the many collisions which it suffers, it will arrive at the substrate having a kinetic energy on the order of 0.1 ev, i.e., thermal energy.

Vapor plating[2] is the process in which a metal-bearing gas is decomposed at a hot surface by hydrogen reduction or thermal decomposition. In this technique, the depositing atoms have only thermal energies. Since the decomposition normally occurs below 1000°C, the kinetic energy of the depositing atoms will be only a few tenths of an electron volt. The gas pressures used for vapor plating vary from greater than 760 torr to 10^{-4} torr.

Vacuum deposition[3] is the deposition of a material from a vaporizing source in a vacuum where the mean free path of the atoms is greater than distance between the source and the substrate. Here again the energies of the depositing atoms are thermal[4] having mean values of a few tenths of an electron volt with maximum values of about 1 ev.

Most other commonly used deposition techniques give the depositing atoms only thermal energies, i. e., a few tenths of an electron volt. An exception to this is the sputtering process.

Sputtering[3] is the atom ejection from a surface subjected to high energy ion bombardment. The surface atoms acquire enough energy by momentum transfer from the bombarding ions to escape from the surface and deposit on a substrate which is usually placed on the anode. Sputtering is done in a gaseous environment with gas pressures of a few microns. It has been shown that under the typical sputtering conditions of bombardment by 900 ev Hg^+ ions, ejected atoms of such materials as copper have mean energies of about 10 ev with a few percent having energies in excess of 100 ev.[5] This was determined using ions normally incident to the surface. It is to be expected that if ions impinge on the surface at a more oblique angle, the energies of the sputtered atoms would be somewhat higher. The sputtering threshold is defined as the minimum energy which a normally incident ion must have and still cause an atom to be ejected from a surface. The sputtering threshold for clean metal surfaces is about four times the sublimation energy of the metal, i. e., 20-30 ev for common metals.[6] The sputtering yield is defined as the number of ejected atoms per incident ion and varies with the energy of the bombarding ion and the crystallographic plane of the target surface. The close packed planes have higher sputtering yields than more open planes since collisions are more probable. Possibly these planes would also yield higher energy sputtered atoms. This difference in sputtering rate with crystallographic plane allows the cathodic etching of a surface.

Substrate Surface

A substrate surface which has been cleaned of gross contaminations such as grease, dirt, etc., will still not be clean on an atomic scale. The remaining contamination may be in the form of physically adsorbed gases which are bound to the surface with 0.1-0.5 ev,[7] chemisorbed gases which are bound with 1-10 ev[8] or compound layers several lattice parameters in extent having bonding of 1-10 ev.[9] It is apparent that the atoms which are deposited having only thermal energies will be incapable of affecting these layers. Only sputtering where the kinetic energy of the depositing atom is on the same order as the binding energy of the adsorbed gases to the surface may appreciably affect the surface. Therefore, a low energy atom impinging on a contaminated surface finds itself not on the substrate but in contact with a contaminating layer.

A low energy atom which strikes the substrate surface must lose its kinetic energy and come to equilibrium with the surface, i. e., condense. Many theoretical papers have been published on the interaction of the atom with the surface and all begin with Langmuir's hypothesis that an atom which strikes the surface is not immediately absorbed or reflected but stays on the surface for a finite "dwell time" (cf., Wexler[10]). It has been experimentally shown that, in most cases, reflected atoms are diffusely reflected, not specularly reflected.

The atom, during this dwell time, moves over the substrate surface making and breaking bonds and thereby losing energy to the surface. If it does not lose sufficient energy, it will be re-evaporated giving a sticking coefficient (ratio of deposited atoms to incident atoms) of less than one. The activation energy for surface migration is a few tenths of an electron volt,[11] much less than the binding energy in a solid (2-5 ev), and its value depends on the crystallographic plane of the surface. Therefore, even if an atom is trapped on a surface, i. e., doesn't have enough energy to be re-evaporated, it will move over the substrate surface. The presence of a monolayer of contaminating gas may change the sticking coefficient drastically since it may prevent the migrating atom from losing energy, hence allowing it to be re-evaporated.

Interface Formation and Nucleation

The mode of nucleation of a thin film on a surface and the type of interfacial region formed between the film and substrate are determined by the materials involved, the deposition technique and the energy available in the interfacial region. The mode of nucleation and type of interface formed determine the resulting structure of the interfacial region and the adhesion between film and substrate. The types of interfacial regions formed may be classified according to some typical characteristics in the following manner:

A. The mechanical interface or tongue and groove type may be formed if the surface contains large pores. In this case, the film material fills the pore and mechanical interlocking provides the adhesion. No chemical reaction between the materials is necessary and the strength of the joint depends on the physical properties of the materials. If one of the material is soft and easily deformed, the adhesion will be low since, under tension, the material will be pulled from the pore. Since the formation of this type of interface requires a very high surface mobility of the depositing atoms, it is not likely to be of importance except in the deposition of low melting point materials such as cadmium where the surface mobility is exceptionally high.

B. The monolayer-to-monolayer type of interface is characterized by an abrupt change from the film material to the substrate material in a distance on the order of the separation between atoms (2-5 Å). This type of interface will be formed if there is no diffusion of the depositing atom into the substrate surface and little chemical reaction between the atoms of the film material and the substrate. With this type of interface the strains due to lattice mismatch between the film and substrate material and due to structural differences, will be confined to a narrow region between the two materials. Strains due to lattice mismatch are to some degree compensated by defect formation.[12]

C. The compound interface is characterized by a constant composition, many lattice parameters thick. The compound is formed by the chemical interaction of the film and substrate material. The compound formed may be: (1) An intermetallic compound, or (2) Some other chemical compound such as an oxide. The intermetallic compounds formed from two metals are usually brittle and easily fractured. In the compound interface, the strains are principally concentrated in two areas, between the film and compound and between the compound and the substrate material. Because of the stress involved, it is to be expected that unusual compound compositions and structures are formed which would be unstable under different circumstances. This type of interfacial region has been detected in electrodeposits.[13]

D. The diffusion interface is characterized by a gradual change in composition and lattice parameter across the interfacial region between the film and substrate. The formation of this type of interface requires that there be diffusion between the film and substrate material which means that there must be some degree of solubility and that energy must be available to overcome the activation energy for bulk diffusion (1-5 ev). This type of interface has been observed in the deposition of copper on gold at room temperature.[14] Here the energy is provided by the condensation of the copper atoms on the surface. A continuously variable lattice parameter change was observed, using electron microscopy, charging from that of gold to that of copper as the deposition proceeded. In this type of interface, the strains due to lattice mismatch are distributed throughout the interfacial region which may be thousands of angstroms in depth. Essentially, the material is "graded" from the substrate material to the film material much as is done in glass technology to compensate for differences in thermal expansion.

These types of interfacial regions may be formed in a low energy environment. Under more extreme conditions, another type of interfacial region may be formed.

E. The term "pseudo-diffusion" will be used to designate an interfacial region formed under high energy conditions. This type of interface will be formed if two molten materials in contact were mixed and then quenched as in the case of fusion welding. Another example is the interfacial region formed by particles impinging on a surface with sufficient kinetic energy to penetrate into the substrate lattice without the need of a diffusion mechanism. Experiments involving the ionization and acceleration of atoms to a substrate surface give penetrations on the order of 50 Å per kiloelectron volt.[15] The penetration depends on the relative masses of the bombarding ions and the target atoms. Focusing collisions may extend this range appreciably.[16] This type of interfacial region allows the "grading" from one material to another without the need for diffusion between materials.

Obviously, a combination of several types of interfacial regions is possible.

A film atom which arrives at a clean substrate surface may be nucleated on the surface in several ways:

1. As the atom moves over the surface, it may find a preferential nucleation or low energy site where there is a higher coordination number than normal. Such sites may be lattice steps in the surface, emergent dislocations or point defects such as vacancies. These allow the migrating atom to be bound to several surface atoms at the same time. Such a nucleation mode allows deposited atoms to be used for the "decoration" of cleavage steps in such materials as mica.[17] Copper depositions on atomically clean titanium show nucleation on isolated sites when investigated using low energy electron diffraction.[18] The density of such low energy sites on a metal surface is low (10^8 -$10^{10}/cm^2$) compared to the number of surface atoms, ($10^{15}/cm^2$). This mode of nucleation leads to widely separated nuclei.

2. The migrating atoms on the surface may collide with each other on the surface and nucleate by coalescence. A nucleus of two or more atoms is more stable than a single atom and is less likely to be reevaporated. This type of nucleation is largely independent of the interaction between the film atom and the substrate material which only acts as a third body to remove energy released on the condensation of two or more atoms. The probability of collision of atoms on the surface, hence the number of nuclei formed, depends on the density of the migrating atoms. The concept of critical beam density is developed in atomic beam theory to give a minimum beam density below which atoms will not nucleate on the surface by collision. The nuclei thus formed may have appreciable mobility on the substrate surface.[19]

3. If there is a strong interaction between the depositing atom and the surface atoms, each surface atom acts as a nucleation site. The depositing atom finds that it is strongly bonded to each surface atom, hence it will rapidly lose energy and come to equilibrium with the surface. Such nucleation would be expected to occur in the deposition of an oxygen active material such as aluminum on an oxide surface where the surface is an exposed oxygen layer.[20] This mode of nucleation would give a number of nucleation sites comparable to the number of surface atoms, i.e., $10^{15}/cm^2$.

Film Growth

To form a continuous film, the nuclei must increase in size and grow together. The two extremes with which nuclei may grow are, laterally along or perpendicularly to the substrate surface. Lateral growth would be expected if there is strong interaction between the film atoms and substrate material and the lattice misfit is small. With this type of growth, the film will become continuous at very small thicknesses and has been noted in the case of alkali metals on glass, gold on bismuth oxide[21] and for aluminum on SiO_2.[22] If there is appreciable misfit, perpendicular or columnar growth may be expected and the average film thickness may be several hundred angstroms before the film becomes continuous. An example where this may be the case is in the vacuum deposition of silver on SiO_2 where there is little interaction between the silver and the oxygen surface layer and the film must be on the order of a hundred angstroms in thickness before it becomes continuous as indicated by electrical measurements.[23] This type of growth may be responsible for the very high surface area measurements made on some type of films using gas adsorption techniques. The mode of growth of these nuclei determines the effective contact area between the film and substrate and the number and size of voids formed in the interfacial region.

Adhesion as a Macroscopic Observable

The term adhesion, as it is commonly used, refers to the ability of two materials to remain in contact under a tensile force. The difficulty in measuring the adhesion of a thin film to a surface lies primarily in the inability to apply a pure tensile stress normal to the interface without attaching a connection to the thin film thereby stressing the film even before the adhesion is measured. Most adhesion tests applied to a thin film on a substrate involve a very complicated mixture of shear and tensile stresses applied to the interfacial region, hence it is difficult to make a comparison between tests. The measurement of the adhesion of a thin film to a substrate only determines the force necessary to pull the materials apart and usually little attention has been given to how and why the failure occurred.

The interpretation of the measured adhesion involves two main considerations:

1. The bonding across the interfacial region.

2. The fracture mechanism which results in failure. The bonding across the interfacial region is a summation of the individual bond strengths which exist, the number of which depends on the effective contact area. The strength of the individual bonds depends not only on the type of bond and the materials involved but also on the stresses in the bonding region. Tensile stress lowers the bond energy. The

effective contact area will be determined by the structure of the interfacial region; if the film is formed by widely separated nuclei having columnar growth, then the effective surface contact area will be less than if formed by closely spaced nuclei having lateral growth.

The fracture mechanism by which a material fails is determined by the ability of a material to relieve stress concentrations by some mechanism.[24] If the material is very ductile, the local stresses will be relieved by the movement of dislocations, i.e., plastic deformation. Fracture will only occur by increasing the strain rate to a point where the dislocations are unable to move fast enough to relieve local stresses and the stresses may build up above a critical value allowing crack propagation. In a ductile material which has been work hardened by increasing the defect concentration, dislocation movement will be hindered and the stresses will exceed the critical value at lower strain rates. If there is no dislocation movement (no ductility), there will be no movement of material and the critical value of stress will be exceeded at low strain rates giving brittle fracture.

Stress concentrations in a material result from imperfections such as voids, microcracks, etc. The stress concentration factor around these imperfections depends on the geometry of the imperfection. A sharp edge on a dish-shaped void will give a stress concentration of 100 or greater, while around a spherical void, it will be much less.

In the case of the thin film on a substrate, the number and geometry of the imperfections is determined by the type of interfacial region formed. In the monolayer-to-monolayer type of interface, the stress due to lattice mismatch and the imperfections formed by incomplete lateral growth lie in one plane and are confined to a narrow region. This enables the fracture plane to be propagated preferentially down this plane from imperfection to imperfection resulting in poor adhesion. Since deposited thin films having a monolayer-to-monolayer interface are, in general, highly defected, dislocation movement in the film will be minimized.

In the diffusion interface, the interfacial stresses and the imperfections are distributed over a broad region. Failure in this case will not occur in a plane but will follow a circuitous path through the interfacial region.

Reasons for Poor Adhesion

There are two general considerations which must be taken into account for the poor adhesion in a particular film-substrate couple: (1) Factors affecting nucleation and interface formation and (2) Factors affecting the failure mechanism.

Several factors may change the mode or extent of nucleation and interface formation and prevent strong bonding. Barrier layers in the form of gross contamination, physically adsorbed gases, chemisorbed gases and compound layers, prevent intimate contact across the interface. Low substrate temperatures decreases the extent of the chemical reactions and diffusion in the interfacial region. The substrate surface structure also is important in determining the type and extent of nucleation and interface formation.

Other factors influence the failure of the adhesive bond between a film and substrate. Stress in the interfacial region will decrease the bond strength and hence decrease the critical value of applied stress necessary for failure. The amount and distribution of the stress in the interfacial region determines the ease of failure between the film and substrate. The structure of the interfacial region also determines the ease of propagation of a fracture. If the interfacial region is highly defected, brittle fracture is more likely to result. The number, distribution and shape of the voids and microcracks in the interfacial region will also be important in the fracture mechanism. If these imperfections are numerous, dish shaped, and in the same plane, failure will occur most readily.

Techniques for Overcoming Adhesion Problems

Obviously the way to overcome adhesion problems is to change the conditions which cause poor adhesion. The barrier layers which are present on the surface may be removed by cleaning using various techniques. Gross contamination may be removed by solvents applied in a variety of ways such as ultrasonic cleaning and vapor degreasing. The removal of the more tenacious surface barrier layers of chemisorbed gases, physisorbed gases and compound layers and the creation of an atomically clean surface requires more extreme measures. These include chemical cleaning, ion bombardment (sputtering) followed by ultrahigh vacuum (UHV) heating, and cleaving in UHV. All of these techniques may give atomically clean surfaces, but the environment in which the cleaning is done determines the time necessary to recontaminate the surface.

For example, if the sticking coefficient of oxygen on a surface is 1.0, the time necessary to form a monolayer coverage of oxygen on an atomically clean surface at 300°K is 0.3 sec at 10^{-5} torr, 30 sec at 10^{-7} torr, and 3000 sec at 10^{-9} torr. Therefore, to be able to maintain a clean surface long enough to deposit a film using the usual techniques requires that the cleaning be done in UHV. Ultrahigh vacuum cleaning and processing is time consuming and not generally applicable to industrial processing.

The only common deposition process which may result in some cleaning during the deposition process is sputtering where the depositing atoms have energies of 10 - 100 ev. These high energy atoms may result in a limited amount of cleaning giving more adherent films than one achieves using other techniques.[25]

The importance of an atomically clean surface is demonstrated in the deposition of gold on molybdenum. In this case, the adherence is usually very poor because the oxide film on the molybdenum acts as a surface barrier with which the gold does not react. It has been shown by desorption studies that if gold is deposited on an atomically clean molybdenum surface the adhesive bonding strength between the gold and molybdenum is of the same order as the cohesive bonding in the gold, i.e., 4.2 ev; but, if the surface is slightly contaminated, the bonding is less than 1.5 ev.[26] Another technique used to overcome the oxide barrier layer problem is the technique of cleaving silicon in a gold electroplating bath with the potential applied so that the gold deposits on a clean silicon surface rather than on a silicon-oxygen surface. This results in an adherent gold film whereas deposition on a silicon-oxygen surface gives poor adhesion.

Surface modification allows the depositing atom to find a different environment on which to deposit. An intermediate material may be used between the film and substrate which is adherent to both film and substrate. This may be in the form of a "strike" as used in electrodeposition or, in vacuum evaporation, the use of an oxygen-active material such as titanium between an oxide substrate and an oxygen-inactive film material such as gold. The ability of a metal to adhere to oxide substrates is directly related to its free energy of oxide formation in many cases.[27] In some cases, an intermediate material is present to provide nucleation sites as in the case of Bi_2O_3 nuclei deposited on oxide glasses prior to gold deposition.

Another technique of surface modification which is similar to cleaning is that of disrupting the surface barrier layer. This disruption may be accomplished mechanically as in the case of ultrasonic welding and compression bonding or by using high energy particles to create local disruption of the barrier layers. The disruption of the barrier layers permits intimate contact between the materials and allows diffusion to take place.

Surface modification may also be in the form of changing the surface structure in order to change the mode or extent of nucleation. Surface defects may be formed by ion bombardment, cold working, or by exposure to reactor irradiation. Increasing the number of nuclei will increase the effective contact area of the resulting film and thus enhance the adhesion between film and substrate. An increased defect concentration will also enhance the diffusion rate giving a more extensive diffusion bond. Enhanced adhesion may also be obtained by changing the extent and/or type of the interfacial region. For example, a monolayer-to-monolayer type of interface where the stresses and imperfections are confined to a plane may be converted to a diffusion type of interface if the substrate is heated and the materials are mutually soluble. Heating also increases the chemical reaction between the film and substrate material.

The Ideal Deposition Technique for Adhesion

The ideal deposition technique would depend somewhat on the materials involved. If the materials are mutually soluble and/or are chemically reactive, the ideal deposition technique would involve providing an atomically clean surface and a means of keeping the surface clean until the film atoms arrive. In addition, the technique should provide some means of surface heating to allow extensive diffusion and chemical reaction. If there is a barrier layer present, it may be sufficient to disrupt the barrier layer enough to allow diffusion. It might also be desirable to create a highly defected surface to increase the number of nucleation sites and enhance diffusion.

If the materials are nonsoluble, it is impossible to have diffusion. In this case, in addition to having a clean and highly defected surface, it would be advantageous to create a pseudo-diffusion type of interface by some technique. This would allow the formation of an interfacial region of appreciable extent.

Such conditions are more easily stated than achieved using conventional deposition techniques. Almost all of the conventional deposition techniques require a prior cleaning operation since the deposition process itself has little or no cleaning ability. This enables the surface to become recontaminated before deposition unless elaborate precautions are taken. A unique deposition technique which fulfills many of the requirements of the ideal deposition process is that termed "ion plating."

Ion Plating Technique

The ion plating deposition technique[28] involves the deposition of atoms and ions while the substrate is being bombarded with inert gas ions. This is accomplished using the apparatus shown in Figure 1. The substrate is made the cathode of a dc high voltage circuit while the filament for the evaporation of the material to be deposited is made the anode. A dc gas discharge is established between the electrodes by admitting an inert gas into the system and applying a high potential between the electrodes.

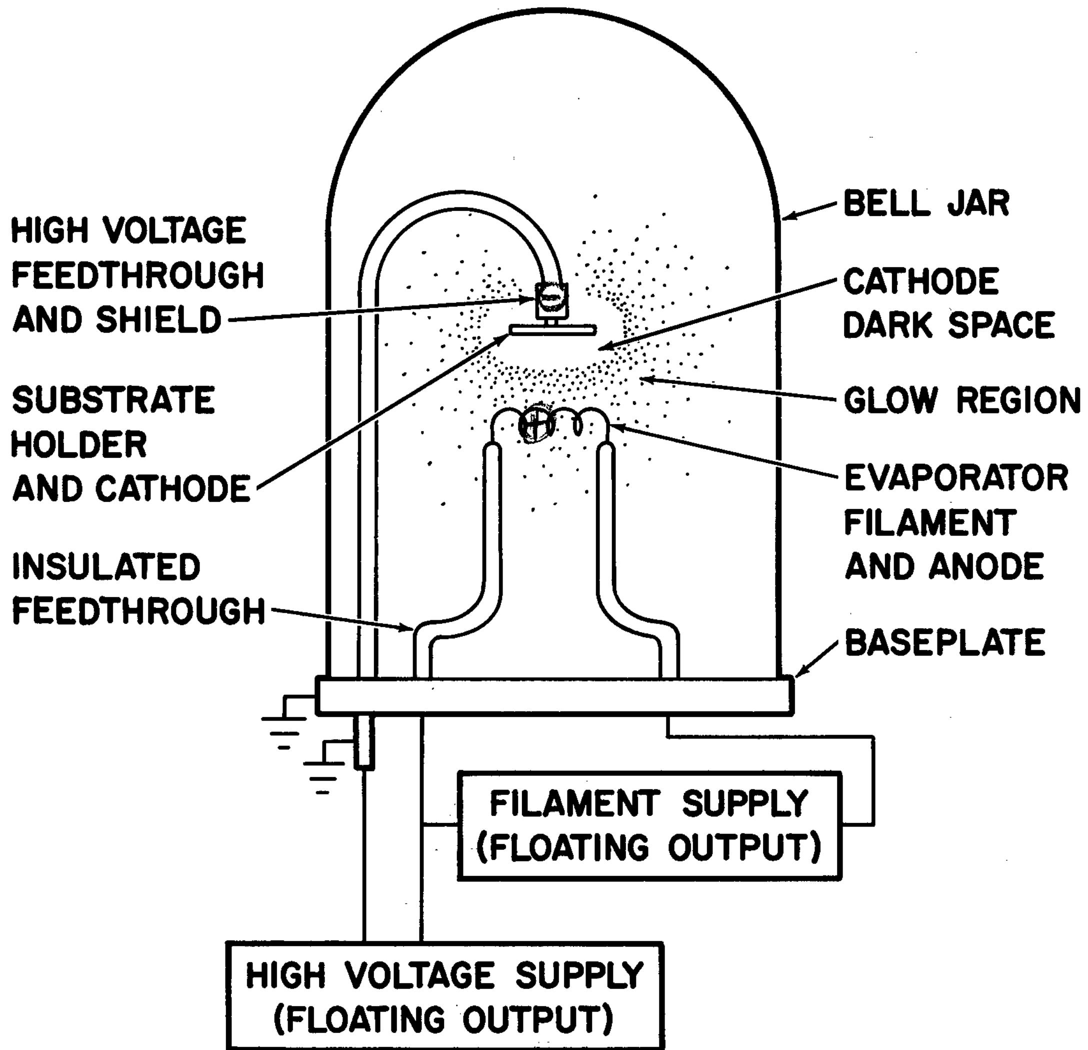

Figure 1. Ion plating apparatus

Cleaning of the substrate is accomplished by inert gas ion bombardment of the substrate surface which sputters contaminating material from the surface. After sufficient ion bombardment to clean the surface, the filament-anode is heated to thermally evaporate the film material into the positive glow region of the gas discharge. A portion of the evaporated atoms is ionized and accelerated to the substrate surface adding to the ion flux to the surface. A resulting film is formed by adjusting the evaporation rate so that the deposition rate of metal atoms and ions is greater than the sputtering rate of material from the surface by the ion bombardment. The particles which are deposited on the surface have an energy distribution ranging from thermal energies (0.2 ev) to energies acquired by acceleration through the maximum of the applied potential[29] (several thousand volts).

This energetic deposition allows the cleaning of the substrate surface by ion bombardment prior to the deposition and the surface is maintained clean up to the formation of the first monolayer of film material. This enables the film to be deposited on essentially an atomically clean surface at rather high working pressures ($>10\ \mu$ argon). The ion bombardment during deposition may be expected to have a cleaning effect similar to that achieved by asymmetric ac sputtering and bias sputtering.[30]

The ion bombardment prior to and during the deposition will create a highly defected surface.[31] It has been shown that bombardment of a surface with argon ions having an energy as low as 100 ev will create detectable surface defects.[32] These defects will increase the number of nucleation sites and aid in the diffusion of soluble materials. In this case, the defects are being produced while the diffusion is taking place and they do not have a chance to anneal out. It should also be pointed out that in a very highly defected material the diffusion mechanism and rate may be quite different than is usually encountered. For example, in the deposition of boron and phosphorous on silicon from a gas discharge it has been found that the diffusion rate of these materials into the silicon during ion bombardment is a factor of 10^4 greater than that achieved by diffusion at the bulk temperature with no gas discharge.[33]

The high energy metal ions impinging on the surface have enough energy to penetrate several lattice parameters into the substrate surface. This will permit the formation of the previously discussed pseudo-diffusion type of interface even if there is no solubility between materials.

Since the energy flux to the substrate is confined to the surface and the energy of the impinging ions is dissipated in the first few thousand angstroms, the effective surface temperature may be many times the bulk temperature. This high surface temperature enhances diffusion and chemical reaction in the surface region. Since a high bulk temperature is unimportant, the substrate may be cooled by being in contact with a heat sink without appreciably affecting the surface temperature.

Typical deposition parameters for the ion plating process are 5000 volts applied potential at 0.5 ma/cm^2 cathode current density using argon gas. Cleaning time is on the order of 30 minutes with evaporation times of several minutes. Evaporation rates vary with different film materials. Gold which sputters readily must be evaporated rapidly. Aluminum which sputters slowly must be evaporated slowly. Deposited film thicknesses are on the order of 10,000 to 250,000 Å. Bulk substrate temperature rise without cooling is 250°C to 350°C with a power input of 2.5 $watts/cm^2$.

Representative Deposition Problems

Several series of test samples were prepared to compare the adhesion of vacuum evaporated films and ion plated films. The test samples were in the form of flat tensile specimens and the adhesion of the film to the substrate was tested by elongating the substrate to detectable coating failure. For poorly adherent films, the film peeled from the substrate after only a few percent elongation. Adherent films cracked during elongation but did not peel from the surface. The results of this type of test depend to some degree on the physical properties of the film but the test gave a good comparison between the adhesion of the different samples.

A film-substrate couple which exhibits complete and continuous solid solubility is that of gold on copper. A series of samples using these materials was prepared by argon ion bombarding the copper substrate for 30 minutes at 5000 volts 0.5 ma/cm^2. At the end of the cleaning period, some samples were ion plated with gold. Other samples had gold vacuum deposited on the copper while still hot from the ion bombardment. A third set was allowed to cool to room temperature under poor vacuum (5×10^{-5} torr) and then gold was vacuum deposited on the cold surface. A fourth set of samples was prepared by heating ion plated samples to 300°C for 20 hours in vacuum to determine if the outgassing of occluded gases was important to the adhesion. On applying the tensile test, the samples prepared by vacuum deposition on a cold surface failed at a few percent elongation. The other films were adherent to the maximum elongation of the copper substrate, 38 percent. It is obvious that a diffusion type of interface was formed when the substrate was heated and there was no apparent advantage of the ion plating process over the best vacuum evaporation technique, i.e., ion bombardment cleaning and a heated substrate. All of the films were approximately 20,000 Å in thickness.

A metal couple which exhibits no solid solubility is that of silver and iron. A series of silver on iron samples were prepared in the same manner as were the gold on copper samples. The tensile test showed the vacuum evaporated film deposited on a cold substrate to fail at less than 2 percent elongation. The vacuum evaporated sample deposited on a hot substrate failed at about 5 percent elongation. None of the ion plated samples showed any failure to rupture of the substrate, 42 percent elongation. All films were approximately 25,000 Å thick. In this case, no diffusion interface would be formed and only the ion plated samples where the surface barrier layer was disrupted and a pseudo-diffusion interface formed showed appreciable adhesion.

Aluminum is a material which forms a very coherent and tenacious barrier layer in the form of an oxide. This oxide layer is difficult to remove using sputtering. Gold which is oxygen inactive was deposited on a series of aluminum tensile specimens in the same manner as in the previous two series. It is doubtful that the aluminum surface was cleaned of oxides by the ion bombardment. Observation of the aluminum surface during the ion plating process showed a very interesting change in surface appearance. A few seconds after the gold evaporation had begun, the surface turned a dark purple which, on continued gold evaporation, gradually turned to a light lavender color before the gold film covered the surface. It was suspected and subsequently shown that this color indicated the formation of a gold-aluminum intermetallic compound. Several ion plated depositions were stopped at various stages in the color transformation of the surface, the substrates allowed to cool to room temperature and gold vacuum

deposited on the cold surface. The tensile test showed that all of the ion plated samples, even those formed by vacuum deposition of gold on the colored surfaces created by limited ion plating of gold, were adherent to failure of the aluminum substrate, 52 percent elongation. The samples formed by vacuum deposition alone peeled at less than 5 percent elongation. Metallographic examination of the interfacial region showed the lavender alloy layer present over about a 15 μ thick region between the film and substrate. Figure 2 shows an electron probe microanalysis across a typical interfacial region showing the distribution of gold and aluminum across the interfacial region. These results show that a rather extensive diffusion type of interface was formed after the disruption of the surface barrier layer as well as a constant composition compound region.

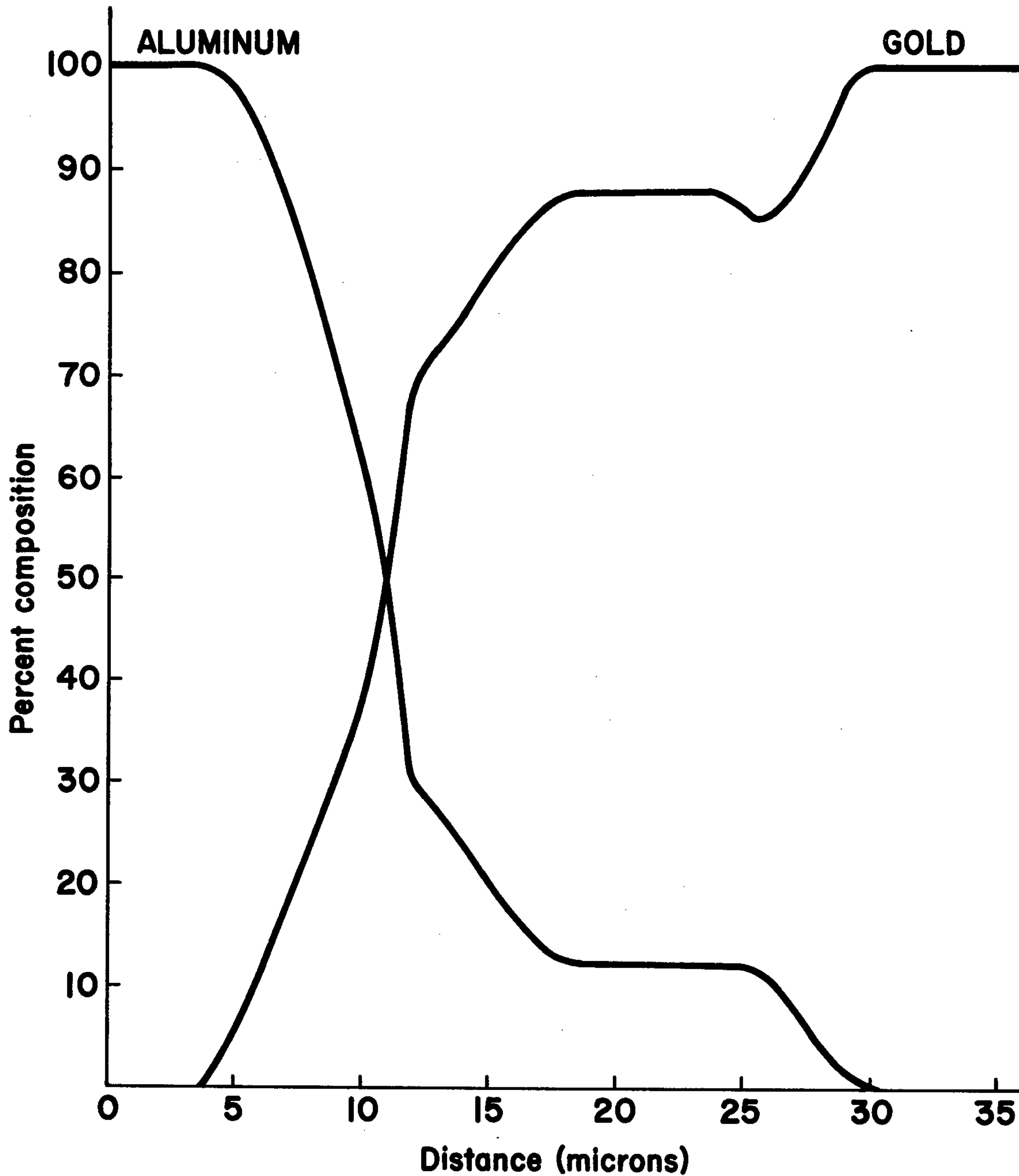

Figure 2. Composition across the interface between the aluminum substrate and the ion plated gold film

Other metal-to-metal depositions of interest are given in Table I. All of these systems exhibited excellent adhesion when deposited using the ion plating process.

TABLE I

Au - Fe^{a}	Cr - Fe^{a}
Au - Al^{abc}	Al - U^{bc}
Au - Cu^{a}	Zn - Nb^{ac}
Cu - Ni^{ac}	Ag - Fe
Al - Fe^{a}	Au - Mo^{c}
Cr - Mo^{ac}	Ag - Ni^{c}
Ni - Pb^{a}	Cu - Mo^{c}
Al - Cu^{a}	Ag - W^{c}
Ag - Ti^{ac}	Al - Mo^{bc}
Au - Ti^{ac}	

[a] Solid solubility[34] (>0.1% below 500°C)

[b] Intermetallic compound

[c] Barrier layer (thin coherent oxides)

Some depositions of metals on semiconductors have been performed for contact purposes. In these cases, the adhesion was tested by soldering a lead to the deposited electrode and pulling the lead to failure. In all cases, failure occurred in the solder or in the semiconductor material. Table II gives the metal-semiconductor couples which have been tested:

TABLE II

Ag - Si	Cu - Ge^{a}
Ag - Ge^{a}	Al - Si^{a}
Cu - Si^{a}	

[a] Solid solubility[34] (>0.1% below 500°C)

The deposition of metal films on insulators can be performed using the ion plating technique with a slight modification in technique.[35] It has been found to be possible to metallize high alumina ceramics using this technique which, after brazing, have joint strengths on the order of the tensile strength of the ceramic. The technique has also been of use in the deposition of electrodes on ferroelectric ceramics. Here joints formed by soldering leads to the deposited electrodes have strengths in excess of the tensile strength of the ceramic.

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