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LOW-ENERGY ACCELERATED
ION DEPOSITION

by

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THE DOW CHEMICAL COMPANY
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U.S. ATOMIC ENERGY COMMISSION
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ABSTRACT

A low energy accelerated ion vapor deposition technique is described which provides superior film adherence when compared to the more common vapor deposition techniques. The significant feature is the ionization of the depositing species by an electron reinforced gas discharge and subsequent acceleration into a substrate held at a low negative potential. In addition to good film adherence, this technique provides a low sputtering rate and only moderate substrate heating.

INTRODUCTION

As Mattox and McDonald⁽¹⁾ have pointed out, film adherence may be increased by increasing the kinetic energy of the impinging vapor atoms. In a later report, Mattox⁽²⁾ showed that excellent film adherence can be achieved by a process called "ion plating." In this technique the depositing species is ionized in a glow discharge set up between the evaporant source and substrate and then accelerated into the highly negative substrate. The impinging particles can attain kinetic energies in the order of kiloelectron volts, as opposed to 1 to 100 electron volts (ev) for sputtering processes and less than one electron volt for thermal deposition techniques. The high energies involved in the ion plating process can result in excessive substrate heating and high sputtering rates from the substrate. The purpose of this report is to describe a method of ion plating which employs a gas discharge independent of the evaporation source and substrate and hence allows lower substrate potentials. The kinetic energy of ionized particles incident upon the substrate, can then be adjusted from thermal energies up to 400 ev or better. Since lower incident particle energies are now involved, the substrate heating and sputtering rates are lessened while still retaining the good adherence properties.

SUMMARY AND CONCLUSIONS

The use of a gas discharge set up perpendicular to the path of the depositing vapor offers several desirable features: (1) greater control over the gas discharge is obtainable, (2) low voltages are employed which lessens the problem of high voltage discharges at undesirable locations, (3) the entire process can be carried out at low pressures thus providing relatively long mean free paths for the evaporant material while still retaining a high ionization efficiency of the material, and (4) substrate heating can be reduced by a factor of two to four over conventional accelerated ion techniques.

The adherence of films prepared by this technique is in most instances comparable to films produced with much higher incident particle kinetic energies. Film adherence is far superior to films prepared by thermal deposition techniques. The abrasion resistance of the resultant films is generally good and again superior to thermally prepared films.

When substrate heating and sputtering cannot be tolerated, the method described is generally superior to the high-energy accelerated ion deposition techniques.

(1) Mattox, D. M., and McDonald, J. E., *J. Appl. Phys.* 34, 2493 (1963).

(2) Mattox, D. M., *Film Deposition Using Accelerated Ions*, Sandia Development Report, November 1963, SC-DR 281-63.

TECHNIQUE AND DISCUSSION

A liquid nitrogen baffled, 6-inch diffusion-pumped vacuum system was employed in this study. The vacuum system, capable of achieving the 10^{-6} torr range within one hour, had a 14-inch collar located on the baseplate in which the vacuum feedthroughs were located. The low-energy accelerated ion apparatus is depicted in Figure 1. In a typical deposition the chamber is first evacuated to a high vacuum, i.e., 10^{-5} to 10^{-6} torr. The tungsten filament, F, is then heated resistively until outgassing from it occurs. In a similar manner the evaporant source, E, is resistively heated to allow outgassing. Caution must be exercised in heating the evaporant source to prevent vaporizing any of the evaporant material in it. When outgassing has ceased, the headgate valve, V, is partially closed and argon is admitted into the chamber through the gas bleed inlet, G. The headgate and bleed valves are adjusted until the chamber pressure stabilizes between 1 to 5 microns. This pressure is read on the thermocouple gauge, TC. The forepressure of the vacuum system generally reads about 30 to 60 microns.

A - ANODE (Ta)
B - FILAMENT SHIELD
S - SUBSTRATE
E - EVAPORANT SOURCE
F - FILAMENT (W)
G - GAS BLEED INLET
TC - THERMOCOUPLE GAUGE
V - HEADGATE VALVE

Figure 1. BLOCK DIAGRAM OF LOW-ENERGY ACCELERATED ION APPARATUS

A positive potential of 40-100 volts is then placed on the tantalum anode, A. The filament, F, is adjusted to its operating range, normally 25 amps at 10 volts depending on the filament dimensions. At this point the apparatus can sustain a discharge if one can be initiated. Discharge initiation can be carried out in several manners. One technique might be to introduce a high potential probe into the chamber, e.g., a Tesla coil. Another method would be to increase the argon gas pressure until breakdown of the gas occurred. The simplest technique is to momentarily create a glow discharge between the evaporation source, E, and the substrate, S. This glow discharge breaks down the gas and once this has occurred, the filament and anode can maintain the discharge. In essence, electrons emitted from the filament, in being accelerated to the anode, ionize some of the argon and thus produce a greater number of free electrons in the chamber. The positive ions tend to bombard the surfaces within the chamber thus cleaning them. This cleaning action (sputtering) can be enhanced on the substrate by placing a negative bias on it, thereby accelerating the ions into it. Increasing the kinetic energy of the ions results in a faster sputtering rate. This cleaning action can be carried out for any desired length of time.

The actual accelerated ion film deposition is begun by placing a negative potential on the substrate, S. This potential can vary from 0 to 400 volts, resulting in bombarding ion energies from thermal (3/2 kt) to nearly 400 ev for the deposition species. The evaporant source is then heated resistively and the material in it allowed to evaporate. Some of the vapor passing through the discharge region is ionized by electron collisions. These ions are then accelerated into the negatively biased substrate, forming the film.

Several things should be kept in mind regarding this process. Because the substrate is placed in a gas discharge and given a negative bias, a positive ion sheath (dipole layer) forms around it. The entire bias voltage is then dropped between the substrate and the edge of this sheath. This region is referred to as the Langmuir dark space.⁽³⁾ An ion diffusing through the gas discharge (whether gas or deposition species) cannot "feel" the effect of the bias unless it happens to arrive at the edge of the sheath. It will then be accelerated across the dark space, and will arrive at the substrate with an energy equal to or less than the bias potential, depending on whether or not it underwent a collision in the dark space.

Another important consideration is that not all of the film material is ionized and accelerated into the

substrate. The majority of the material never becomes ionized and some which is ionized recombines with an electron before reaching the ion sheath. Thus, the resulting film is formed by both accelerated ions and thermal atoms. The thermal atoms may have different energies compared to the energies they had when they left the evaporation source (3/2 kt) because they undergo collisions with gas atoms.

When the bias is impressed upon the substrate, a current appears in the substrate circuit. This current is the consequence of both argon and impurity ions colliding with the substrate surface. The effect of impurity ions is discussed in the Appendix. During the film deposition process, the substrate current increases due to the additional deposition of specie ions colliding and sticking to the surface. This current increase becomes a relative measure of the amount of evaporant material that is ionized and reaches the substrate. As the evaporation rate is increased the current increases proportionately. This current is normally expressed as a current density having the units ma/cm². Values of current density range between 0.1 ma/cm² to 10 ma/cm², with typical values of 0.3 ma/cm² to 1.0 ma/cm². The effect of increasing current from increasing evaporation rate apparently results from the greater density of evaporant vapor in the discharge allowing a greater probability of ionization. In addition to evaporation rate, the current density also depends upon the chamber pressure, substrate potential, filament and anode parameters, and the system geometry. In the majority of this work the source-substrate distance was 15 cm.

A portion of the bombarding particle energy is dissipated in the form of heat, thus resulting in a temperature rise of the substrate. Temperature measurements of the substrate were made with an iron-constantan thermocouple in contact with it. Readings were taken at 5-minute intervals and recorded on a Varian G-11 recorder. Because the negative bias on the substrate caused extraneous readings, each data point was taken with the bias off and the discharge parameters adjusted to just sustain the discharge. In all temperature measurements the substrate was a 1/2-inch diameter copper rod, 1/2 inch long, imbedded in Bakelite plastic. In a typical situation with 300 volts impressed upon the substrate at a current density of approximately 1 ma/cm² the temperature increased from 38°C to 98°C in 35 minutes. No data were taken with the evaporation source on and this could increase the substrate temperature still further. Much of the radiant energy from the evaporation source, however, could be baffled out to prevent the substrate from "seeing" it. Since deposition times are normally short (<10 minutes), little substrate heating by ion bombardment results in this period. Most substrate heating occurs during the lengthy cleaning process.

(3) Cobine, J. D., *Gaseous Conductors*, New York, Dover Publications, Inc., 1958, pp 134-42.

In an attempt to determine the extent of ionization of the depositing species a simple technique was used. Two 1-1/2 inch diameter stainless steel substrates were placed equidistance from, and normal to, a dimpled pan evaporation source. The substrate-substrate-evaporation source plane was perpendicular to the electron flow sustaining the discharge. The substrates were mounted in an insulating material so that only the front surface was exposed.

By placing a bias on one of the substrates it was possible to deposit an accelerated ion film simultaneously with a thermal film. It was assumed that both substrates should receive the same amount of neutral vapor. Thus the biased substrate should receive the neutral vapor plus the accelerated ions, resulting in a greater film thickness. The mass of material deposited was determined by weighing the substrates before and after deposition. An apparent ionization efficiency was then defined as

$$\frac{M_A}{M_A + M_T} \times 100\%$$

where M_A is the mass of material deposited by accelerated ions and M_T is the mass deposited by neutral vapor. It should be pointed out that this efficiency is not defined as the portion ionized out of the total mass of the deposition species. Rather it defines the portion of the total that reaches the substrate in an ionized state. The number of ions reaching the substrate is influenced by the substrate bias, pressure, etc. Material that is ionized and recombines with an electron before reaching the substrate is not included in the efficiency expression. Some data representative of the

efficiency measurements are given in Table I. In the table, the deposition species is given in brackets in the first column; the substrate with the bias impressed on it is followed by accelerated ion (AI). All data were obtained at a chamber pressure of 3-4 microns. The anode and filament were adjusted so that the anode parameters were 4 amps at 60 volts.

Substrates were prepared by polishing with 360-grit paper followed by a 600-grit paper. They were then ultrasonically cleaned in trichloroethylene for 10-15 minutes followed by an acetone rinse. After the pre-deposition weighing, they were again rinsed in acetone and mounted in the vacuum chamber. Ion bombardment cleaning was not performed before deposition because of the weight change that might occur during this process. The current density listed in Table I is an average of the starting and maximum current density values because the current increases when the deposition process starts. The film thicknesses listed in column seven are calculated from the weight change data by the expression

$$t = m/A\rho$$

where m is the mass in grams of the film material, and A and ρ are film area (cm^2) and density of film material (g/cm^3) respectively. This expression is valid if the film thickness is uniform and film density is that of the bulk material.

Column eight (Table I) lists the theoretical film thickness for a vacuum evaporation process. This value is included for the purpose of comparison only. The deposition process described violates the assumptions

TABLE I

APPARENT IONIZATION EFFICIENCY DATA

Trial No.	Stainless Steel Subst. No.	Avg. Weight Before Dep. (grams)	Avg. Weight After Dep. (grams)	Weight Change (gram)	Current Density (ma/cm^2)	Film Thickness ($\text{\AA}$)	Theo. Film Thickness ^c ($\text{\AA}$)	AI Efficiency (%)
4/6(Au) ^a	34(AI) ^b	13.1832	13.2041	0.0209	0.28	9,800	2400	29
	41	13.5798	13.5954	0.0149	—	7,000	2400	
4/7(Cu)	34(AI)	13.1538	13.1644	0.0061	0.35	6,200	2600	5
	41	13.5676	13.5734	0.0058	—	5,800	2600	
4/8(Cu)	28(AI)	12.7745	12.7855	0.0110	0.49	11,000	3000	41
	20	12.5495	12.5560	0.0065	—	6,600	3000	
4/8A(Cu)	16(AI)	13.6206	13.6327	0.0121	0.55	12,000	2600	50
	9	13.7590	13.7651	0.0061	—	6,000	2600	

^a The terms in brackets following the trial number represent the deposition species.

^b The bracketed term following substrate number stands for accelerated ion. This is the substrate with the bias impressed on it.

^c See the text above, column two, last paragraph, regarding this column.

upon which the theoretical film-thickness expression has been derived by Holland.⁽⁴⁾ The reader is referred to Holland for these assumptions and the derivation of the film-thickness equation. The equation, derived for a point on the substrate perpendicular to a point evaporation source, is

$$t = \frac{m}{4\pi\rho h^2}$$

In this expression m is the mass of the material evaporated, ρ the density, and h is the source to substrate distance.

The last column of Table I gives the apparent ionization efficiency as determined by the expression given previously. Unfortunately, individual evaporation rates were not obtained but in general ranged from 2 mg/sec to 15 mg/sec. The reason for the low ionization efficiency in trial 4/7(Cu) was because the evaporation rate was less than in trials 4/8(Cu) and 4/8A(Cu), i.e., roughly 2 mg/sec as opposed to 3-4 mg/sec.

FILM QUALITIES

Basically the qualities of the film prepared by the low energy accelerated ion technique that have been examined are adherence, abrasion resistance, and film surface appearance. In most cases the degree of film adherence is dependent on the abrasion resistance.

The adherence of the film is tested by three means. The first of these is the standard cellophane tape test. The second involves an acetone rinse during which the

film is briskly rubbed with a paper towel. Normally most films easily passed these two qualitative tests. The third technique employs a stainless steel or aluminum block fastened to the film surface with epoxy. The substrate and block combination are then placed in a tensile tester and pulled apart. The force required to separate the film from the substrate is thus obtained. There are several apparent flaws in this approach and therefore the results are semi-quantitative.

The epoxy used was two parts D.E.R.®* resin 334 to one part D.E.H.®* resin 12. The epoxy was cured for one hour at 100°C to 125°C. The epoxy joint between film and block failed frequently when the film material was gold (no explanation for this failure has been found). Because of this the values obtained for the gold films are merely lower limits. Table II gives some tensile data for copper and gold films on stainless steel. The force per unit area required to separate the film from the substrate, listed in column five, is an average value because two blocks were fastened to each film and pulled individually. The value given is the average of these two values. The copper films listed are the same as those given in Table I. The trend seems to be a greater adherence with increasing current density.

The adherence of some couples was rather poor, e.g., silver on stainless steel. For this reason, together with the fact that ionization efficiency measurements of silver on stainless steel yielded erratic and low values, it was felt that very few silver ions were reaching the substrate. Since a green glow was observed with silver, indicating that excitation or ionization had occurred, the silver ions must have been recombining with electrons before arriving at the ion sheath surrounding the substrate.

(4) Holland, L., *Vacuum Deposition of Thin Films*, New York, John Wiley & Sons, Inc., 1961, pp 141-6.

* Trademark of The Dow Chemical Company.

TABLE II

FILM ADHERENCE ON STAINLESS STEEL

Trial No.	Substrate No.	Film Material	Type of Film Preparation	Average Adherence (psi)	Comments
3/8	1	Au	Accelerated	925	Epoxy Failed
3/9	7	Au	Accelerated	990	Epoxy Failed
4/7	34	Cu	Accelerated	2020	Small Spot Cu Off
4/8	28	Cu	Accelerated	2270	Small Spot Cu Off
4/8A	16	Cu	Accelerated	3150	Removed Cu
4/7	41	Cu	Thermal*	830	Removed Cu
4/8	20	Cu	Thermal*	1225	Removed Cu
4/8A	9	Cu	Thermal*	960	Removed Cu

* These thermal films were prepared simultaneously with the Cu accelerated films, i.e., with an argon pressure of 3-4 microns and a discharge present in the chamber.

The abrasion test was crude so yielded only qualitative information. This test involved scratching the surface with a sharp point (an X-acto knife blade). On most films prepared thermally, a single stroke will scratch through the film to the substrate. On the accelerated films, however, it was more difficult to scratch through the film.

Surfaces of films prepared by thermal and accelerated ion techniques have been examined by electron microscopy methods. Since the films were generally too thick to use transmission techniques, the films were replicated. Examination of the accelerated gold film replicas reveals a surface with random pits and what appears to be ion etching along grain boundaries. The surface of a gold

film prepared simultaneously with the accelerated ion film but with no substrate bias displays a columnar type structure. It is assumed that this structure is a result of the partial pressure of argon in the chamber. As deposition species vapor undergoes collisions with argon atoms the angles of incidence for neutral atoms onto the substrate vary considerably. The columnar type structure is associated with this scattering of incident vapor. Since the majority of vapor reaching the substrate is neutral, the accelerated films should also display this columnar type structure although perhaps masked because of the simultaneous deposition of ions. The results do indicate that this is the case, except as previously mentioned there is etching occurring due to the ion bombardment.

APPENDIX

A film being deposited in vacuum by any process (thermal, sputtering, or accelerated ion techniques) in the presence of a partial pressure of some impurity will trap some of the impurity. According to Maissel and Schaible⁽⁵⁾ the concentration of impurities in the film, g , can be written as

$$g = \frac{aN}{aN + R}$$

where a is the sticking coefficient for impurities on the film, N is the number of neutral impurities striking the film per unit area per second, and R is the deposition rate in atoms per unit area per second.

In the situation where a bias is applied to the substrate, the impurity concentration expression is drastically changed. Now besides neutral impurity atoms impinging on the substrate there are accelerated impurity ions colliding with it, as well as argon ions (and deposition specie ions) sputtering impurities and film material from the surface.

Maissel and Schaible⁽⁵⁾ point out that the impurity atoms are more easily removed than the atoms of the film material, so that bombardment results primarily in removing impurity atoms from the film.

Consider first the case where a bias is placed on a substrate with a gas discharge in the chamber, but where the deposition specie is not ionized, i.e., a sputtering process. The substrate surface is now bombarded with argon and impurity ions that are accelerated across the Langmuir dark space. Neglecting the sputtering yield (atoms sputtered per incident ion) of impurity atoms knocked from the surface by impurity ions, a value S can be defined as the absorbed gas atoms sputtered off the film per incident argon ion. Impurity ions accelerated across the dark space can still contribute to the impurities trapped in the film, and with this as a basis the concentrations of impurities can be written as

$$g = \frac{aN - j/q (S - \beta)}{aN - j/q (S - \beta) + R}$$

In this expression j is the bias current density, q the electronic charge, and β the fraction of the bias current due to impurity ions. Actually j should be $j/(1 + \gamma)$, where γ is the secondary electron emission coefficient by the ions. In many cases this term may be considered

negligible at the low energies involved.⁽⁶⁾ It is pointed out⁽⁵⁾ that S is essentially an "effective" sputtering yield rather than a "true" sputtering yield. One reason for this is that as impurity atoms are cleaned off the surface, the chance that an argon ion will strike an impurity becomes progressively less. Thus the true sputtering yield, S_t , would be related to the effective yield by

$$S = fS_t$$

where f would be the ratio of surface impurities to the total flux of bombarding particles. The second aspect which makes S an effective yield is that an ion may experience a collision while traveling the dark space. A collision results in deflection of particles from a normal angle of incidence and also reduced energies.

The situation where a portion of the film material is also accelerated is slightly more involved. Now impurities can be sputtered by both argon and deposition specie ions, and hence two sputtering yields must be considered. Let S' be the effective sputtering yield for impurities sputtered off the film by deposition specie ions and let S'' be the effective sputtering yield of film material by deposition specie ions.

An expression for impurity concentration can then be written as

$$g_z = \frac{aN + (j^1/q)(\beta - \delta S - \eta S')}{aN + (j^1/q)(\beta - \delta S - \eta S') + j^1/q (\eta - \eta S'') + R}$$

The symbol j^1 is now used to represent the total bias current resulting from argon, impurity and deposition specie ions. The fractions of the bias current caused by argon, impurity and deposition specie ions are labeled δ , β , and η respectively. It should be kept in mind that in the bias expression term no correction for secondary electron emission is made. Actually the ion current would be expressed correctly as

$$\left(\frac{\delta}{1 + \gamma_a} + \frac{\beta}{1 + \gamma_i} + \frac{\eta}{1 + \gamma_d} \right) j^1$$

where γ_a , γ_i , γ_d are coefficients of secondary electron emission by argon, impurities and deposition ions respectively (see Reference 7 for a discussion of the electron emission coefficients).

(6) Loeb, L. B., *Basic Processes of Gaseous Electronics*, Berkeley, University of California Press, 1960, Chapter 9.

(5) Maissel, I. I., *loc. cit.*, p 7.

(7) McDaniel, E. W., *Collision Phenomena in Ionized Gases*, New York, John Wiley & Sons, Inc., 1964, pp 629-49.

(5) Maissel, I. I., and Schaible, P. M., *J. Appl. Phys.* 36, 237 (1965).

In the expression for g_2 , three terms have been omitted. These are: impurities sputtered by impurities, film material sputtered by impurities, and film material sputtered by argon. It is assumed at the low incident particle energies involved that these terms can be considered negligible. The resultant equation for g_2 is thus considered to be applicable to the low energy accel-

erated ion technique. It is, however, not very workable for several reasons. First, it is not easy to obtain effective sputtering yields, and secondly the portions of the bias currents ascribed to various ions are not easily ascertained. As such the expression has been included only to illustrate the nature of impurities which might occur in a film prepared by this technique.