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VACUUM ACCELERATED-ION DEPOSITION

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VACUUM ACCELERATED-ION DEPOSITION

Robert G. Kurtz and T. Van Vorous

Abstract. A new evaporation technique has been investigated which utilizes the thermal energy of a resistance source to ionize, either directly or indirectly, an evaporant metal placed in the source. The ionized evaporant is accelerated towards a substrate by placing a high negative potential on the substrate. Not all metals exhibit this ability to be ionized. Of twenty-two metals investigated, only nine showed measurable current during evaporation.

INTRODUCTION

A film deposition technique utilizing the thermal energy of a resistance source to vaporize the evaporant metal, as well as to ionize a fraction of the metal vapor, has been partially evaluated. Twenty-two metals have been investigated and only nine of these exhibited an apparent ability to be ionized. These ionized vapors are accelerated towards the substrate by making the substrate the negative electrode of a high voltage system. The evaporation source serves as the positive electrode. The extent of the ionization appears to be influenced by the substrate material. Uranium and copper have been utilized as substrate materials.

Equipment:

The vacuum system used was a 4-inch oil diffusion pump backed by a 15-cubic feet per minute mechanical pump. The fore valve and roughing valve were pneumatically operated while the high vacuum valve and leak valve were manually operated. This latter feature permitted flexible and fast control of the inert-gas pressure during ion-bombardment cleaning and accelerated-ion plating,¹ with argon. An 18-inch feedthrough collar and an 18-inch diameter glass bell jar were mounted on the base plate of the vacuum system and contained the fixturing shown in Figure 1.

Experimental Procedure:

The experimental procedure included the following steps.

1. Electropolish the substrate. This was accomplished by taking the substrate (a 1/2-inch diameter by 1 3/8-inch long rod of depleted uranium or copper), mounting it on the end of a stainless steel wire, and then hanging it in a plastic beaker containing *Power Clean*.² The electrical connections were made to a 300 volt, 10-amperes DC power supply. The cathode lead was connected to a metal plate in the bottom of a beaker and the anode lead was connected to the substrate. The power supply was turned on and adjusted to give approximately 2 amperes and 10 volts. The cleaning continued for two to three minutes after which time, the substrate was removed from the *Power Clean*, rinsed in water, and then in alcohol.
2. Mount the substrate on the high voltage lead inside the vacuum chamber and position the ground shield around the ceramic portion of the high voltage lead.
3. Place a 0.25 gram of evaporant metal in a boat-type evaporation source of appropriate material.
4. Evacuate the chamber to at least 1×10^{-6} torr.
5. Back-fill the chamber with pure argon to a pressure of 20 microns. The system must be in a dynamic state; i.e., the high vacuum valve must be partially closed and the argon leak valve partially opened to maintain a vacuum chamber pressure of 20 microns and a diffusion pump fore-pressure of 50 to 70 microns.
6. Turn on the high voltage power supply and the recorder, and then adjust the voltage to 2000 volts.

¹D. M. Mattox. *Film Deposition Using Accelerated Ions*. Sandia Laboratory Report SC-DR 281-63. Sandia Corporation, Albuquerque, New Mexico. November 1963.

²Trade name of Moleetrics Inc., 459 N. Eucalyptus Ave., Inglewood, California.

FIGURE 1. Fixturing for Vacuum System.

7. Keeping the voltage and gas pressure constant, continue ion-bombardment cleaning until the current (read out on the recorder) stabilizes at some minimum value. This usually requires 20 to 30 minutes.
8. Turn off the high voltage power supply, close the argon leak valve, and open the high vacuum valve. Continue pumping until a pressure of at least 1×10^{-6} torr is attained.
9. Turn on the high voltage power supply and adjust the voltage to 2000 volts. (Recorder should read zero milliamperes.)
10. Turn on the filament power supply and resistively heat the evaporation boat to evaporate the metal in the boat.

This same basic procedure was used for the argon accelerated-ion work except that after Step 7, the current was noted and the evaporation proceeded at the same argon pressure. The evaporation boat was heated up to just below the melting point of the evaporant metal and held there until the argon pressure was again stable. This step permitted outgassing of the source and the evaporant metal so that these gases would have no effect on the current measured during the actual evaporation.

After completion of the evaporation and while the evaporation source remained at temperature, the current was noted. This current represents the amount of ionization of gases or other impurities resulting from thermionic emission of the hot evaporation source, and does not result from ionized evaporant metal.

DISCUSSION

The results obtained using the above procedure on twenty-two different metals are given in Table I. The values given for evaporation current is that which was measured by heating up the evaporation source and evaporating the metal onto the substrate. Compensation has been made of base current values taken before and after the evaporation, while the source was hot. That is, any current obtained from outgassing the source and evaporant or resulting from a hot source (which is the residual current after evaporation was completed) is not included

TABLE I. Ion Current during Evaporation for Several Metal-Substrate Combinations.

Evaporant Metal	Substrate	Argon Accelerated-Ion Current (milliamperes)		Vacuum Accelerated-Ion Current (milliamperes)	
		Start	Peak	Start	Peak
Beryllium	Copper	9.0	15.0	0	0
Beryllium	Uranium	-	-	0	0
Aluminum	Uranium	16.0	16.0	0	35.0
Aluminum	Copper	-	-	0	0
Magnesium	Uranium	19.0	36.0	0	0
Titanium	Uranium	15.8	18.5	0	13.0
Titanium	Copper	-	-	0	0
Chromium	Uranium	15.6	50.5	0	13.0
Chromium	Copper	-	-	0	0
Manganese	Uranium	20.0	50.5	0	0
Iron	Copper	10.0	7.0	0	0
Iron	Uranium	-	-	0	0
Nickel	Copper	10.5	5.0	0	0
Nickel	Uranium	-	-	0	0
Copper	Uranium	8.0	7.5	0	6.5
Gallium	Copper	8.5	7.0	0	0
Silver	Uranium	7.5	4.0	0	0
Cadmium	Uranium	16.0	0	0	1.5
Cadmium	Copper	-	-	0	0
Indium	Copper	9.0	3.0	0	0
Indium	Uranium	-	-	0	32.5
Tin	Uranium	16.0	1.0	0	0
Antimony	Copper	13.0	2.5	0	0
Antimony	Uranium	-	-	0	0
Barium	Copper	9.0	50.0	0	0
Lanthanum	Copper	9.0	19.5	0	13.0
Lanthanum	Uranium	-	-	0	50.0
Cerium	Uranium	15.7	45.6	0	5.5
Cerium	Copper	-	-	0	0
Palladium	Uranium	18.5	5.0	0	0
Neodymium	Copper	-	-	0	0

in the values shown in Table I. Thus evaporation current for vacuum accelerated-ion deposition is that resulting from ions of *apparent* thermally ionized evaporant material being collected or deposited on the substrate.

There also appears to be a relationship between the evaporant material and the substrate that is influencing either the existence of or the extent of ionization. Lanthanum is the only evaporant that showed measurable current during vacuum acceleration onto both copper and uranium. Eight other metals showed measurable current when deposited onto uranium and not on the copper substrate.

The *apparent thermal ionization* of the evaporant metals could be caused by one of the following:

1. Thermal ionization resulting from the metal vapor being heated by the resistance source. This is a distinct possibility as noted from the following equation,³ a form of the law of mass action.

$$\left(\frac{P}{1+x} \right) \left(\frac{x^2}{1-x} \right) = \frac{2W_i}{W_a} \left(\frac{2\pi mk}{h^2} \right)^{3/2} (kT)^{5/2} \left(\frac{e^{-u}}{kT} \right)$$

x — fraction of all atoms that are ionized

W_i — multiplicity of normal state of the ion

W_a — multiplicity of normal state of the atom

m — electronic mass

u — energy of ionization in electron volts

P — pressure in atmospheres

h — length

k, e — constants

Solving the equation for various temperatures and at various energy levels, the values of x are given in Column 3 of Table II. Inspection of the table

TABLE II. Fraction of Atoms Ionized at Various Temperature and Energy Levels.

Temperature (°K)	Energy of Ionization (u) (electron volts)	Fraction Ionized (x)
1000	1	0.999647
1000	3	6.70711×10^{-4}
1000	5	1.19637×10^{-8}
1000	7	2.13397×10^{-13}
1000	9	3.80647×10^{-18}
1000	11	6.78970×10^{-23}
1000	13	1.21110×10^{-27}
1000	15	2.16027×10^{-32}
1000	17	0
1000	19	0
2000	1	1.0
2000	3	0.985519
2000	5	2.45392×10^{-2}
2000	7	1.03671×10^{-4}
2000	9	4.37844×10^{-7}
2000	11	1.84920×10^{-9}
2000	13	7.80995×10^{-12}
2000	15	3.29847×10^{-14}
2000	17	1.39308×10^{-16}
2000	19	5.88358×10^{-19}
3000	1	1.0
3000	3	0.999977
3000	5	0.968339
3000	7	0.100834
3000	9	2.64811×10^{-3}
3000	11	6.91906×10^{-5}
3000	13	1.80783×10^{-6}
3000	15	4.72352×10^{-8}
3000	17	1.23417×10^{-9}
3000	19	3.22467×10^{-11}

³Earle H. Kennard. *Kinetic Theory of Gases*. McGraw-Hill Book Company, Inc. New York. 1938. Page 426.

reveals only what one might expect; i.e., the higher the temperature and the lower the energy of ionization, the larger the fraction of atoms being ionized becomes. Since most atoms have a first ionization potential in the range of 5 to 8 electron volts, it can be seen that if other conditions are favorable, a good possibility exists of having ionization occur.

Such other conditions would involve electron density, the density of vaporized metal atoms, the condition of the walls of the chamber, etc. Since these later items were not evaluated or controlled in these experiments, it must be mentioned that they could have an influence on the measured values of *apparent thermal ionization*.

2. Ionization brought about by gases present or absorbed in the evaporant metal or absorbed onto the source itself. These gases could be ionized when evolved and could be enhancing or causing some ionization of the evaporant metal. This is a definite possible cause because all of the metals indicating a measurable current during vacuum acceleration also showed measurable current during argon acceleration. (Indium and lanthanum were not evaluated using uranium substrates under argon acceleration conditions.)

The extent of the ionization could be a function of the amount of gases included in the metal. All of these metals are reactive in air to form oxides. These metals also have high potential for argon absorption during the initial sputter-cleaning step.

3. A third possible cause is Auger emission.⁴ This process involves the electronic interaction between ions and conduction electrons of a metal. Interaction occurs when the potential energy recovered from neutralization of the incoming ion is sufficient to extract a neutralizing electron and to excite a second electron above the potential energy barrier at the surface of the metal.

SUMMARY

The current discussion describes what was done, what results were obtained, and presents possible reasons for the resultant data. The report is not intended to define the mechanism that produced these results, but rather present initial speculation. A further program has been established to complete this project and define the mechanism of *apparent thermal ionization*. A more sophisticated setup will be used which will provide for a lower level and a more accurate current measurement. External conditions which may influence the data will also be more closely controlled.

In addition, it must be apparent that a different type of film structure is obtained during vacuum acceleration than that obtained during thermal evaporation or argon accelerated-ion evaporation. These films will be characterized and the interface areas examined.

⁴R. W. Roberts and T. A. Vanderslice. *Ultrahigh Vacuum and Its Applications*. Prentice-Hall Inc., Englewood Cliffs, New Jersey. 1963. Pages 161-164.