DEPOSITION OF ALUMINUM-COPPER ALLOY ON LAMINATED POLYIMIDE SUBSTRATES FROM AN RF INDUCTION SOURCE

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ABSTRACT

A physical vapor deposition process with an rf induction vapor source has been developed to deposit 11.2-μm aluminum-copper alloy on polyimide laminate substrates. The average thickness uniformity (standard deviation/average thickness) of the deposit acquired by a beta backscatter technique was approximately 1 percent for these deposits. The aluminum-0.3 weight percent copper vapor charge results in a copper content in the deposit of 0.12 weight percent. The copper shows no preferential deposition pattern, as related to the surface of the laminate and its dispersion throughout the deposit. The resistivity of the aluminum-copper deposits is 3.0 μΩ-cm and is stable from one deposition run to another. Also, the resistivity was not related to the geometry of the domed substrate. The density of the 11.2-μm-thick aluminum-copper film was within 1 percent of theoretical, and its adhesion to the polyimide exceeds that required for post-deposition operations and handling. The deposited films exhibited a specular reflectance above 90 percent with a 632.8 nm wave length source and a grain size of 0.6 μm throughout the deposit.

ILLUSTRATIONS

INTRODUCTION

The process of vacuum metallizing is well established as a means of imparting a decorative metallic finish to a variety of plastic components. Vacuum deposited aluminum and aluminum-copper alloys are widely used as conductors on integrated circuits. In either case, advantages exist to allow successful application of these films. Usually in providing highly reflective aluminum films on plastic components for decorative purposes, films of less than 1 μm are used to maintain the high reflectance requirement. The use of aluminum and its alloys for integrated circuit applications, has the advantage of low outgasing substrate materials. Combining the basic disadvantages of large multilayered plastic substrates and the requirement for thick (>10 μm), reflective highly uniform aluminum and aluminum-copper films demands the utmost of vacuum deposition technology.

This paper reports on a process for vacuum deposition of aluminum-0.3 weight percent copper films, 11 μm thick on three-layer laminated substrates. These substrates consist of two polyimide (Kapton) layers and one aluminum foil layer bonded with a thermosetting adhesive. The required film properties were highly uniform deposits, reflective, consistant resistivity near bulk values, adequate film adhesion, and all properties to be repeatable over a long-time period.

EXPERIMENTAL

Deposition Equipment

The deposition system was a stainless steel bell jar chamber pumped by a liquid nitrogen - trapped oil diffusion pump. Chamber pressure before deposition was in the low 10^{-4} Pa range. The vapor source was a radio frequency, induction-heated source powered by a 5-kW, 450-kHz generator, which is connected to a five-turn induction coil. The vapor source is mounted inside the induction coil and consists of a boron nitride-titanium diboride composite crucible held by dense alumina insulators. The power to the source was manually controlled. The thickness of the deposit is monitored continuously during deposition by a quartz crystal thickness monitor. A three part planetary system was used to rotate the substrates above and around the centrally located vapor source. The source material was high purity aluminum-0.3 weight percent copper alloy. A calibrated reference thermocouple was used to monitor substrate temperature and quartz radiant heaters were used for chamber and substrate bakeout. The deposition chamber was equipped with a quadrapole mass spectrometer for residual gas analysis.

Substrate Composition

The substrates are made from laminated polyimide (Kapton) and aluminum foil. Two layers of polyimide, 0.127 mm thick, and one layer of aluminum, 0.102 mm thick, are formed into domed segments which are then bonded together with a thermosetting adhesive. The aluminum foil acts as an outer backing layer for the polyimide. These substrates have a surface area of approximately $600 cm^2$.

Recognizing that the polyimide-laminate substrates are a source of contamination, they must be thoroughly cleaned and thermally treated before depositing the aluminum-copper alloy. Dirt particles, lint, fingerprints, and films from the Kapton/Kapton/aluminum foil bonding-forming operation, as well as other contaminants, must also be removed to acquire good quality deposits with acceptable adhesion. A preliminary chemical cleaning procedure does not remove all of these sources of contamination. Additional substrate cleaning before deposition is accomplished by rinsing the laminates with ethyl alcohol, blowing them dry with nitrogen, and baking them in a 150°C atmosphere for two hours. The selection of 150°C was based on mass spectrometric analyses of laminated substrates exposed to various temperatures and conditions. These data indicated that a two-hour bake-out between 140 and 150°C removed most of the water and air from the organic laminates. Further heat treatment is done in the vacuum chamber prior to deposition.

Process Description

The developed deposition process is as follows: After the vacuum chamber is roughed down to nine Pa (50 μ), the diffusion pump is valved in to take the chamber down to 0.13 mPa (10^{-6} torr). At this pressure, the heatup of the vapor source begins. Normally the vapor source is under continuous power (15 percent) to reduce temperature cycling of the BN-TiB_2 crucible.

During initial power soak (at 35 percent power), the temperature of the crucible is brought up to a red stage, and a preheat is initiated at 95 percent power for four minutes. The rf power is then reduced to approximately 80 percent for one minute, and the shutter is opened to begin deposition of the aluminum-0.3 weight percent copper charge. Power is then adjusted to achieve the desired rate of deposition. Typically, a rate of five nm/s is used for total thickness requirements of 11.2 μm. When the target thickness is reached, the shutter is automatically or manually activated to terminate the deposition. Power is reduced to a 15 percent level and a 25 minute cooling cycle begins. After sufficient cooling of the coated substrates, the system is vented, and the three planets containing substrates are removed. The system can then be prepared for another deposition cycle. It should be noted that before the actual deposition process begins, the laminates are baked under vacuum in the deposition chamber until their temperature in the chamber reaches 150°C, and then are cooled in vacuum to 75°C prior to coating.

PROCESS CHARACTERIZATION

Residual Gas Analysis

Deposition characteristics are dependent on the vacuum environment.[1] Consequently, the vacuum deposition environment was monitored with a quadrapole mass spectrometer. After monitoring several deposition runs to verify the consistency of results, typical gas spectra and species were documented (Figure 1). Figure 1 shows the relative intensities for baseline vacuums prior to and during deposition. The resulting spectra before bake-out and deposition indicated hydrogen, nitrogen, water, carbon monoxide, oxygen, and carbon dioxide. All of these species are expected during thermal treatment of the laminated polyimide substrates in a high vacuum environment. After vacuum bake-out, the water and oxygen peaks are reduced substantially. During deposition, the major constituents are hydrogen, nitrogen, water, and carbon monoxide. The increased hydrogen is due to the dissociation of the water by the reactive aluminum and the formation of aluminum oxide and hydrogen.

The increased carbon monoxide and nitrogen intensity (28 amu) during deposition comes primarily from the boron nitride-titanium diboride composite crucible in the vapor source. Deposition runs were made without the laminated substrates and show a similar increase in the 28-amu peak, to confirm that $BN-TiB_2$ crucibles in the vapor source constitute the main contributor to this observed

28-amu peak. The observed intensities of oxygen and water during deposition represent partial pressure to deposition rate (five nm/s) ratios of 0.18 nPa•s/nm (1.4 x 10^{-11} torr•s/Å) for oxygen and 8.1μPa•s/nm (6.2 x 10^{-9} torr•s/Å) for water. These partial pressure values for oxygen and water are below the critical points expressed by F. d'Heurle.[1] A mass spectra scan above 50 amu during deposition at a rate of five nm/s did not reveal any other significant amount of evaporated species in that range.

Material Distribution from RF Vapor Source

The aluminum-copper alloy vapor distribution from the rf induction source is highly dependent on several features. These include the power level being applied to the crucible, temperature of the crucible, material composition of the crucible, geometry of the crucible, position of the crucible relative to the induction coil, purity and composition of the evaporated aluminum -0.3 percent weight copper source material, and the vacuum in the chamber during deposition. Consequently, steps were taken to control these effects to assure consistent deposits.

A deposition rate gradient for the five nm/s deposition rate was generated (Figure 2), using the cosine distribution for a surface source, as described by Behrndt.[2,3] To acquire uniform deposit thickness over the entire surface of the curved substrate, the substrates are rotated to take advantage of the rate gradient.

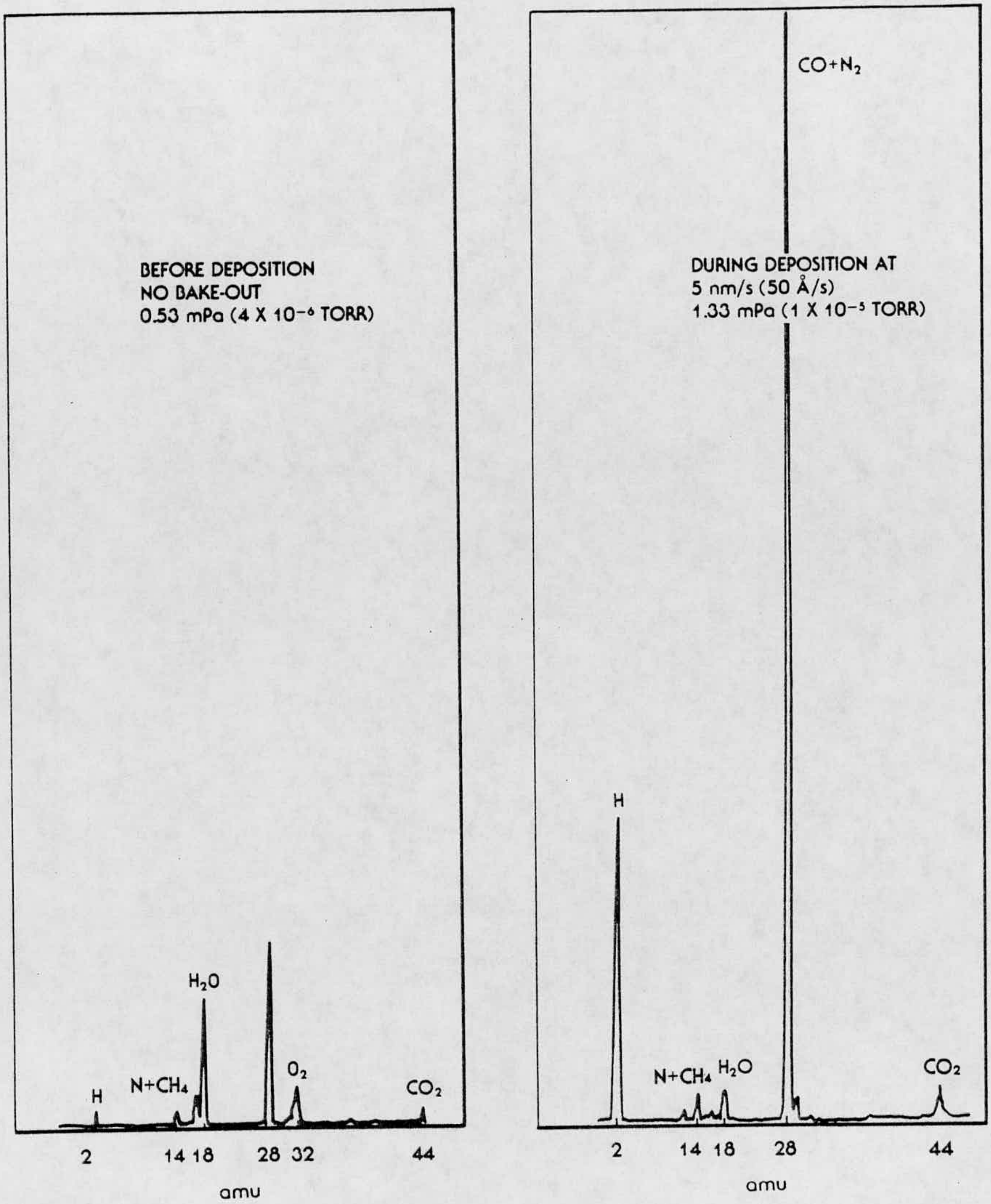


Figure 1. Quadrapole Mass Spectrometric Analyses

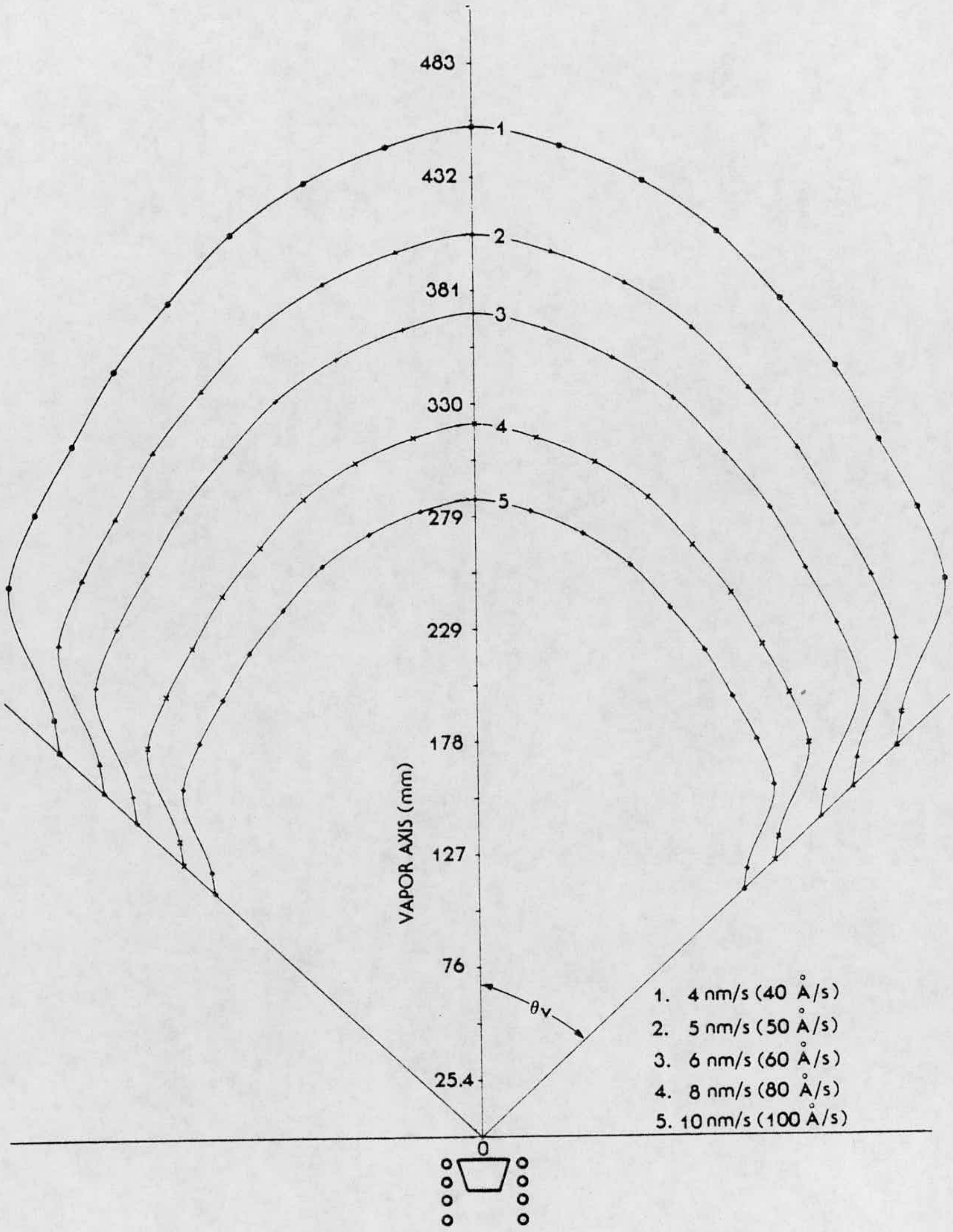


Figure 2. Deposition Rate Gradient (Target Deposition Rate 5 nm/s)

The observed deviation in the region of the 45-degree vapor angle is believed to be caused by the crucible dimensions that inhibit an ideal surface condition.

Deposition Temperature

The maximum temperature experienced during deposition for the previously thermal-treated laminated substrates is a very important parameter in the deposition process. It can affect the appearance of the final aluminum-copper deposits, primarily by the amount and type of outgassing species from the heated substrates that occur during the deposition. An alumel-chromel thermocouple, placed off the surface of the substrate, serves as a stationary reference thermocouple to provide deposition temperature data on a run-to-run basis. Typically the five nm/s deposition rate resulted in a maximum substrate temperature of 190°C.

Thickness and Uniformity of the Deposit

The thickness and uniformity of the deposit on the 600cm^2 substrates were established, using the beta backscatter technique,[4,5] by measuring thirty precisely located points on the surface of the coated laminates. The average total thickness and uniformity were then established, after defining the uniformity as the standard deviation divided by the average thickness.

Data from a typical laminate are given in Table 1. The average total thickness was 11.17 μm with a standard deviation of 0.13 μm. This is equivalent to a thickness uniformity number, or coefficient of variation, of 1.14 percent. The matrix average gives the thickness deviations for concentric contour rings at various angles from the pole of the laminate and deviations in thickness of wedge sections of the part from center to outside. Each contour ring is represented by five beta backscatter measurements at some angle from the pole of the laminate. For instance at an angle of four degrees the five measurements show a thickness average of 11.33 μm with a deviation of 0.0736 μm, while at an angle of 36 degrees the five measurements show a thickness average of 11.056 μm and a deviation of 0.0793 μm. The six contour rings all recorded very consistent deviations with slightly decreasing thickness, from 11.33 μm in the central area to 11.06 μm near the outside of the curved laminate. The wedge sections represent six beta backscatter measurements taken from four to 36 degrees from the pole of the laminate. Five equally spaced wedge sections were measured, and the thickness average was found to be very consistent.

The average uniformity number for 100 similarly curved laminates that were plated to 11.2 μm total thickness in the Knudson sphere position was 1.21 percent, as determined for a full 30 beta backscatter measurements performed on each sample.

TABLE 1. Matrix Average for Beta Backscatter Thickness Measurements

	Angle From Pole of Laminate (Degrees)						Wedge Sections	
	4	12	20	24	31	36	Average	Deviation
	Thickness (µm)						(µm)	(µm)
Contour	11.3347	11.3247	11.2362	11.1475	11.0171	10.9943	11.1758	0.1483
Ring	11.23	11.109	11.1871	11.0516	11.1232	10.9709	11.112	0.093
	11.32	11.2318	11.1715	11.1941	10.9517	11.0756	11.1575	0.1285
	11.4367	11.2824	11.1917	11.1726	10.994	11.0644	11.1903	0.1574
	11.3444	11.2842	11.3209	11.1238	11.0283	11.1729	11.2124	0.1246
	Average							
	11.3332	11.2464	11.2215	11.1379	11.0229	11.0556		
	Deviation							
	0.0736	0.0836	0.0606	0.055	0.0633	0.0793		

Total Thickness Average - 11.17 µm
Standard Deviation - 0.13 µm
Uniformity - 1.14 percent

DEPOSIT CHARACTERIZATION

Microstructural Analysis of Deposit

Typical surfaces and a fracture cross section of the aluminum-copper alloy deposits are shown in Figure 3. The periodic hillocks (white abnormalities) in Figure 3b and 3c on the film's surface are localized nucleation sites which are typical of thick PVD aluminum deposits.[2,6,7] The addition of the 0.3 weight percent copper in the aluminum significantly reduced the initial number of these hillocks observed for pure aluminum deposits.[6,8,9]

Defects typically originate from fingerprints, dirt, lint, and fibers that collect on the polyimide surface prior to loading a substrate into the vacuum chamber. The initial surface conditions of the polyimide substrate prior to deposition definitely determine the density of these defects on the deposit. Typical particulate defects are illustrated in Figure 4. Figure 4a shows a fibrous defect resulting from lint fibers present on the polyimide before deposition. Since lint and dirt particles are strongly attracted to the polyimide by electrostatic charges, special handling and preparation techniques must be followed to reduce these defect sources. When these particulate-coated substrates are vapor deposited, defects such as those shown in Figures 4a and 4b are present.

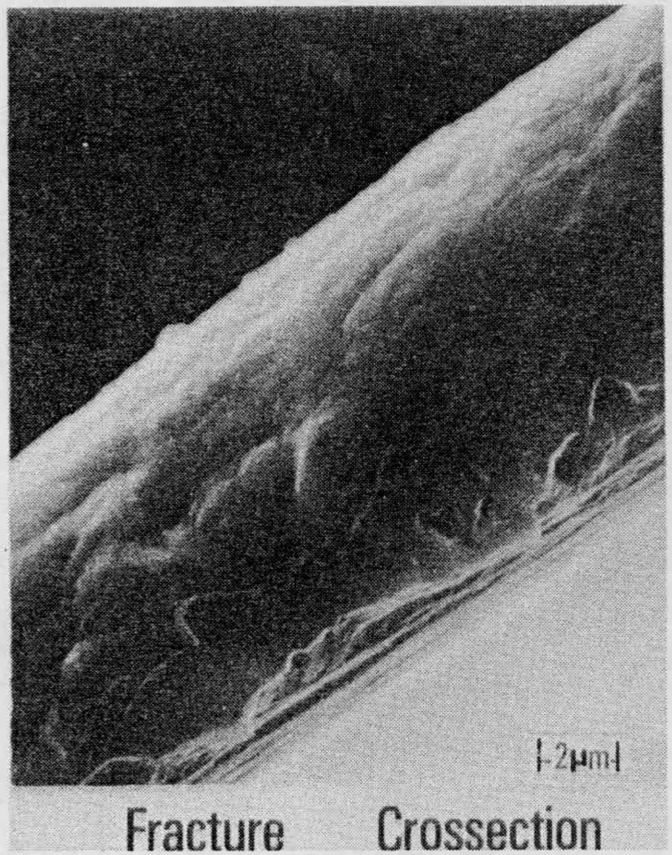


Figure 3A

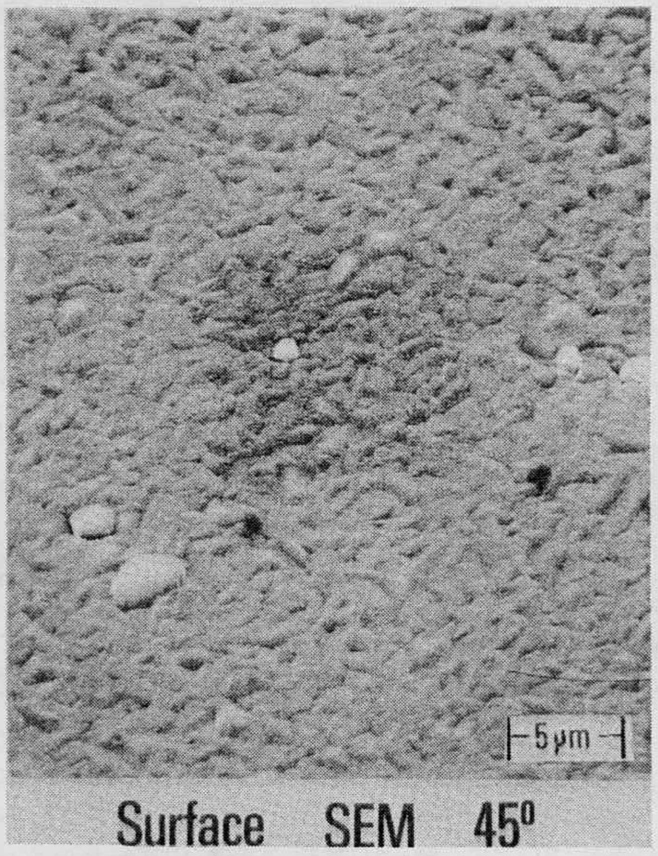


Figure 3B

Figure 3. Fracture Crossection And Surface of Aluminum-Copper Film, 11.5 µm Thick

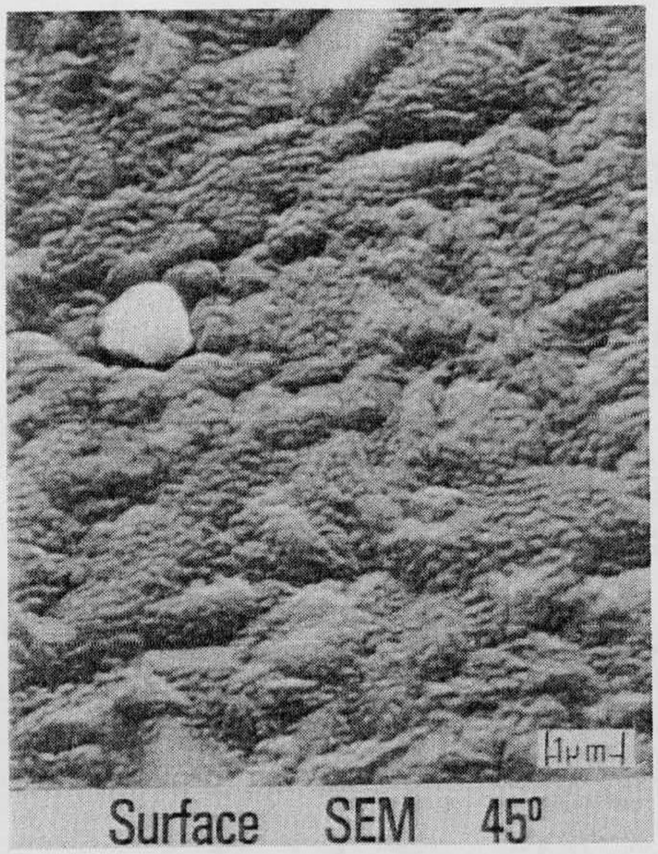
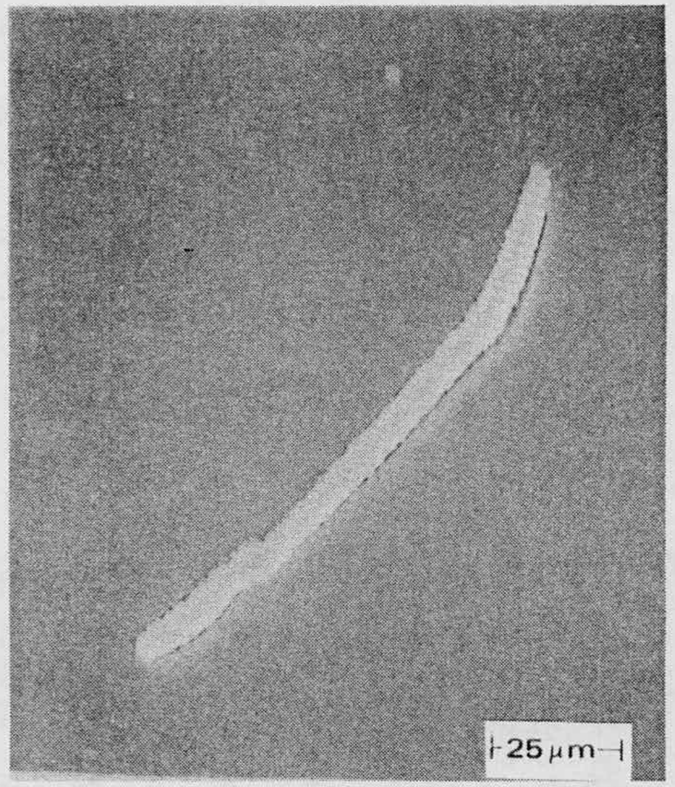
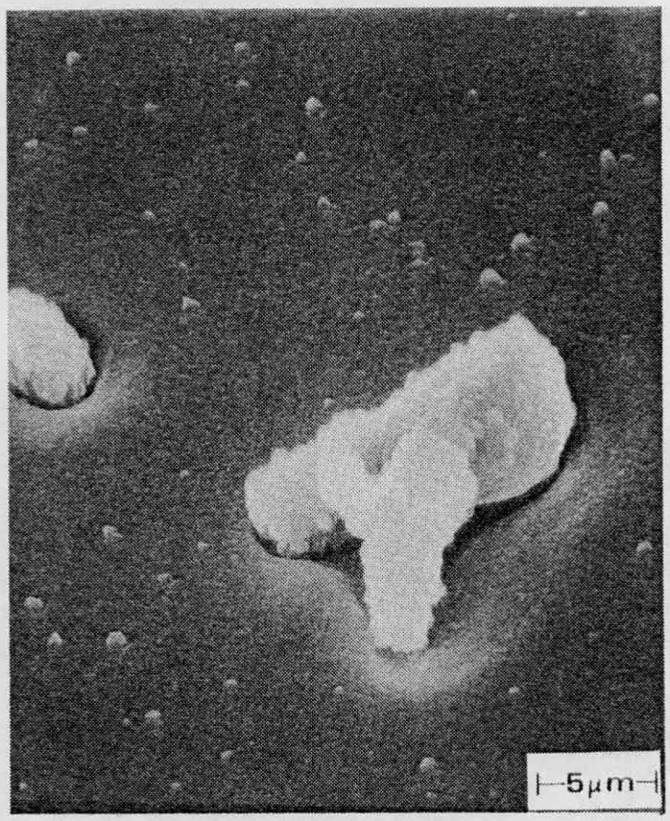


Figure 3C

Figure 3 Continued. Fracture Crossection And Surface of Aluminum-Copper Film, 11.5 µm Thick

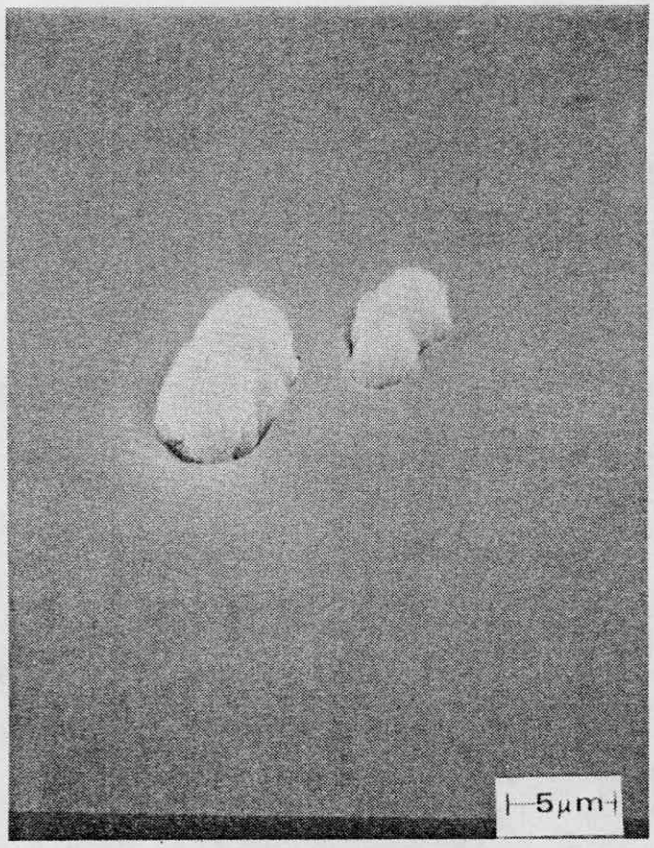


4A. Lint Defect, After Deposition

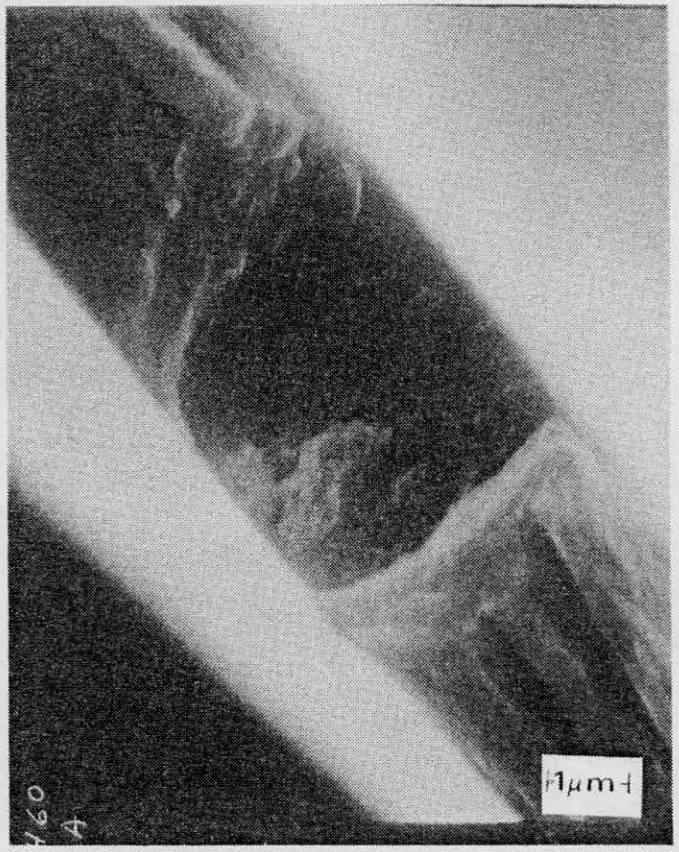


4B. Dirt Defect, Originating on Substrate

Figure 4. Observed Defects in Deposited Aluminum-Copper Films (SEM Photomicrographs)



4C. General Defect, Originating on Substrate



4D. Crossection of Affected Deposit

Figure 4 Continued. Observed Defects in Depostied Aluminum-Copper Films (SEM Photomicrographs)

In Figure 4b, the smaller whitish protrusions are the hillock-type defects mentioned above. Other defects shown in Figure 4c typify those that originate from contaminated or deformed polyimide surfaces. A cross section (Figure 4d) through a defect (Figure 4c) illustrates its origin at the polyimide surface.

Reflectance

The reflectance of the metal films was measured using an integrating sphere technique[10]. The total reflectance of the aluminum-0.12 weight percent copper film using a 632.8-nm-wave length source was 89 percent. This is comparable to results others have acquired for pure aluminum films in the 0.1 μm (1000Å)[11] and thickness ranges 10 to 12 μm[18]. The amount of reflected light that was specularly reflected was in the 90 percent range. This level of specular reflectance corresponds to a mirror-like surface.

Copper Content Distribution

Thin films deposited from a liquid alloy source will normally have compositions different from their source.[12] The degree of difference was investigated for the aluminum-copper alloy, using the electron microprobe and atomic absorption analytical techniques. The electron microprobe was also used to evaluate the copper distribution in the deposit on a domed polyimide laminate. An elemental distribution analysis was performed with an electron beam size of approximately one μm being scanned across seven regions of a metallurgically prepared deposit. Ten data points for each of these seven locations were used to determine an average aluminum and copper content. Quantitative data indicated that the copper contents were 0.12 weight percent within ±0.02 weight percent and homogeneously distributed across the aluminum-copper films.

Consecutive runs using the identical aluminum-0.3 weight percent copper starting material were expected to result in a copper enrichment of the vapor load and ultimately the deposit. The trend was evaluated, using 91 aluminum-copper deposits from seven different crucibles. The atomic absorption technique was used to determine the average copper content of coated polyimide coupons that had been placed in the vacuum system for each consecutive run. Atomic absorption results indicated that the average increase in weight percent copper per consecutive deposition was approximately 0.003 percent. In addition, the atomic absorption data of these 91 coupons show the average copper content to be 0.12 ±0.04 weight percent, which agrees with the electron microprobe data from the domed substrate referred to above.

Resistivity

The resistivity of the vacuum deposited aluminum-0.12 weight percent copper alloy on polyimide laminates was measured, using a four-point in-line probe system. This resistance and the film thickness measured with the beta backscatter technique were used to calculate the resistivity of the deposited film.

The theoretical room temperature resistivity of pure aluminum thicker than one μm is 2.71 μΩ-cm.[13,15] This reported value is dependent upon other effects, such as grain size, deposition rates, and substrate conditions, as well as the inherent errors in the resistance and thickness measurements.

Three polyimide laminates with aluminum-0.12 weight percent copper deposits were evaluated, using the four-point probe system. Thirty points per part were measured. The resulting average resistivity for each of the parts was 2.92, 3.01, and 3.03 μΩ-cm.

These resistivities appear relatively constant for the aluminum-copper deposited films from the rf induction source and do not vary from pole to skirt. As mentioned, grain boundaries and interstitial contaminants introduced by the high temperature exposure of the laminated substrates during deposition affect resistivity. However, the observed resistivity values for the different parts from different deposition runs do not reveal these effects. As previously discussed, mass spectrometric analysis data suggest another contaminant source because of the species outgassed from the laminate that could be co-deposited with the aluminum-copper film. However, organic contamination from the substrate was not observed to any degree from the gas analysis test performed during deposition. It appears, however, that the major contaminating contributor was coming from the BN-TiB_2 crucible, as detected by mass spectrometric analysis during deposition. (Refer to above discussion of Residual Gas Analysis.)

Density

Density of the aluminum-0.12 weight percent copper films was examined using a trioptic measuring machine, a light section microscope, a contact interferometer, and an analytical balance. Optical flats were weighed and then deposited with the aluminum-copper alloy. The average density of the deposits was 2.68 g/cm^3 with an uncertainty of ± 4 percent. The theoretical density of aluminum-0.12 weight percent copper is 2.71 g/cm^3 at 20°C.[14] These data indicated that the thick aluminum-copper films are within one percent of theoretical density. This difference in density between theoretical and the PVD material could have easily resulted from the measurement uncertainties of the technique and the equipment used.

Adhesion

Traditionally, adhesion tests of vacuum deposited films have shown them to be rather subjective and dependent upon the application and the individual performing the tests. Therefore, comparable adhesion results are not available. The capability to establish a comparable strength value for the aluminum-copper film and polyimide interfacial adhesion is limited. The predeposit cleaning and vacuum thermal treating procedures used throughout this activity on the laminated samples and the deposition process have provided aluminum-copper films with good adhesion. Consequently, adhesion has not been a problem, but is a film property which should be characterized.

To establish a semiquantitative measure of adhesion of the aluminum-copper deposit on polyimide, a direct pull test was developed which used cyano-acrylic adhesive-coated aluminum cylinders (64.5 mm^2 pull face) to sandwich the aluminum-copper deposited polyimide specimens. The specimens are pulled and identified as to fracture strength and location.

The results of the adhesion testing did not indicate any particular relationship between the deposit's vapor source composition, thickness, substrate temperature, and the achieved adhesion values. The pull strength values were not indicative of the aluminum-copper deposit/polyimide interfacial adhesion. The failure regions in all cases were in the cyano-acrylic adhesive zone either between the aluminum plug and the polyimide substrate, or the aluminum-copper deposit and the aluminum plug. The highest pull strength value achieved before the adhesive failed was 17.13 MPa. In general, the results of this pull test showed the adhesion of the deposited films to be above that of the cyano-acrylic adhesive used to bond the coated samples to the aluminum plugs. In addition, deposit/polyimide adhesion is more than satisfactory to withstand subsequent processing and handling.

Crystal Orientation and Grain Size

Several deposits were analyzed with a pole figure device[16] using Cu Kα radiation. The 11-μm-thick deposits had a preferred crystallographic orientation of the (111) parallel to the substrate. Vacuum deposited face-centered cubic metals often exhibit (111) orientation.[17] Specimens near the polyimide/aluminum-copper interface, central and outer surface regions of the deposited film were prepared for examination with the transmission electron microscope. Resulting data indicated that the grain size was 0.6 μm throughout the deposit.

SUMMARY

A physical vapor deposition process, utilizing a radio frequency induction source, was developed for routinely producing 11.2-μm aluminum-0.12 weight percent copper alloy deposits on polyimide laminates. The normal operating vacuum during deposition is 2.6 mPa (2×10^{-5} torr), and the optimized deposition rate is five nm/s. The resulting substrate temperature for the five-nm/s rate is 190°C.

Residual gas analysis (RGA) during deposition shows the normal hydrogen, oxygen, and water but an increased carbon monoxide and nitrogen (28 amu) contribution as a result of outgassing of the composite BN-TiB_2 crucible.

The uniformity of the aluminum-copper films at the 11.2-μm thickness is 1.2 percent.

Some defects observed in the deposited film appear inherent in the metallizing process. However, with the appropriate substrate preparation before deposition it is possible to reduce noticeably the quantity of these defects. The specular reflectivity of the deposited films was in the 90 percent range. The vapor source material is an aluminum-0.3 weight percent copper alloy. The resulting deposit contains approximately 0.12 weight percent

copper. Electron microprobe analysis indicates little copper variation in the cross section of the deposit. Four-point-probe electrical resistivity measurements on typical deposits recorded values of 3.0 $\mu\Omega$-cm. The density of the deposits 11.2 μm thick was within one percent of theoretical. Grain size was found to be 0.6 μm throughout the deposit and a preferred (111) crystallographic orientation was determined for the 11.2-μm-thick aluminum-copper deposits.

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