United States Patent Office

3,360,349

Patented Dec. 26, 1967

1

3,360,349

COPPER LAYER BONDED TO A NON-CONDUCTIVE LAYER BY MEANS OF A COPPER ALLOY

Alfred A. Adomines, Wayne, Pa., assignor to Sperry Rand Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Apr. 1, 1965, Ser. No. 444,849
8 Claims. (Cl. 29—195)

ABSTRACT OF THE DISCLOSURE

This invention relates to structures containing electrodeposited copper. More particularly, this invention relates to structures containing electrodeposited copper and an inert, non-conductive substrate and to improving the adhesion of electrodeposited copper to selected substrate materials, particularly inert, non-conductive substrate materials, such as glass, alumina, ceramic materials, organic plastic materials, e.g., Mylar film, and the like. This is accomplished by using a particular alloy containing copper.

To obtain satisfactory adhesion of electrodeposited copper to an inert, non-conductive substrate material, such as glass, it has been necessary heretofore to subject the substrate material to intensive cleaning. This intensive cleaning of the substrate material prior to electrodeposition of copper thereon in order to obtain good adhesion of the electrodeposited copper has been time consuming and expensive. Even then in many instances the adhesion of the electrodeposited copper would be less than desired.

Accordingly, it is an object of this invention to provide a method of preparing structures containing electrodeposited copper whereby the intensive cleaning of the substrate surfaces prior to the electrodeposition of copper thereon in order to obtain good adhesion is substantially eliminated or greatly reduced.

Another object of this invention is to provide structures containing electrodeposited copper which exhibits excellent and improved adhesion to the underlying material.

Still another object of this invention is to provide an improved method of preparing structures containing electrodeposited copper.

How these and other objects of this invention are accomplished will become apparent in the light of the accompanying disclosure. In at least one embodiment of this invention at least one of the foregoing objects will be achieved.

In accordance with this invention it has been discovered that in structures containing electrodeposited copper improved adhesion of the electrodeposited copper is obtained by electrodepositing the copper onto vapor deposited material which is chemically similar to copper. More particularly, in accordance with one embodiment of this invention an improved structure containing electrodeposited copper, as evidenced by the improved adhesion of the electrodeposited copper, is provided by a structure made up of an inert, non-conductive substrate, vapor deposited material chemically similar to copper deposited thereon and an electrodeposited copper deposited upon said vapor deposited material.

Those vapor deposited materials which are useful for improving and increasing the adhesion of electrodeposited copper include substantially all materials chemically similar to copper and capable of volatilization and vapor deposition upon the inert, non-conductive substrate materials. Examples of vapor-deposited materials useful in accordance with the practice of this invention for improving the adhesion of electrodeposited copper include the various copper alloys, particularly the bronzes, such as the aluminum bronzes and chromium bronzes. Copper

2

alloys capable of volatilization and vapor deposition in accordance with the practice of this invention and analyzing 20–95% copper and higher and 80–5% other alloying metal or metals, such as aluminum and chromium, have been found to be suitable.

In accordance with one embodiment of the practice of this invention it has been found that improved adhesion is obtained by effecting the deposition of the vapor deposited material, such as copper-containing alloy, onto a heated substrate, such as glass, alumina ceramic surface and the like, maintained at a substantially elevated temperature in the range 200–400° C., more or less, during the vapor deposition operation. Satisfactory results, however, are also obtained while carrying out the vapor deposition operation at substantially room temperature conditions with respect to the temperature of the substrate material. This type of operation is particularly useful when the inert, non-conductive substrate material comprises a thermally decomposable material, such as organic polymer material, e.g., Mylar, polyethylene, polypropylene, cellophane and the like.

The following is illustrative of the practice of this invention. A tungsten boat charged with a mixture comprising about 75–80% by weight copper and 20–25% by weight aluminum was placed in a vacuum system. There was also placed in the system a substrate material, such as a glass plate or slide, the glass plate or slide being separated from the tungsten boat by a shutter.

The system was then evacuated to a low pressure, about 1×10^{-6} mm. Hg. The copper and aluminum in the tungsten boat were slowly heated to the melting point and the glass substrate material was heated by suitable means to a temperature of about 300° C. The shutter between the tungsten boat and the glass substrate material was removed for a desired period of time with the result that there was deposited by vapor deposition onto the glass substrate material a layer of aluminum-copper metallic material of about 4,000 A. thickness. This aluminum-copper material thus vapor deposited on the heated glass substrate analyzed 92% by weight copper and 8% by weight aluminum.

After the desired amount of the aluminum bronze material, i.e., the copper-aluminum-containing material analyzing 92% copper and 8% aluminum, had been vapor deposited the shutter was closed and the system shut down and permitted to cool under vacuum for approximately 4 hours or to about room temperature. The resulting copper-aluminum coated glass substrate material was removed from the system and a layer of copper was electroplated thereon, such as a layer of copper of about 1 mil in thickness.

The electrodeposited copper exhibited superior and excellent adhesion to the aluminum-copper coated glass substrate material. For example, the electrodeposited copper layer could not be removed or peeled by the conventional test methods, such as peeling with Scotch tape or scraping with a razor or scribing and prying at the edges with a razor. Further, the layers thus deposited on the glass substrate material, i.e., the copper-aluminum vapor deposited layer and the electrodeposited copper layer, were easily etched by conventional copper etchant solutions, such as ferric chloride copper etching solution, and this combination of layers showed no obvious difference from pure copper except for the superior and excellent adhesion of the electrodeposited copper to the underlying substrate material.

Excellent results with respect to the adhesion of the electrodeposited copper were also obtained by means of other vapor deposited copper-aluminum films or layers, even those analyzing up to about 80% by weight aluminum. Also, excellent results were obtained in accordance with this invention by means of vapor deposited copper chromium layers, particularly a copper-chromium layer analyzing about 10% by weight chromium. Also, tests carried out showed that the advantages of this invention were also obtainable on substrates maintained at about room or ambient temperature during the vapor deposition operation.

The advantages in accordance with the practice of this invention of employing a vapor deposited film, such as aluminum bronze or chromium bronze or other metallic materials chemically similar to copper, in addition to improving the adhesion of the electrodeposited copper include the fact that the vapor deposited material does not contaminate the copper plating bath during the copper electrodeposition operation. Further, by following the practices of this invention the electrodeposited copper film is extremely bright and suitable for electrodeposition thereon of an additional metallic film, such as a magnetic nickel-iron film. Therefore, the practice of this invention is particularly suitable for the preparation of a firm, well-adhering copper base layer for integrated circuit mountings and as a sub-layer in an electroplated memory structure.

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many substitutions, alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A structure comprising an inert, non-conductive substrate, copper alloy material analyzing 20–95% copper and 80–5% of a metal selected from the group consisting of aluminum and chromium deposited on the surface of said substrate and copper electrodeposited on said copper alloy material.

2. A structure comprising an inert, non-conductive substrate, copper alloy material deposited on the surface of

said substrate and copper electrodeposited on said copper alloy material, said copper alloy material analyzing 5–80% aluminum and 95–20% copper.

3. A structure in accordance with claim **1** wherein said copper alloy material comprises 92% copper and 8% aluminum.

4. A structure comprising an inert, non-conductive substrate, copper alloy material deposited on the surface of said substrate and copper electrodeposited on said copper alloy material, said copper alloy material analyzing 5–80% chromium and 95–20% copper.

5. A structure comprising an inert, non-conductive substrate, copper alloy material deposited on the surface of said substrate and copper electrodeposited on said copper alloy material, said copper alloy material comprising about 90% copper and 10% chromium.

6. A structure in accordance with claim **1** wherein said copper alloy material has a thickness in the range of 500–50,000 A.

7. A structure in accordance with claim **1** wherein said copper alloy material has a thickness of about 4,000 A.

8. A structure comprising an inert, non-conductive substrate, copper alloy material deposited on the surface of said substrate and copper electrodeposited on said copper alloy material, said copper alloy material having the composition 92% by weight copper and 8% by weight aluminum and a thickness of approximately 4,000 A. and said electrodeposited copper having a thickness of about 1 mil.

References Cited

UNITED STATES PATENTS

2,482,178	9/1949	Harris	29—195
2,966,427	12/1960	Breining	117—107.2
2,988,630	6/1961	Moore	29—199
3,206,325	9/1965	Averbach	117—107.2
3,294,654	12/1966	Norman	204—38

HYLAND BIZOT, *Primary Examiner.*