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ELECTROPLATING ONTO MOLYBDENUM SURFACES

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This invention relates to electroplating of gold onto molybdenum substrates. Molybdenum is a highly desirable material of construction for semiconductor devices and has been selected for use in various microwave device components. These include PIN silicon current limiters, silicon epitaxial varactor diodes, computer diodes for PCM, and gallium arsenide cryogenic packages. The selection of molybdenum is mainly based on its high thermal conductivity, the suitability of its coefficient of thermal expansion and its nonmagnetic character at low temperatures. It is often used alloyed with manganese on metalizing tape to produce thin metal films on ceramics.

For such applications the molybdenum or molybdenum-manganese alloy must be gold plated in order to provide a surface which will alloy readily with semiconductors and which additionally is suitable for thermocompression bonding.

Attempts to plate gold on molybdenum substrates using conventional prior art techniques result either in nonadherent plates or plates that do not survive subsequent processing. This has been found true of substrates that have been carefully cleaned so that surface contamination is not a cause of failure. It is well known that molybdenum forms an oxide (MoO_3) which is stable at low temperatures and it is this oxide which forms a barrier and prevents adherence between the gold plate and the molybdenum substrate.

The plating technique of this invention produces a tenacious gold plate on molybdenum surfaces using a unique plating-surface preparation. The molybdenum substrate is initially oxidized and the oxide hydrated, a step contrary to the conventional practice, and a very thin strike plate of gold is applied. The intermediate hydrated oxide coating is thereafter reduced by heat treatment in a reducing atmosphere. The hydrated oxide is thereby converted to metal and a continuous metal-to-metal interface is produced. The bond between the gold plate and the molybdenum obtained in this manner has exceptional integrity. The gold plate can then be built up to the desired thickness in the conventional way.

The process of this invention is believed to be successful because of the formation of a porous surface oxide rather than the normally encountered MoO_3 surface. The molybdenum is oxidized, for instance, by hydrogen peroxide ammonium hydroxide solutions to form hydrated molybdenum-oxides according to the reaction:

$$Mo+3H_2O_2 \rightarrow MoO_3 \cdot XH_2O+(3-X)H_2O \quad (1)$$

where $X=1$ or 2.

The vigorous etching action provides a fresh and clean Mo/MoO_3 surface. Any MoO_2 present before the treatment will be converted to the hydrated forms of MoO_3.

When the substrate is removed from the etching solution the hydrated oxide remaining on the surface is thin and porous. Upon immersion in the plating bath, the plating solution penetrates the oxide and comes into contact with the Mo surface. After the gold flash, treatment with hydrogen reduces the hydrated molybdenum oxide to Mo by the reaction.

$$MoO_3 \cdot XH_2O+3H_2 \rightarrow Mo+(3+X)H_2O \quad (2)$$

where X is 1 or 2.

This produces a two-phase interface. The gold is mechanically trapped in the reduced oxide and provides an adherent initial plate upon which to continue plating to the desired final thickness.

The following examples are given as illustrative embodiments of the invention:

Example I

In this example a gold plate was produced on a molybdenum-manganese metalized ceramic. The molybdenum alloy surface was degreased in an alkaline solution and rinsed in acetone. To complete the preliminary surface preparation the piece was fired at 1000° C. in dry hydrogen for ten minutes. The molybdenum alloy surface was then oxidized and hydrated to form the molybdenum oxide hydrate described above. This was done by immersing the part in a solution of four parts ammonium hydroxide, 28% assay, reagent grade, and one part "Superoxol" (hydrogen peroxide 30%, 25–33% assay, preservative free) at room temperature for approximately eight seconds. The hydrated surface thus formed is rinsed in deionized water. A very thin gold strike plate was then applied by electroplating the part as cathode in an acid citrate gold plating bath according to procedures well known in prior art. The thickness of the strike plate was carefully controlled to less than .06 mils. The plated part was again rinsed in deionized water and blown dry with nitrogen. The coating was then fired in dry hydrogen at 900° C. for ten minutes. This step effectively reduces the molybdenum hydrate intermediate layer to molybdenum metal so that a continuous molybdenum-gold interface is obtained. To build up the plate to the desired thickness by conventional means the part was again strike plated at 250 ma./in.^{2} and gold plated to .3 mils at 25 ma./in.^{2}. The piece was thereafter rinsed and dried as before.

Example II

In this example a pure molybdenum part was gold plated. The part was degreased in alkaline solution and rinsed in acetone. The surface was then oxidized as before by treatment in ammonium hydroxide and "Superoxol" for ten seconds at room temperature. After rinsing in deionized water a strike plate was applied to the hydrated molybdenum oxide surface as in Example I. Again the strike plate was restricted to less than .06 mils in thickness. It was convenient to plate 0.02 mils at a current density of 250 ma./in.^{2}. The part was again rinsed, dried, and fired in hydrogen at 900° C. for ten minutes. The plate was then built up to a desired thickness of 0.3 mils by electroplating in the same bath at 25 ma./in.^{2}.

Example III

The procedure of Example I was followed with the exception of the oxidizing and hydrating step. In this example the clean molybdeum piece was treated in water at room temperature for a period of eight seconds. This was found to give an adequate molybdenum hydrate coating. The subsequent processing was identical to that of Example I. A tightly adherent gold electroplate was obtained.

In each of the foregoing examples the electroplated film was found to be continuous, and tightly inherent to the molybdenum substrate.

The oxidization of the molybdenum substrate surface to form the desired oxide hydrate according to Equation 1 can be carried out in various ways which will be apparent to those skilled in the art. Various oxidizing agents are adequate, such as H_2O_2, and H_2O_2—NH_4OH mixtures. The hydrate can be formed in separate successive operations of oxidation and hydration if desired but the one-step procedure used herein is believed to be superior in that a greater degree of permeability to the reducing gas is obtained. The solution used in Examples I and II has been found to be particularly effective for this pur-

pose. The proportions of ammonium hydroxide and hydrogen peroxide in the solution can be varied appreciably. Water has also been found to be useful as illustrated by Example III. Thus, for the purposes of this invention the required treatment to form the hydrate is specified as immersion in an aqueous solution. The term aqueous solution is intended to mean a solution in which water is the predominant ingredient (by volume). Treatment for at least five seconds has been found adequate.

The gold plate can be applied by any conventional plating technique. It has been found that this procedure is effective irrespective of the particular electrolyte used in the electroplating operation or the other variables in the plating processes. However, it is essential that the thickness of the initial strike be limited to .08 mil or less. Such thicknesses are capable of being permeated by a subsequent reducing atmosphere so that complete reduction of the entire thickness of the hydrate film can be obtained. The reducing operation used to reduce the intermediate hydrate layer can be varied according to well-known considerations. Heat treatment in a dry reducing gas such as hydrogen, appears to be most convenient. Treatments in hydrogen at a temperature of at least 700° C. for periods of at least ten minutes have been found successful. Hydrogen reduction at a temperature of 900° C. for a period of twenty minutes has been particularly successful. Reduction of the hydrate by chemical solutions or other alternative procedures which completely reduce the hydrate to molybdenum metal may be used as well.

This invention is applicable to molybdenum substrate and molybdenum alloy substrates in which the molybdenum content predominates.

These and other aspects of the invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of this invention.

What is claimed is:

1. A method for electroplating gold onto a substrate comprising molybdenum by the steps of oxidizing the surface to be plated in the presence of water to form molybdenum oxide hydrate, electroplating a strike film of gold and into the molybdenum oxide hydrate said film being less than 0.08 mils in thickness, treating the electroplated surface with a reducing agent to completely reduce the hydrated molybdenum oxide and electroplating gold onto the strike film to the desired thickness.

2. A method for electroplating gold onto a substrate comprising molybdenum which method comprises the steps of exposing the surface to be plated to aqueous solutions of hydrogen peroxide and ammonium hydroxide to form a film of molybdenum oxide hydrate, electroplating a strike film of gold onto and into the molybdenum oxide hydrate film said strike film not exceeding 0.08 mil in thickness, reducing the molybdenum oxide hydrate film to molybdenum metal thus forming a molybdenum-gold interface, and electroplating gold onto the gold strike to the desired thickness.

3. The method of claim **2** wherein the composition of the aqueous solution comprises H_2O_2 and NH_4OH.

4. The method of claim **3** wherein the surface to be plated is exposed to the said solution for a period of approximately ten seconds at room temperature.

5. The method of claim **2** wherein the molybdenum oxide hydrate film is reduced by treating the film in hydrogen at a temperature of at least 700° C. for a period of at least ten minutes.

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