

[54] **METHOD FOR MAKING THIN FILM
TUNGSTEN-THORIUM ALLOY**

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[51] Int. Cl. **C23b 7/02, C23b 5/52, C23b 5/32**

[58] Field of Search **204/43 R, 12, 37 R**

[56] **References Cited**

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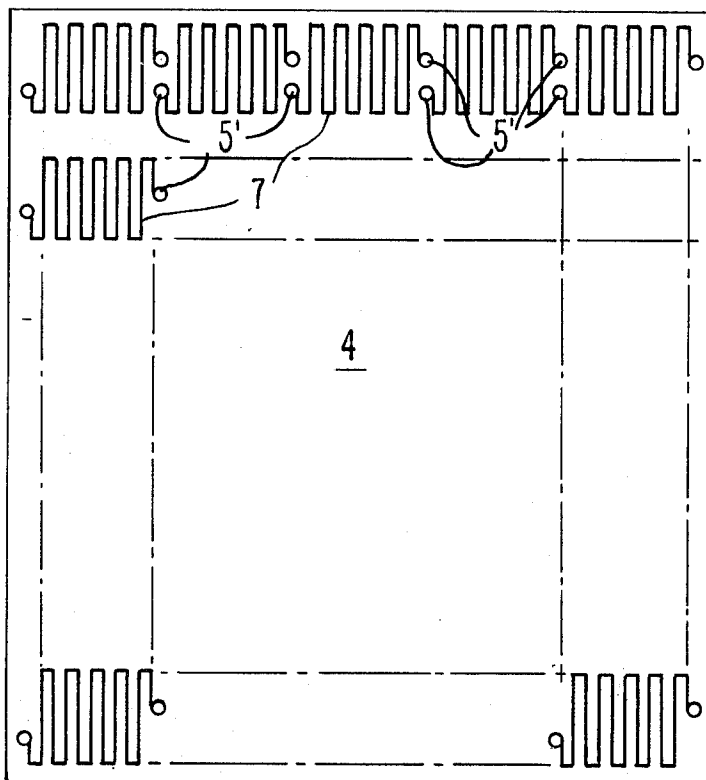
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Attorney, Agent, or Firm—Norman R. Bardales

[57] **ABSTRACT**

A thin film tungsten-thorium alloy is fabricated by a method utilizing an electroplating technique. In some applications, the W—Th alloy subsequently remains as a layer on the object on which it is deposited. In other applications, it is subsequently completely or partially removed from the object. Also, in applications where it is desired to have the W—Th alloy in a single crystal state, it is subsequently annealed.

12 Claims, 8 Drawing Figures



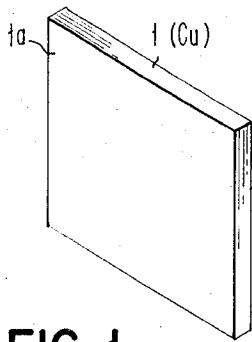


FIG. 1

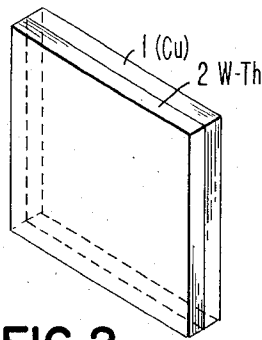


FIG. 2

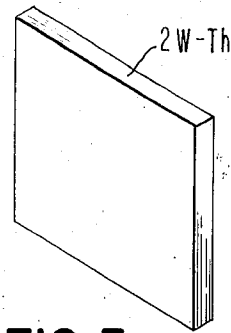


FIG. 3

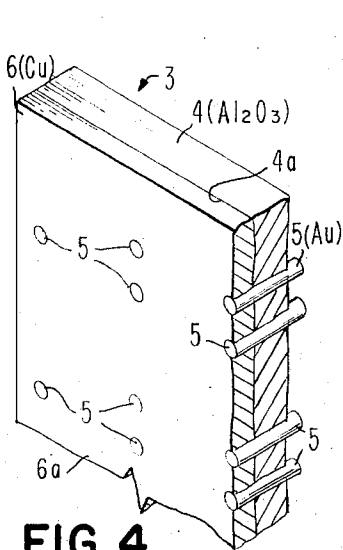


FIG. 4

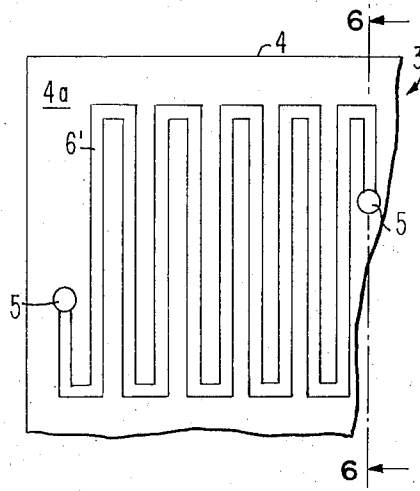


FIG. 5

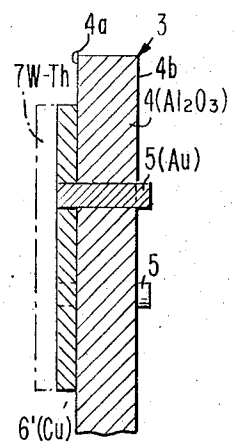
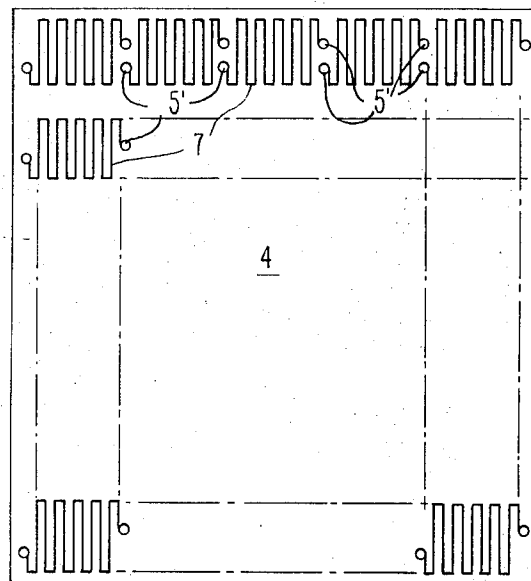
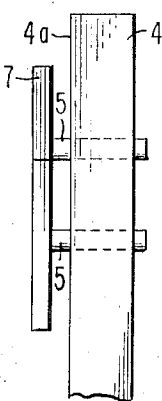


FIG. 6

FIG. 8

FIG. 7



METHOD FOR MAKING THIN FILM TUNGSTEN-THORIUM ALLOY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is related to a method for making tungsten-thorium alloys and in particular a method for making thin film tungsten-thorium alloys.

2. Description of the Prior Art

It is well known in the prior art to use tungsten-thorium alloy as wire filaments for incandescent lamps, displays and the like because it can be made in a single crystal state. A thermal compression extruding method is used in the prior art for making these devices. It requires the providing of a powdery mixture of the tungsten and thorium ingredients, concurrently subjecting the mixture to high temperature, circa 2,000°C., and high pressure conditions, and extruding the mixture under these conditions through a wire forming die. As such, the extruded wire is in a polycrystal state. In order to make it a single crystal, the wire is subsequently annealed at an elevated temperature, e.g., 1,800°C., for approximately 2 hours. As is well known to those skilled in the art, a single crystal tungsten-thorium alloy filament has an extended life expectancy as compared to a polycrystal one.

The aforescribed prior art extrusion method is not conducive to making thin film W—Th alloys such as thin film plates and sheets, or layers, and particularly thin films of 10 microns or less. Thus, for example, it is not conducive to making a thin film W—Th alloy in the form of a protective layer or coating used for anti-thermal, anti-corrosive, and/or wear resistance purposes. Furthermore, this prior art method cannot be employed for making W—Th alloy components used in printed and/or integrated circuits.

It is known in the prior art to make planar, i.e., printed circuit type, pure W filaments by chemical vapor deposition. Because W has a high boiling point, i.e., 5,660°C., chemical vapor deposition is not particularly suitable for depositing pure W in these type applications. Accordingly, a W compound, such as WF_6 , is used in combination with a suitable reducing agent, e.g., H, to provide the pure tungsten deposit at temperatures of 600°C. approximately. In addition, the pure W filament when formed is in a polycrystal state. As is well known to those familiar with the art, pure W cannot be produced in single crystal state form. Hence, the polycrystal pure W filament suffers from the defect of short life expectancy.

It has been suggested to make printed circuit type filaments of a W—Th filament by the method of chemical vapor deposition. However, because the boiling point of Th is also relatively high, i.e., 4,790°C., this method is not suitable for these applications. Moreover, the system would require that the W and Th each to be compounded with other elements and a suitable and compatible reducing agent to be utilized. Thus, the system complexity is increased and thereby the system's reliability is decreased. Hence, the use of chemical vapor deposition for making thin film W—Th alloy bodies is not deemed practical.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a method of making single crystal or polycrystal thin film tungsten-thorium alloys.

Another object of this invention is to provide a method for making thin film W—Th alloys as incandescent filaments.

Still another object of this invention is to provide a method of making thin film W—Th alloys as components for printed circuits and/or integrated circuits.

Still another object of this invention is to provide a method for making thin film W—Th alloy bodies and in particular bodies which are substantially planar such as plates or sheets and the like.

Another object of this invention is to provide a method for making thin film W—Th alloy bodies as a coating or layer for an object and in particular protective coating used for anti-thermal, anti-corrosive and/or wear resistance purposes.

The method for making a thin film tungsten-thorium alloy according to the invention includes providing a plating bath comprised of a first aqueous solution of WO_3 , $NaPO_4$ and H_2O at a predetermined temperature. The bath has immersed in it predetermined cathode and anode electrode means. The cathode and anode electrode means are energized to provide a predetermined current density for a predetermined time period. During the energizing, another aqueous solution of a predetermined concentration of $Th(SO_4)_2$ is added to the bath at a predetermined rate to produce plating of the thin film tungsten-thorium alloy on an appropriate substrate which may be part of the cathode electrode means.

The foregoing and other objects, features, and advantages of the invention will be apparent from the following more particular description of the preferred embodiments of the invention, as illustrated in the accompanying drawing.

DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective view of a member used to apply thereto a thin film W—Th alloy according to the method of the present invention;

FIG. 2 is a perspective view of the W—Th alloy layer or coating applied to the member of FIG. 1;

FIG. 3 is a perspective view of a thin film W—Th alloy body after the member of FIG. 1 has been removed from the structure of FIG. 2;

FIG. 4 is an enlarged partial perspective view of another member useful in applying thereto a W—Th alloy according to the method of the present invention;

FIG. 5 is an enlarged partial front view of the member of FIG. 4 at a different stage of its formation;

FIG. 6 is an enlarged partial cross-sectional view of the member of FIG. 5 taken along the line 6—6 thereof;

FIG. 7 is an enlarged partial cross-sectional view of a thin film W—Th alloy filament formed on the member of FIGS. 5—6 according to the method of the present invention; and

FIG. 8 is an enlarged front view, shown partially in schematic, of a W—Th alloy filament display of FIG. 7.

In the figures, like elements are designated with similar reference numerals.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method for making a thin film tungsten-thorium alloy according to the present invention broadly contemplates electrodepositing, i.e., electroplating, a W—Th alloy by passing an electric current through a

heated bath consisting essentially of an aqueous solution of WO_3 and Na_3PO_4 and to which is added at a controlled rate a second aqueous solution of $\text{Th}(\text{SO}_4)_2$. Preferably, the aqueous solution of WO_3 , Na_3PO_4 and H_2O is in the ratio of the order of about 35:100:200 parts by weight, respectively; a 10 percent concentration of $\text{Th}(\text{SO}_4)_2$ is used in the second aqueous solution; and the bath is heated to a temperature of about 80°C .

The W—Th alloy is deposited on a substrate which is immersed in the bath. The substrate is conductive and may be permanent, temporary or partially temporary depending on the particular application. For example, in the application where the W—Th alloy is to be used as a protective type coating such as a thermal, anti-corrosive and/or anti-abrasive type for an object, the object would be immersed in the bath. As such, the object acts as the substrate and is of the permanent type. In an application, for example, where an W—Th alloy body is required such as W—Th sheet it can be deposited on a planar substrate which substrate is subsequently removed by, for example, a suitable etchant or other means. Since the substrate is conductive, it also acts as the cathode electrode of the electroplating system.

Accordingly, referring to FIG. 1, member 1 is a planar conductive body of, for example, Cu. Assume, for example, it is desired to coat surface 1a of member 1 with a thin film W—Th alloy. An appropriate anti-plating masking process is used to mask the opposite surface and edges of member 1. In addition, a suitable lead-in conductor is attached to the member 1 in non-obstructing relationship with surface 1a so that member 1 will also serve as the cathode electrode. The anode electrode, not shown, and cathode electrode are immersed in the aforescribed heated bath and connected to a suitable electrical supply that passes the plating current through the bath at the same time, i.e., concurrently, the $\text{Th}(\text{SO}_4)_2$ aqueous solution is being added. As a result, the W—Th alloy coating 2, cf. FIG. 2, is deposited on the surface 1a of member 1.

In certain applications the member 1 is retained after the electrodeposition such as, for example, the aforementioned applications where the coating 2 is a protective type coating.

However, if it is desired in certain applications to provide a body, such as flat sheet of the W—Th alloy, the member 1 is removed by any suitable means such as etching with a compatible etchant that removes the member 1 without adverse effects to the W—Th alloy. For the given copper substrate example, the etchant may, for example, be FeCl_3 . As a result, the W—Th alloy member 2, cf. FIG. 3, becomes an independent body which is substantially rigid and of high strength even at thicknesses of 10 microns or less.

In certain applications the W—Th alloy is annealed after the electrodeposition process. One such application is for use of the W—Th alloy as an incandescent filament where annealing changes the W—Th alloy to a single crystal state. The annealing may be done with or without the member 1 being attached to the W—Th alloy film 2. Preferably, the annealing is done below the melting point of the member 1 when it is attached to the film 2. Thus, for the given Cu example which has a melting point of $1,083^\circ\text{C}$., the annealing temperature may be 900°C ., for example. If the member 1 is not at-

tached, then the film 2 may be annealed at higher temperatures, e.g., $1,800^\circ\text{C}$.

There is next described another embodiment of the present invention for making thin film tungsten filaments for an alpha-numeric character display in which a part of the substrate is temporarily provided during the electrodeposition process and subsequently removed. Referring to FIG. 4, the substrate 3 includes a ceramic planar member 4. A preferred and suitable ceramic for this purpose is Al_2O_3 . Imbedded in the ceramic member are an array of conductive posts 5 of a suitable material. Preferably, posts 5 are high temperature materials such as Au. Alternatively, posts 5 may be of W. The posts 5 may be formed, for example, by drilling holes in the ceramic member 4 at spatial locations corresponding to the desired post array. Next, the insides and around the periphery of the holes so formed are electroplated with gold using well known sensitizing and electroplating techniques.

Substrate 3 also includes a conductive layer 6 which is different from the material of the posts 5. Preferably the layer 6 is copper. It is formed on the face of the ceramic member 4 by printed circuit deposition techniques. The exposed surface of the layer 6 is co-planar with the end surfaces of the posts 5 which protrude above the front surface 4a, as viewed in FIG. 4. This can be done, for example, by controlling the thickness of the layer 6 during its deposition and/or by subsequent lapping.

Referring now to FIGS. 5 and 6, in the preferred embodiment, the copper layer 6 is next processed using well known printed circuit techniques to form a composite conductive pattern 6' made up of individual conductive segments formed between mutually exclusive pairs of posts 5. One such technique which is preferred is to form the pattern using photoresist methods. The composite pattern corresponds to the pattern desired for the W—Th alloy filament to be formed on the substrate 3 and more particularly on the members 5, 6' thereof. The pattern 6' comprises a rectangular array of individual segments each of which is square wave-shaped in form and only one segment of which is shown in FIGS. 5 and 6 for sake of clarity. By way of example, a typical array includes 35 such segments arranged in a 5×7 matrix as will be apparent hereinafter. Preferably, the ends of post 5 protruding outwardly from the rear surface 4b of member 4 are coated with a suitable masking material to prevent depositing of the W—Th alloy thereat in the subsequent electroplating, i.e., electrodeposition, process.

In accordance with the principles of the present invention, an aqueous solution of WO_3 , Na_3PO_4 , and H_2O is provided as part of the plating bath. The bath is heated to an elevated temperature of approximately 80°C . Immersed in the bath is the substrate 3 of FIG. 5. The copper segments 6' and gold posts 5 act as the cathode of the electroplating system. A platinum anode is also immersed into the solution and a plating current density of approximately 160 milliamperes per square inch is conducted between the electrodes and through the bath. An appropriate electrical supply is provided for this purpose. A plating time of between 15 to 30 minutes is utilized. During the plating process an aqueous solution having a concentration of about 10 percent of $\text{Th}(\text{SO}_4)_2$ is added to and is part of the plating bath at the rate of approximately 20 drops per minute. As shown in phantom outline, the tungsten-thorium

alloy film 7 is deposited at the completion of the plating process on the exposed copper pattern 6' and exposed gold end surfaces of the posts 5 of the substrate 3 and thus, has the desired display pattern configuration.

After the layer 7 has been deposited and the composite structure of elements 4, 5, 6' and 7 is removed from the bath, an etching process takes place with an etchant that attacks only the conductive segments 6' but does not effect the ceramic member 4, W—Th alloy film 7, or posts 5. For the preferred choice of materials, to wit: Cu, Al_2O_3 and Au, an etchant such as the aforementioned FeCl_3 is preferred. As a result, the conductive segments 6' are removed and the W—Th filament pattern 7 is affixedly supported to the posts 5 as shown in FIG. 7.

Subsequently, the film 7 is annealed to place the film 7 in a single crystal state.

In one way of annealing, a temperature is utilized which is below the temperature associated with the material of the members 4, 5 and 7 having the lowest melting point. For the preferred materials of Al_2O_3 , Au and W—Th, a suitable annealing temperature is 900°C ., for example.

A preferred way of annealing the W—Th filament pattern 7 is to pass an electrical current through it while it is located in a vacuum or inert atmosphere. The relative high resistance W—Th generates heats and incandescences. The W—Th is thus at a very high temperature which is controlled by the amount of current being passed. Preferably, the temperature is about $1,800^\circ\text{C}$.. Even though the material of posts 5 may have a melting point below this temperature, they will not be adversely affected if they are judiciously selected to have a low resistance, i.e., be a good conductor such as gold, so that the heat generated therein by the current passing through the posts 5 is at a temperature well below their melting point. This operation may be performed prior to mounting the W—Th filament pattern 7 in its associated display housing, or alternatively may be performed after it is mounted in the housing and the housing is evacuated.

After annealing, a suitable printed circuit conductive pattern may be provided on the rear surface 4b of the ceramic member 4 to provide lead-in electrode connections to the individual filament segments located on the front face 4a, cf. FIG. 8. When incorporated in a suitable evacuated display housing, the filament segments via their respective electrode connections are selectively energized to provide the desired character to be read out. In FIG. 8, the reference numbers 5' indicate the W—Th alloy plated end surfaces of the posts 5 for sake of clarity.

An example of the plating bath suitable for use in the present method, is as follows:

WO_3	35 grams
Na_3PO_4	100 grams
H_2O	200 grams

In one such thin film W—Th alloy built in accordance with the principles of the present invention, the film was approximately 4 microns thick.

It should be understood that alternatively a co-extensive W—Th alloy thin film can be deposited directly on the exposed surface 6a of layer 6 and the exposed co-planar end surfaces of posts 5 of substrate 3 shown in FIG. 4 in accordance with the principles of

the inventive method. After the W—Th film is deposited, the pattern 7 is formed using printed circuit techniques. Preferably, a conventional photoresist is applied to the exposed surface of the deposited W—Th film. Photoresist is exposed through a mask containing the desired conductive display pattern and developed. Thereafter, subsequent etching processes are employed to remove the unwanted portions of the W—Th alloy film and to remove the temporary copper layer 6. A mixture of $\text{K}_3\text{Fe}(\text{CN})_6$ and NaOH is a suitable etchant for removing the W—Th alloy and FeCl_3 is a suitable etchant for removing the copper layer 6. Thereafter, the remaining W—Th filament pattern is annealed to place the W—Th alloy in a single crystal state. As a result, a W—Th alloy filament display identical to the one shown in FIGS. 7—8 is provided.

Thus, it has been demonstrated from the foregoing description that the W—Th alloy in some applications remains on the object on which it is deposited, cf. FIG. 2. In other applications, it is completely removed from the object, cf. FIG. 3. Still in other applications, it is only partially removed, cf. FIGS. 7—8.

However, while the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

I claim:

1. The method of electrodepositing thin film W—Th alloy on a conductive substrate, said method comprising the steps of:

passing an electric current through a heated plating bath containing the substrate, said substrate forming the cathode of the electrical system used to pass said electrical current, said bath comprising two aqueous solutions, the first solution consisting of WO_3 , Na_3PO_4 and H_2O , and the second solution consisting of $\text{Th}(\text{SO}_4)_2$ and H_2O , and adding concurrently to passing said current said second solution to said first solution at a predetermined rate.

2. The method of claim 1, wherein the WO_3 , Na_3PO_4 and H_2O of said first solution are in the ratio of the order of about 35:100:200, respectively, by weight, and said second solution has a 10 percent concentration of $\text{Th}(\text{SO}_4)_2$.

3. The method of claim 2, wherein said bath is at a temperature of about 80°C .

4. The method of claim 3, wherein said electric current has a current density of about 160 milliamperes.

5. The method of claim 1, further comprising the subsequent step of annealing said thin film W—Th alloy to place said alloy in a single crystal state.

6. The method according to claim 2, wherein said predetermined rate is about 20 drops per minute.

7. The method according to claim 1, wherein said current is passed through said bath for a predetermined time period of not more than 30 minutes or less than 15 minutes.

8. The method of claim 1, wherein said W—Th alloy is used as an incandescent filament.

9. The method according to claim 1, comprising in combination therewith the subsequent step of separating the W—Th film from said substrate.

10. The method according to claim 1, comprising in combination therewith the subsequent step of etching the substrate to separate the W—Th film therefrom.

11. The method of making a single crystal thin film W—Th alloy, said method comprising the steps of:

providing a first aqueous solution consisting of WO_3 , Na_3PO_4 and H_2O in the ratio of the order of about 35:100:200, respectively, by weight,

providing a second aqueous solution consisting of $\text{Th}(\text{SO}_4)_2$ and H_2O , said second solution having a 10 percent concentration of $\text{Th}(\text{SO}_4)_2$,

adding said second solution to said first solution at the rate of about 20 drops per minute to provide an electroplating bath,

heating said bath to maintain it at a temperature of about $80^\circ\text{C}.$,

immersing predetermined anode and cathode electroplating means in said bath, said cathode elec-

trode means comprising a substrate on which the W—Th film is to be formed,

passing an electric current having a current density of about 160 milliamperes between the two said electrode means and through said bath to electrodeposit said thin film W—Th alloy on the substrate, said steps of passing and adding being performed concurrently,

removing the substrate having thin film deposited therein, and

subsequently annealing said thin film W—Th alloy at a temperature of about $1,800^\circ\text{C}.$ to place said W—Th alloy in a single crystal state.

12. The method according to claim 11, further comprising the step of:

removing at least part of said substrate prior to the step of annealing.

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