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Archer et al.

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[54] **METHOD FOR PRODUCING REFRACTORY METAL MEMBERS BY VAPOR DEPOSITION, AND RESULTING PRODUCT**

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[51] **Int. Cl.**..... **B44d 1/18**

[58] **Field of Search**..... 117/107.1, 107.2 R, 107, 117/227, 231, 219, 224, 225, 217; 75/176, 177

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[57] **ABSTRACT**

Method of preparing tungsten, molybdenum or zirconium members such as can be used in light sources wherein a metallic member has vapor-deposited thereon additional metal by a chemical vapor deposition process. For the process of fabrication of tungsten filament wire, the required dopants can also be chemically vapor deposited in the desired concentration. There is also provided the product produced by this process. The method of chemical vapor deposition of members is particularly adapted to continuous production techniques wherein after deposition, the member is mechanically reduced to its original cross-section area and wherein a portion of the mechanically reduced material has deposited thereon additional material to provide a continuous chemical vapor deposition method preparation.

4 Claims, 2 Drawing Figures

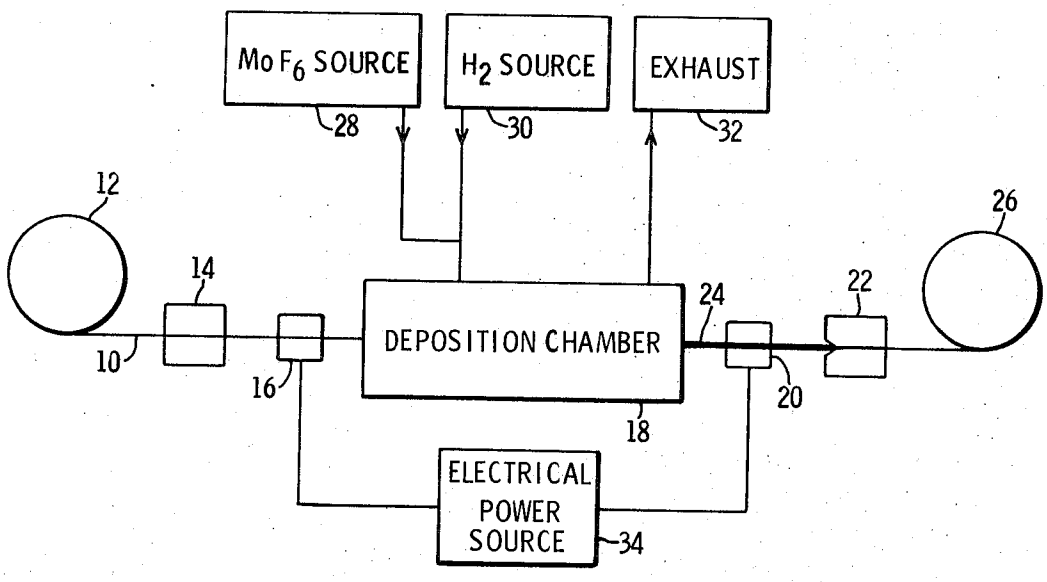
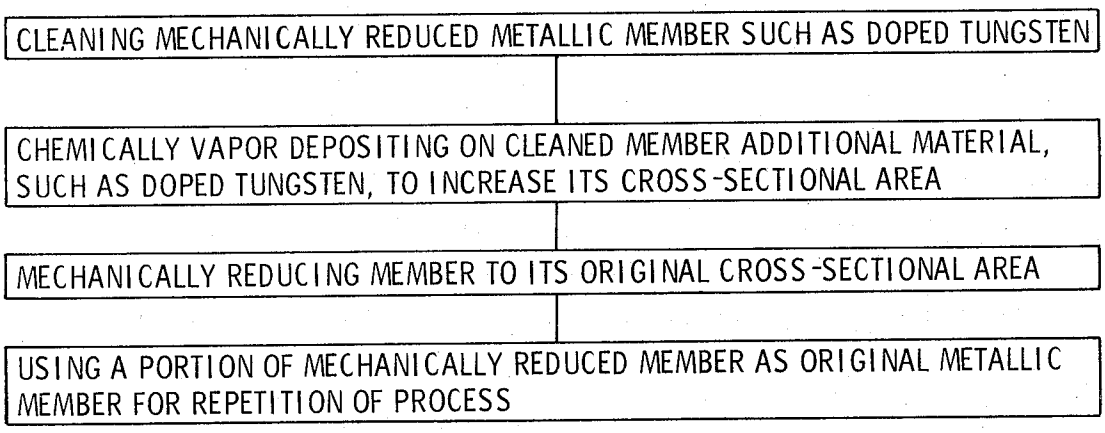


FIG. 1


CLEANING MECHANICALLY REDUCED METALLIC MEMBER SUCH AS DOPED TUNGSTEN
CHEMICALLY VAPOR DEPOSITING ON CLEANED MEMBER ADDITIONAL MATERIAL, SUCH AS DOPED TUNGSTEN, TO INCREASE ITS CROSS-SECTIONAL AREA
MECHANICALLY REDUCING MEMBER TO ITS ORIGINAL CROSS-SECTIONAL AREA
USING A PORTION OF MECHANICALLY REDUCED MEMBER AS ORIGINAL METALLIC MEMBER FOR REPETITION OF PROCESS

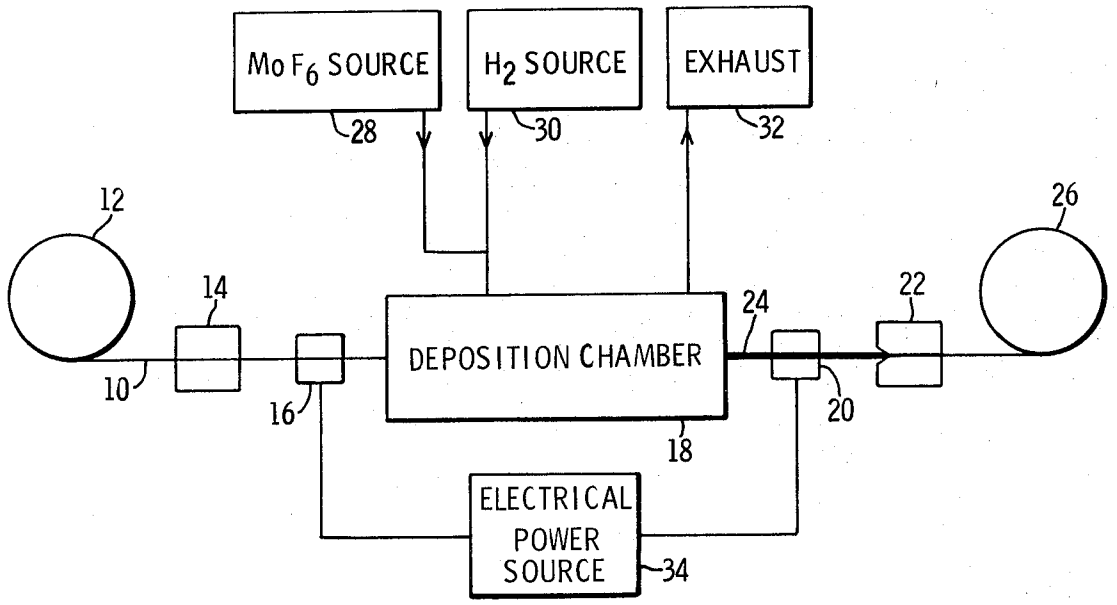

Mo F6 SOURCE
28
H2 SOURCE
30
EXHAUST
32
12
26
14
22
24
DEPOSITION CHAMBER
10
16
20
18
ELECTRICAL POWER SOURCE
34

FIG. 2

METHOD FOR PRODUCING REFRACTORY METAL MEMBERS BY VAPOR DEPOSITION, AND RESULTING PRODUCT

CROSS REFERENCE TO RELATED APPLICATION

In copending application, Ser. No. 210,952, filed Concurrently herewith by R. Stickler and L. E. Brecher, and owned by the present assignee is disclosed a method for preparing doped tungsten powders by the simultaneous chemical vapor deposition of tungsten and dopant.

BACKGROUND OF THE INVENTION

This invention relates to preparation of metallic members such as are used in the fabrication of lamps and, more particularly, the preparation of such metallic members by chemical vapor deposition.

Chemical vapor deposition as used herein, is a reaction between gases at a heated surface which deposits one or more of the constituents of the gases on the heated surface. This process is a chemical reaction, differing from the part of the well known tungsten-halogen cycle which uses thermal decomposition of tungsten-halogen gas to deposit tungsten on a lamp filament. The decomposition in the tungsten-halogen cycle is described in U.S. Pat. No. 2,883,571 dated Mar. 3, 1958.

Zirconium, molybdenum, tungsten, and doped tungsten members are all normally fabricated by similar powder metallurgy processes. In these processes the ore is converted into a purified oxide, which oxide is then reduced to the metal. In the case of doped tungsten for filament wire, the dopants are mixed in with the oxide prior to reduction. The reduced powder is then compacted and sintered to a high-density mass or sintered ingot. The ingot is swaged down, typically by many steps each of which successively reduces cross-sectional area. The material is then further reduced by drawing, again typically through a series of successive reductions. These processes are expensive due to the labor and equipment required, and in the case of tungsten, more than 50 percent material loss normally occurs due to oxidation and breakage in the many high temperatures steps which are required.

The chemical vapor deposition of undoped tungsten, and of zirconium, and molybdenum by hydrogen reduction of their halides is known, but this technique has apparently never heretofore been used for continuous production. In the known noncontinuous preocesses, the member is placed in a chamber, the air in the chamber evacuated, the member heated and the reaction gases introduced, the chamber again evacuated, the member allowed to cool, air allowed to enter the chamber, and the member removed. Non-continuous production is slow and expensive due to time required for heatup, and cool down, and problems in changing to an atmosphere containing H_2 and back to air. In a non-continuous process production at near final size is generally not practical.

The use of dopants to improve performance of tungsten filament wire is also known. In the prior art, however, dopants are not homogeneously introduced, being generally mixed in micron sized grains of powder. The compacting, sintering, and the multiple reductions, first by swaging and later by drawing, distributes the dopant particles somewhat more evenly and thereby reduces offsetting and sagging of the wire, but the dopants still are not distributed in the tungsten in a homogeneous manner. Apparently because of the initial inhomogeneity, expensive multiple reductions are required to distort the original dopant particles in order to produce filament quality wire. Even after the multiple reductions, the remaining nonhomogeneity renders the wire more likely to fail by either offsetting or sagging.

SUMMARY OF THE INVENTION

There is provided an improved method for preparing elongated tungsten, doped tungsten, zirconium or molyddenum molybdenum wherein the member of the material which is being processed is heated to a temperature of at least 450°C in an atmosphere which comprises hydrogen and a halide of the same metal of the member being processed. The atmosphere is heated to a temperature at least equal to the boiling point of the halide. Contact with the heated member causes the halide to react with the hydrogen in the atmosphere at the surface of the heated member to deposit thereon the metal component of the halide. This deposition is continued until a predetermined thickness of deposited metal is obtained. This deposition is practiced with a continuous process and/or a process where tungsten and dopant are simultaneously or alternately deposited. In the continuous process, a common moving means moves the member into, and, after a predetermined time, out of the atmosphere. The moving means may also be used to pass the member through a mechanical reducing means where the member's cross section is reduced to about its original cross section, such that a portion of the resulting member may be recycled for repetition of the process.

In the processing of doped tungsten, gas comprising at least the metallic constituents of preselected dopant and at a predetermined temperature of at least 100°C is introduced into contact with the heated member, which gas upon contact with the heated member will deposit the dopant on the heated member in an atom ratio of dopant to tungsten of between 1 ppm and 500 ppm.

BRIEF DESCRIPTION OF THE DRAWING

For a better understanding of the invention, reference may be had to the preferred embodiment, exemplary of the invention, shown in the accompanying drawings in which:

FIG. 1 is a flow chart illustrating the steps of the method used to prepare a member, such as doped tungsten for lamp filaments.

FIG. 2 is a schematic diagram illustrating the preparation of molybdenum wire by a continuous process where the wire cross section is the same on both the feed and the take-up reels, but the take-up reel will have a greater length of wire due to the material added by deposition.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to FIG. 1 there is shown a flow chart of typical steps in the production of a member such as filament quality tungsten wire in accordance with this invention. The first step is preferably a cleaning operation. The initial member generally has on its surface a

graphite lubricant applied in previous drawing. The member is placed in a bath containing a 50—50 mixture of KNO_3-KNO_2 at greater than 400°C where the graphite lubricant is removed. Following the bath any KNO-KNO_2 adhering to the surface of the member is removed by a water rinse.

In the next step the cleaned member is heated to preferably between 450°–1,200°C in an atmosphere where, depending on the particular gases introduced, reactions such as are described in the following equations deposit additional doped tungsten:

$WF_6+3H_2 \rightarrow W+6HF$
$WCl_6+3H_2 \rightarrow W+6HCl$
$WOCl_4+3H_2 \rightarrow W+4HCl+H_2O$
$2WBr_5+5H_2 \rightarrow 2W+10HBr$
$ZrCl_4+2H_2O \rightarrow ZrO_2+4HCl$
$ThCl_4+2H_2O \rightarrow ThO_2+4HCl$
$2AlCl_3+3H_2 \rightarrow Al_2O_3+6HCl$
$SiCl_4+2H_2O \rightarrow SiO_2+4HCl$

It will be noted that water vapor for doping reactions may be introduced through the use of an oxy halide. The following reactions may also directly or indirectly occur:

K (vapor) → K (dissolved in tungsten)
K (vapor)+HCl → KCl (in tungsten)+½ H_2
$2KCl+H_2O \rightarrow K_2O+2HCl$

The exact reaction when potassium is introduced either in the form of KCl, or K (vapor), is not known, but experiments have shown the potassium-doped tungsten has resulted when eigher KCl or K (vapor) is introduced. Sodium or lithium can be introduced in a manner similar to potassium. For doped tungsten deposition the pressure of the atmosphere is maintained at about 5–800 torrs. Gas flow rates and deposition times are preferably selected to give from 5–30 percent increase in cross-sectional area of the member.

On completion of deposition, the quantity of the filament quality tungsten has been increased and the process could be considered ended at this point. It is convenient, however, to render the process self-sustaining as far as the initial doped tungsten is concerned. This is done by reducing the tungsten member's cross section, by for example drawing or swaging, to its original size. The increased length of the member which has resulted from the preceding step is then cut off and doped tungsten member of the original length is reinserted at the beginning of the process. The end product is the increased length of filament quality tungsten. While the steps just described can be performed by batch processing, they can also be performed continuously.

With reference to FIG. **2** there is shown a diagram of a system for continuous production of a 25 mil (0.635 mm) molybdenum member. In this system, an original 25 mil (0.635 mm) molybdenum member **10** is fed from a feed reel **12** which is preferably heated greater than 200°C. The member is pulled through a cleaning means **14** which preferably includes KNO_3-KNO_2 heated to greater than 400°C and a water rinse, then into a first electrical contact **16** which is preferably a mercury bath, into a deposition chamber **18** which contains an atmosphere heated to between 100° and 400°C, through a second electrical contact **20** which is similar to the first electrical contact, through mechanical reducing means **22,** such as a diamond die, reduce the now enlarged member **24** to the original 25 mil (0.635 mm) diameter, with the mechanical reducing means being heated preferably to greater than 400°C, and then onto a take-up reel **26** which is preferably heated to greater than 200°C.

The MoF_6 source **28** and a H_2 source **30** are sufficient to supply gas flow rates of up to 500 standard cc's of MoF_6 and 1,500 standard cc's of H_2. The H_2 source **30** is used to permit prolonged periods of deposition, by replenishing the H_2 atmosphere which is otherwise depleted by the halide-hydrogen reaction. The flow rates of the halide gas and of the H_2 gas are preselected to give a predetermined concentration of the halide gas in the deposition chamber **18,** and the mol ratio of H_2 to halide is at least 3 to maintain the H_2 atmosphere. An exhaust **32** is preferably controlled to provide approximately one atmosphere pressure inside the deposition chamber **18,** but pressures from 5 torrs to 5 atmospheres be used for deposition of undoped material. An electrical power source **34** is used which is of sufficient capacity to heat the 25 mil (0.635 mm) molybdenum wire to between 450° and 1200°C using the resistance of the molybdenum wire itself to generate the required heat.

Molybdenum can be deposited from its chloride in such a system merely by changing the MoF_6 source to a $MoCl_6$ source and, in order to keep the halide in gaseous form, maintaining the atmosphere at 300°–400°C. The continuous system for tungsten or zirconium member production is quite similar except that the halide source would be a WF_6 source with a room temperature to 400°C atmosphere a WCl_6 source with a 350°–400°C atmosphere or a $ZrCl_4$ source with a 350°–400°C atmosphere.

Depositions of molybdenum and zirconium, and undoped tungsten are described in the following equations:

$WF_6+3H_2 \rightarrow W+6HF$
$WCl_6+3H_2 \rightarrow W+6HCl$
$MoF_6+3H_2 \rightarrow Mo+6HF$
$2MoCl_5+5H_2 \rightarrow 2Mo+10HCl$
$ZrCl_4+2H_2 \rightarrow Zr+4HCl$

The system for continuous production of doped tungsten is also similar to the system in FIG. **2** with the exception that a source of the gas comprising at least the metallic constituents of the preselected dopant is also required and a pressure of 5–800 torrs is used. A first predetermined temperature which is sufficient to allow hydrogen reduction of the tungsten halide and which is at least 450°C is maintained on the member. A second predetermined temperature which is sufficient to maintain both the tungsten halide contained in the hydrogen atmosphere and the gas comprising the metallic constituents of the dopant in gaseous form and which is at least 100°C is maintained in the atmosphere. The second predetermined temperature is at least 300°C when $SiCl_4$ or $AlCl_3$ are used and at least 100°C is required in the case of all of the other dopants described herein.

For continuous deposition of either doped or undoped material, the members are preferably processed at about the size to be used in lamp fabrication.

The following specific examples describe in greater detail various combinations which are possible using this method, and the first six examples demonstrate method of preparation and, when dopant and tungsten are deposited simultaneously, these examples set forth a method of achieving the homogeneous doped tungsten composition. Flow rates in all the examples are on the basis of a two foot long deposition chamber and if

a longer or shorter deposition chamber is used, the gas flow rates should be adjusted in direct proportion.

EXAMPLE I

The following conditions will produce a deposition rate of about 5 mils per hour on a 9 mil diameter tungsten member which is doped with silica, alumina and potassium: a temperature of the chamber **18** of approximately 400°C, a temperature of the member **10** of approximately 600°C, a pressure in the chamber **18** of approximately 20 torrs, a flow rate of $SiCl_4$ of 0.0014 standard cubic centimeters (scc) per minute, a flow rate of $AlCl_3$ of 0.073 gram per minute, a flow rate of potassium of 0.12 gram per minute, a flow rate of hydrogen of 1,430 scc per minute, a flow rate of water vapor of 2 scc per minute, and a flow rate of WCl_6 of 0.53 gram per minute.

EXAMPLE II

A deposition rate of about 25 mils per hour on a 9 mil diameter thoria doped tungsten member is obtained as follows: a temperature of the chamber **18** of approximately 100°C, a temperature of the member **10** of 850°C, a pressure in the chamber **18** of 5 torrs, a flow rate of hydrogen of 7,150 scc per minute, a flow rate of water vapor of 10 scc per minute, a flow rate of WCl_6 of 2.65 grams per minute, and a flow rate of $ThCl_4$ as produced by 150 scc per minute of helium flowing through a canister containing $ThCl_4$ at 170°F and at one atmosphere.

EXAMPLE III

Zirconia doped tungsten is produced by the procedures specified in Example II by replacing the $ThCl_4$ with $ZrCl_4$.

EXAMPLE IV

A deposition thickness of about 5 mils is obtained in about 6 minutes on a 90 mil diameter tungsten member doped with silica, alumina and sodium as follows: a temperature of the outer edge of the chamber **18** of 300°C, a temperature of the member **10** of 700°C, a pressure in the chamber **18** of 800 torrs, a flow rate of hydrogen of 14,300 scc per minute, a flow rate of $SiCl_4$ of 0.014 scc per minute, a flow rate of $AlCl_3$ of 0.73 gm/min., a flow rate of Na of 0.69 gm/min., and a flow rate of WCl_6 of 5.3 gms/min.

EXAMPLE V

Tungsten doped with silica, alumina and lithium is produced in the same manner as Example IV except that the flow rate of sodium is replaced with a flow rate of lithium of 0.22 gram per minute.

EXAMPLE VI

A 9 mil diameter tungsten wire doped with silica, alumina, and potassium is precleaned, increased to 10 mil diameter by deposition in the 2 foot long chamber and reduced by a die to 9 mil diameter with deposition conditions as follows: a wire velocity through the precleaning, deposition chamber, and into the die of about 200 foot per hour, a temperature at the outer edge of the chamber **18** of 300°C, a temperature of the wire **10** of 450°C, a pressure in the chamber **18** of 10 torrs, a flow rate of $SiCl_4$ of 0.014 scc per minute, a flow rate of $AlCl_3$ of 0.73 gram per minute, a flow rate of potassium of 1.2 grams per minute, a flow rate of hydrogen of 14,300 scc per minute, a flow rate of water vapor of 20 scc per minute, and a flow rate of WF_6 of 3.98 grams per minute.

All of the depositions in the six preceding examples are calculated to give tungsten doped with about the following concentration of dopant, when that dopant is included in the conposition: silicon 1 ppm, and all other dopants in amount of 100 ppm each. Flow rates of the gas comprising the metallic constituent of the dopant can be adjusted to give a predetermined concentration of the gas in the chamber **18**, and thereby vary the concentration of any of the dopants in the range of 1 ppm to 500 ppm.

EXAMPLE VII

A continuous deposition rate of approximately 80 mils per hour of molybdenum on a 25 mil diameter member **10** is obtained as follows: a temperature at the outer edge of the chamber **18** of 400°C, a temperature of the member **10** of 800°C, a pressure in the chamber **18** of 1 atmosphere, a flow rate of hydrogen of 1,500 scc per minute, and the flow rate of MoF_6 of 500 scc per minute.

EXAMPLE VIII

A continuous deposition rate of about 300 mils per hour of tungsten on a 25 mil diameter member is obtained as follows: the chamber **18** is maintained at room temperature, a temperature of the member **10** at 700°C, a pressure of the chamber **18** at 2 atmospheres, a flow rate of hydrogen of 6,000 scc per minute, and a flow rate of MF_6 of 2,000 scc per minute.

EXAMPLE IX

A continuous deposition rate of about 80 mils per hour is obtained on a 1 mil by 40 mil zirconium foil as follows: a temperature of the chamber **18** of 400°C, a temperature of the foil of 800°C, pressure in the chamber **18** of approximately 1 atmosphere, a flow rate of hydrogen of 1,500 scc per minute, and a flow rate of ZrF_6 of 500 scc per minute.

EXAMPLE X

A continuous deposition rate of about 5 mils per hour of molybdenum on a 100 mil diameter member is obtained as follows: a temperature of the chamber **18** of 600°C, a temperature of the member **10** of 600°C, a pressure in the chamber **18** of 1 atmosphere, a flow rate of hydrogen of 6,000 scc per minute, and a flow rate of $MoCl_6$ of 2,000 scc per minute. It should be noted that, in this example, some deposition will occur on the chamber walls.

The deposition rate which is given in some of the preceding examples occurs on all surfaces of the member and accordingly a diameter of the member **10** increases at twice the deposition rate.

The temperature at the outer edge of the chamber atmosphere is at least high enough to prevent condensation of the particular gases used, and is preferably not more than 400°C to prevent deposition on, for example, the chamber walls. When the temperature of the member **10** is above the temperature of the chamber **18**, the member **10** must be directly heated and is preferably self-resistance heated by passing electric current directly through the member **10**. The member **10** may also be directly heated by conduction from a heating

means in contact with the member **10** or by induction heating.

We claim as our invention:

1. A method of preparing a tungsten member containing one metal selected from the group consisting of potassium, sodium, and lithium together with at least one metal oxide selected from the group consisting of silica and alumina as dopants from which lamp filament wire can be prepared, which method comprises:

a. heating an elongated doped tungsten member to a temperature of at least 450°C in an atmosphere comprising hydrogen, said atmosphere being heated to a temperature of 300°–400°C, and surrounding said heated tungsten member with tungsten halide gas which in the presence of said atmosphere comprising hydrogen will cause said tungsten halide gas to react upon contact with said heated tungsten member to deposit metallic tungsten thereon; and

b. introducing a vapor comprising one metal selected from the group consisting of K, Na and Li and at least one metal chloride selected from the group consisting of $AlCl_3$ and $SiCl_4$ into contact with said heated tungsten member to deposit preselected dopant on said heated member in an atom ratio of dopant to tungsten of between 1 ppm and 500 ppm.

2. The method as specified in claim **1**, wherein said elongated doped tungsten member is self-resistance heated by passing an electric current through said tungsten member.

3. A method of preparing a tungsten member containing one metal selected from the group consisting of potassium, sodium, and lithium together with at least one metal oxide selected from the group consisting of silica and alumina as dopants from which lamp filament wire can be prepared, which method comprises:

a. heating an elongated doped tungsten member to a temperature of 450°–1,200°C in an atmosphere comprising hydrogen, said atmosphere being a pressure of between 5 and 800 torrs and being heated to a temperature of 300°–400°C, and surrounding said heated tungsten member with tungsten halide gas selected from the group consisting of WCl_6 and WF_6 which in the presence of said atmosphere comprising hydrogen will cause said tungsten halide gas to react upon contact with said heated tungsten member to deposit metallic tungsten thereon; and

b. simultaneously introducing a vapor comprising one metal selected from the group consisting of K, Na and Li and at least one metal chloride selected from the group consisting of $AlCl_3$ and $SiCl_4$ into contact with said heated tungsten member to simultaneously deposit preselected dopant on said heated member in an atom ratio of dopant to tungsten of between 1 ppm and 500 ppm.

4. The method as specified in claim **3**, wherein said vapor consists essentially of water vapor, $SiCl_4$, $AlCl_3$, and K.

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