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(54) **Metal halide lamp and method of making the same.**

(57) A metal halide lamp is made by coating the inner surface of a luminous tube made of quartz glass with hafnium oxide, uranium oxide, hafnium oxide partially stabilized with yttrium oxide or uranium oxide partially stabilized with yttrium oxide by introducing therein a vapour of metal chelate containing hafnium (Hf), uranium (U) or yttrium (Y) and oxygen (O_2), nitrogen suboxide (N_2O) or ozone (O_3) as a reaction gas, and sealing the inside of the luminous tube with a halogenide of alkali metal, mercury and argon.

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BACKGROUND OF THE INVENTION:

1. Field of the Invention

The present invention relates to a quartz luminous tube to be used for a metal halide lamp, a high pressure mercury lamp, etc. and a method of making the same.

2. Description of the Prior Art

In order to improve luminous efficiency and coloring property of metal halide lamp, high pressure mercury lamp, etc., generally, a metal iodide or mercury and rare gas are sealed in the quartz luminous tube of such lamp (e.g. Japanese Patent Laid-open Publication No.50-12881/1975).

In a lamp of this kind, there is utilized a phenomenon that, during the illumination, the additive is present as a stable metal iodide in the vicinity of the luminous tube and does not corrode quartz or quartz glass, but at the central part of the arc, it is dissociated into metal atoms and iodine atoms, and vapor of said metal is excited in arc and radiates the spectrum peculiar to the metal.

In general, in a metal halide lamp or high pressure mercury lamp, during the operation of the lamp, the alkali metal or metal iodide sealed in the lamp turns into a state of being dissociated into a metal atom or an ion to cause a reaction with the quartz luminous tube, with the result that the quartz may be crystallized or discolored, giving rise to remarkable lowering of the lamp life. In order to dissolve these problems there is proposed a method of coating the inside of the quartz luminous tube (e.g. Japanese Patent Laid-open Publication No.53-35392/1978, Japanese Patent Publication No. 46-21432/1971, Japanese Patent Laid-open Publication No.50-27677/1975, U.S. Patent 3,390,298).

However, these conventional methods and coating materials have defects such that it is difficult to make the film having no defect, and no large improvement of the lamp life can be made.

SUMMARY OF THE INVENTION:

An object of the present invention is to provide a metal halide lamp having extremely excellent durability and a method of making the same.

In order to attain the above object, quartz glass tube is coated on its inner surface with an oxide which has a higher heat resistance than that of quartz and chemical stability, preferably any one of hafnium oxide (HfO_2), uranium oxide (UO_2), especially preferably HfO_2 or UO_2 partially stabilized with yttrium oxide (Y_2O_3), by a chemical vapour deposition (CVD) using metal chelate.

The CVD to be used in the present invention is to introduce a vapour of metal chelate containing hafnium (Hf), uranium (U), yttrium (Y), preferably hafnium acetyl acetone [$Hf(C_5H_7O_2)_4$], uranium acetyl acetone [$U(C_5H_7O_2)_4$], yttrium acetyl acetone [$Y(C_5H_7O_2)_3$],especially preferably hafnium dipivaloylmethane [$Hf(C_{11}H_{19}O_2)_4$], uranium dipivaloylmethane [$U(C_{11}H_{19}O_2)_4$], yttrium dipivaloylmethane [$Y(C_{11}H_{19}O_2)_3$], hafnium hexafluoroacetylacetone [$Hf(C_5HF_6O_2)_4$], uranium hexafluoroacetylacetone [$U(C_5HF_6O_2)_4$], yttrium hexafluoroacetylacetone [$Y(C_5HF_6O_2)_3$], and oxygen (O_2), nitrogen suboxide (N_2O), or ozone (O_3) as a reaction gas into a quartz glass tube which is subjected to reduced pressure, and heat the quartz glass tube or excite with plasma the inside of the quartz glass to form an oxide-of hafnium (HfO_2), an oxide of uranium (UO_2) or an oxide of hafnium which is partially stabilized with yttrium (Y_2O_3) on the inner wall of the quartz glass tube. The reason why HfO_2 or UO_2 obtained by such a method does not react with the metal halide, which is a material sealed in the lamp, at a high temperature during lighting of the lamp (during the lighting of the lamp, the inner wall of the quartz glass is about 950° C) is not only because HfO_2 or UO_2 is a substance having the higher melting point and higher density than the quartz glass (HfO_2's melting point is 2810° C and density is 9.68 g/cm^3, UO_2's melting point is 2800° C and density is 10.96 g/cm^3), but also because the oxide film formed by CVD using an active metal chelate is dense.

As described above, according to the present invention, a dense oxide film is formed by CVD using an active metal chelate. Accordingly, the present invention is a useful invention which can extend the life of the halide lamp to a great extent.

BRIEF DESCRIPTION OF THE DRAWINGS:

Fig. 1 schematic constitution views of a reduced pressure CVD apparatus in an embodiment of the present invention;

Fig. 2 is a sectional view of a metal halide lamp in an embodiment of the present invention;

Fig. 3 is a schematic constitution view of a high frequency plasma CVD apparatus in an embodiment of

the present invention; and

Fig. 4 is a schematic constitution view of an ECR plasma CVD apparatus using a microwave in an embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS:

Hereinafter, a method of making a metal halide lamp produced by coating an inside surface of a quartz luminous tube with an oxide film by CVD using a metal chelate is explained with reference to the drawings.

Fig. 1 shows a schematic view of a CVD apparatus. In the drawing, the part 11 is a luminous tube sealed with main electrodes at both ends, 12 is a heater for heating the luminous tube 11, 13 is a gas introducing tube for flowing a reaction gas, 14 is an exhaust pipe for gas, 15 is a bubbler containing a material gas, 16 is an introducing port for carrier gas, 17 is a pump for exhausting the luminous tube under reduced pressure.

First, the luminous tube is subjected to reduced pressure inside with a rotary pump 17 to remove adsorbed gases and the like. Next, the luminous tube is heated with the heater 12, a metal chelate is placed on the bubbler 15, the bubbler is heated, and the vapour thereof is introduced into the luminous tube 11 through the introducing port 13 along with the oxygen carrier to carry out reaction, by which an oxide is formed into a film of 0.1 μm - 3.0 μm (preferably, 0.2 μm - 2 μm) on the inner surface of the luminous tube. Thereafter, introduction of the carrier gas is stopped, the heater is switched off to cool the luminous tube, and the gas introducing tube 13 is tip sealed at a position as near as possible to the luminous tube. Thereafter, metal iodide and mercury (Hg) as sealing materials are packed from the exhaust pipe 14. After discharging gas, an argon gas as a gas for starting is introduced into the pipe, the exhaust pipe 14 is tip sealed to complete the lamp. The process is shown in more detail in the following examples.

Example 1

First, as shown in Fig. 1, the luminous tube was subjected to reduced pressure inside to 2×10^{-2} Torr with a rotary pump 17 to remove adsorbed gas and the like. Next, using a heater 12, the luminous tube was heated to 600° C hafnium acetyl acetonate [$Hf(C_5H_7O_2)_4$] was placed in a bubbler 15, the bubbler was heated to 125° C, and its vapour, along with the oxygen carrier (flow rate, 10 cc/min.), was introduced into the luminous tube 11 through the introducing port 13, and a reaction was carried out for 5 minutes to form a film of hafnium oxide of about 1.0 μm on the inner surface of the luminous tube. Thereafter, the introduction of the carrier gas was stopped, the heater was switched off to cool the luminous tube, and the gas introducing tube 13 was tip sealed at a position as near as possible to the luminous tube. Thereafter, as sealants, cesium iodide (CsI) 3.0 mg, neodium iodide (NdI_3) 1.0 mg and mercury (Hg) 40 mg were filled from the exhaust pipe 14, and after exhaustion, an argon gas was introduced as a gas for starting, followed by tip sealing the exhaust pipe to complete the lamp.

Next, the discharge lamp was lighted with 100 volts and 1.5 amperes (at that time, the color temperature was about 6500° K) . Also, the beam maintenance factor after lighting the lamp for 5000 hours was 84%.

The results are shown as Sample No.1 in Table 1.

Fig. 2 shows a sectional view of the lamp produced in the above manner, in which 21 is a quartz luminous tube, 22 is a coated oxide film (HfO_2), and 23 is a tungusten starting electrode.

Example 2

First, as shown in Fig. 1, the luminous tube was subjected to reduced pressure inside to 2×10^{-2} Torr with a rotary pump 17 to remove adsorbed gas and the like. Next, using a heater 12, the luminous tube was heated to 600° C, a mixture of 95 mol % hafnium acetyl acetonate [$Hf(C_5H_7O_2)_4$] and 5 mol % yttrium acetyl acetone [$Y(C_5H_7O_2)_3$] was placed in a bubbler 15, the bubbler was heated to 125° C, and its vapour, along with the oxygen carrier (flow rate, 10 cc/min.), was introduced into the luminous tube 11 through the introducing port 13, and a reaction was carried out for 5 minutes to form a film of hafnium oxide of about 1.1 μm on the inner surface of the luminous tube. Thereafter, the introduction of the carrier gas was stopped, the heater was switched off to cool the luminous tube, and the gas introducing tube 13 was tip sealed at a position as near as possible to the luminous tube. Thereafter, as sealants, cesium iodide (CsI) 3.0 mg, neodium iodide (NdI_3) 1.0 mg and mercury (Hg) 40 mg were filled from the exhaust pipe 14, and after exhaustion, an argon gas was introduced as a gas for starting, followed by tip sealing the exhaust pipe to complete the lamp.

Next, the discharge lamp was lighted with 100 volts and 2.5 amperes (at that time, the color

temperature was about 6500° K). Also, the beam maintenance factor after lighting the lamp for 5000 hours was 88 %.

The results are shown as Sample No.2 in Table 1.

Fig. 2 shows a sectional view of the lamp produced in the above manner, in which 21 is a quartz luminous tube, 22 is a coated oxide film (HfO_2), and 23 is a tungsten starting electrode.

Example 3

First, as shown in Fig. 3, the luminous tube was subjected to reduced pressure inside to 10^{-2} Torr with a rotary pump 37 to remove adsorbed gas and the like. Next, using a high frequency power source (13.56 MHz) 32, a current of 200 W was applied to generate a plasma. Next, hafnium acetyl acetonate [$Hf(C_5H_7O_2)_4$] was placed in a bubbler 35, the bubbler was heated to 125° C, and its vapour, along with the oxygen carrier (flow rate, 10 cc/min.), was introduced into the luminous tube 31 through the introducing port 33, and a reaction was carried out for 7 minutes to form a film of hafnium oxide of about 1.1 μm on the inner surface of the luminous tube. Thereafter, introduction of the carrier gas was stopped supply of the high frequency power was stopped, and the gas introducing pipe 33 was tip sealed at a position as near as possible to the luminous tube. Thereafter, as sealants, cesium iodide (CsI) 3.0 mg, neodium iodide (NdI_3) 1.0 mg and mercury (Hg) 40 mg were filled from the exhaust pipe 34, and the air inside was once exhausted from the exhaust pipe 34. Thereafter, about 20 Torr of argon gas (Ar) was introduced as a gas for starting from the exhaust pipe 34, followed by tip sealing the exhaust pipe 34 to complete the lamp. Next, the lamp was lighted with 100 volts and 2.5 amperes (at that time, the color temperature was about 6500° K). Also, the beam maintenance factor after lighting the lamp for 5000 hours was 85 %.

The results are shown as Sample No.3 in Table 1.

Example 4

First, as shown in Fig. 4, the luminous tube was subjected to reduced pressure inside to 10^{-3} Torr with a turbo molecular pump 47 to remove adsorbed gas and the like. Next, using a microwave power source (2.45 GHz) 42, a power of 200 W was applied to generate a plasma. Next, hafnium acetyl acetonate [$Hf(C_5H_7O_2)_4$] was placed in a bubbler 45, the bubbler 45 was heated to 125° C, and its vapour, along with the oxygen carrier (flow rate, 10 cc/min.), was introduced into the luminous tube 41 through the introducing port 43, and a reaction was carried out for 6 minutes to form a film of hafnium oxide of about 1.2 μm on the inner surface of the luminous tube. Thereafter, the introduction of the carrier gas was stopped, supply of the microwave power was stopped, and the gas introducing pipe 43 was tip sealed at a position as near as possible to the luminous tube. Thereafter, as sealants, cesium iodide (CsI) 3.0 mg, neodium iodide (NdI_3) 1.0 mg and mercury (Hg) 40 mg were filled from the exhaust pipe 44, and the air inside was once exhausted from the exhaust pipe 44. Thereafter, about 20 Torr of argon gas (Ar) was introduced as a gas for starting from the exhaust pipe 44, followed by tip sealing the exhaust pipe 44 to complete the lamp. Next, the lamp was lighted with 100 volts and 2.5 amperes (at that time, the color temperature was about 6500° K). Also, the beam maintenance factor after lighting the lamp for 5000 hours was 87 %

The results are shown as Sample No.4 in Table 1.

Hereinafter, similar tests were carried out by varying the kind of the metal chelate and the kind of the reaction gas to be contained in the bubbler, temperature of the bubbler, reaction method, heating temperature of the luminous tube, pressure of the luminous tube, reaction time, etc., and their results are shown as Sample Nos. 4 - 13 in Table 1.

The Sample No. 14 is a comparative example lying outside the scope of the present invention.

Table 1 (1)

Sample No.	Kind of metal chelate	Kind of reaction gas	Temperature of bubbler (°C)
1	$Hf(C_5H_7O_2)_4$	Oxygen	125
2	95 mol% $Hf(C_5H_7O_2)_4$ 5 mol% $Y(C_5H_7O_2)_3$	"	"
3	$Hf(C_5H_7O_2)_4$	"	"
4	"	"	"
5	"	Ozone	"
6	"	Nitrogen suboxide	"
7	$Hf(C_{11}H_{19}O_2)_4$	"	100
8	$Hf(C_5HF_8O_2)_4$	"	95
9	$U(C_5H_7O_2)_4$	Ozone	120
10	$U(C_{11}H_{19}O_2)_4$	"	110
11	$U(C_5HF_8O_2)_4$	"	100
12	95 mol% $U(C_{11}H_{19}O_2)_4$ 5 mol% $Y(C_{11}H_{19}O_2)_4$	"	110
13	$Hf((C_{11}H_{19}O_2)_4$	"	100
14*	Without coating		

* 14 is comparative example.

Table 1 (2)

Reaction method	Heating temperature of luminous tube (°C)	Pressure of luminous tube (Torr)	Reaction time (Min.)
Red.press.CVD	600	2×10^{-2}	5
"	"	"	"
RF plasma CVD	200	1×10^{-2}	7
ECR plasma CVD	50	1×10^{-3}	6
"	"	5×10^{-3}	5
"	"	1×10^{-4}	15
Red.press.CVD	500	1×10^{-4}	4
"	"	1×10^{-3}	10
RF plasma CVD	150	5×10^{-1}	3
"	"	2×10^{-2}	4
"	"	3×10^{-3}	6
Red.Press.CVD	600	2×10^{-1}	5
ECR plasma CVD	50	1×10^{-4}	6
Without coating			

Table 1 (3)

Kind of oxide film	Film thickness (μm)	Beam maintenance factor after lighting for 5000 hrs. (%)
HfO_2	1.0	84
Partly stabilized HfO_2	1.1	88
HfO_2	1.1	85
HfO_2	1.2	87
"	1.2	88
"	1.5	87
"	1.2	88
"	1.3	87
UO_2	1.1	82
UO_2	1.2	83
UO_2	1.5	84
Partly stabilized UO_2	1.2	85
HfO_2	1.1	87

As described above, it can be observed that, according to the present invention, it is possible to extend the life of a metal halide lamp to a remarkable degree (with less lowering of beam maintenance factor) by coating with any one of HfO_2, UO_2, HfO_2 partially stabilized with Y_2O_3 and UO_2 partially stabilized with Y_2O_3, by a chemical vapour deposition (reduced pressure CVD, high frequency plasma CVD, ECR plasma CVD) using a gas of metal chelate.

Claims

1. A metal halide lamp having formed on an inner surface of a luminous tube a thin film comprising any

one of hafnium oxide (HfO_2), uranium oxide (UO_2), HfO_2 partially stabilized with yttrium oxide (Y_2O_3) and UO_2 partially stabilized with yttrium oxide.

2. A method of making a metal halide lamp which comprises introducing in a pipe made of quartz glass which is subjected to reduced pressure of 10^{-1} - 10^{-4} Torr a vapour of metal chelate containing any one or two elements of hafnium (Hf), uranium (U) and yttrium (Y) and oxygen (O_2), nitrogen suboxide (N_2O) or ozone (O_2) as a reaction gas to coat an inner surface of a quartz glass tube with any one of HfO_2, UO_2, HfO_2 partially stabilized with Y_2O_3 and UO_2 partially stabilized with Y_2O_3, followed by sealing inside said tube with a halogenide of alkali metal, mercury and argon.

3. A method of making a metal halide lamp which comprises causing a high frequency (RF) discharge in the inside of a quartz glass tube which is subjected to reduced pressure of 5×10^{-1} - 3×10^{-3} Torr, introducing therein a vapour of metal chelate containing any one or two elements of hafnium (Hf), uranium (U) and yttrium (Y) and oxygen (O_2), nitrogen suboxide (N_2O) or ozone (O_2) as a reaction gas to coat an inner surface of the quartz glass tube with any one of HfO_2, UO_2, HfO_2 partially stabilized with Y_2O_3 and UO_2 partially stabilized with Y_2O_3, followed by sealing inside the quartz glass tube with a halogenide of alkali metal, mercury and argon (Ar).

4. A method of making a metal halide lamp which comprises causing a discharge using an electron cyclotron (ECR) in the inside of a quartz glass tube which is subjected to reduced pressure of 5×10^{-3} - 10^{-4} Torr, introducing therein a vapour of metal chelate containing any one or two elements of hafnium (Hf), uranium (U) and yttrium (Y) and oxygen (O_2), nitrogen suboxide (N_2O) or ozone (O_2) as a reaction gas to coat an inner surface of the quartz glass tube with any one of HfO_2, UO_2, HfO_2 partially stabilized with Y_2O_3 and UO_2 partially stabilized with Y_2O_3, followed by sealing inside the quartz glass tube with a halogenide of alkali metal, mercury and argon (Ar).

5. A method of making a metal halide lamp according to any one of Claims 2 to 4, wherein the metal chelate is hafnium acetyl acetone [$Hf(C_5H_7O_2)_4$], hafnium dipivaloylmethane [$Hf(C_{11}H_{19}O_2)_4$] hafnium hexafluoroacetylacetone [$Hf(C_5HF_6O_2)_4$], uranium acetyl acetone [$U(C_5H_7O_2)_4$], uranium dipivaloylmethane [$U(C_{11}H_{19}O_2)_4$], uranium hexafluoroacetylacetone [$U(C_5HF_6O_2)_4$], yttrium acetyl acetone [$Y(C_5H_7O_2)_3$], yttrium dipivaloylmethane [$Y(C_{11}H_{19}O_2)_3$], or yttrium hexafluoroacetylacetone [$Y(C_5HF_6O_2)_3$].

Fig. 1

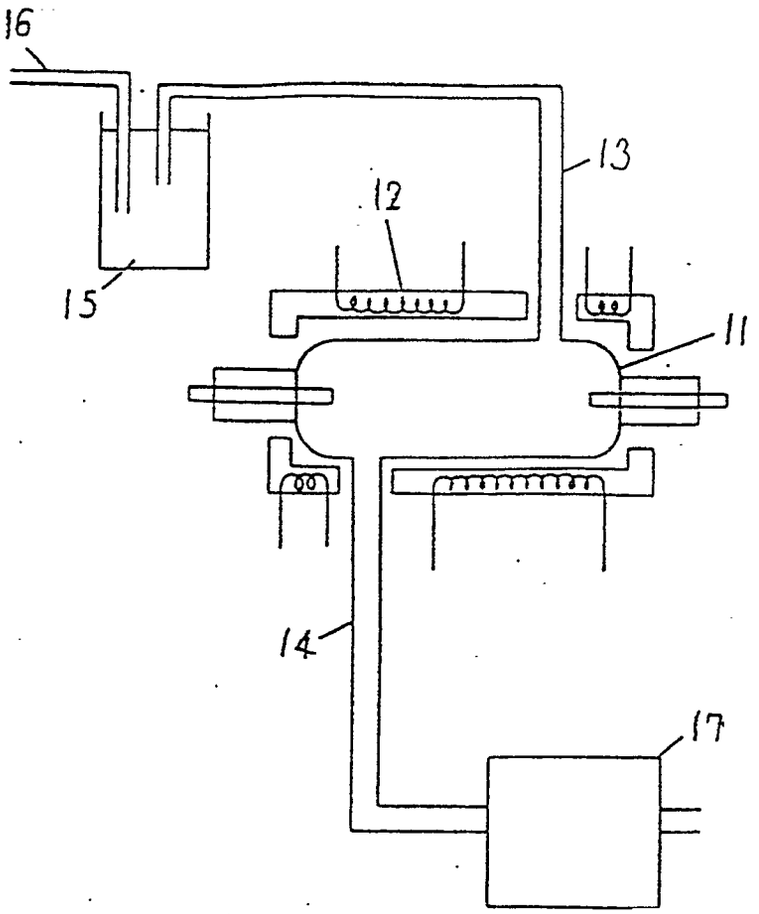

Fig. 2

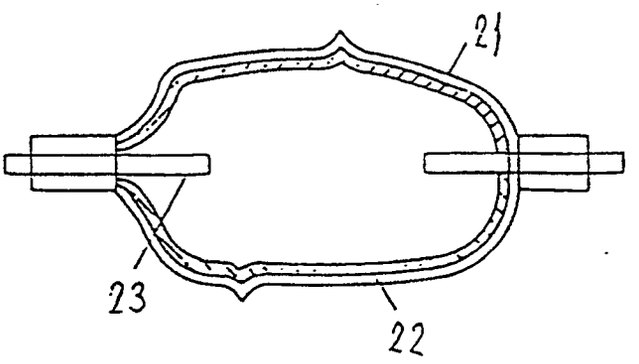

Fig. 3

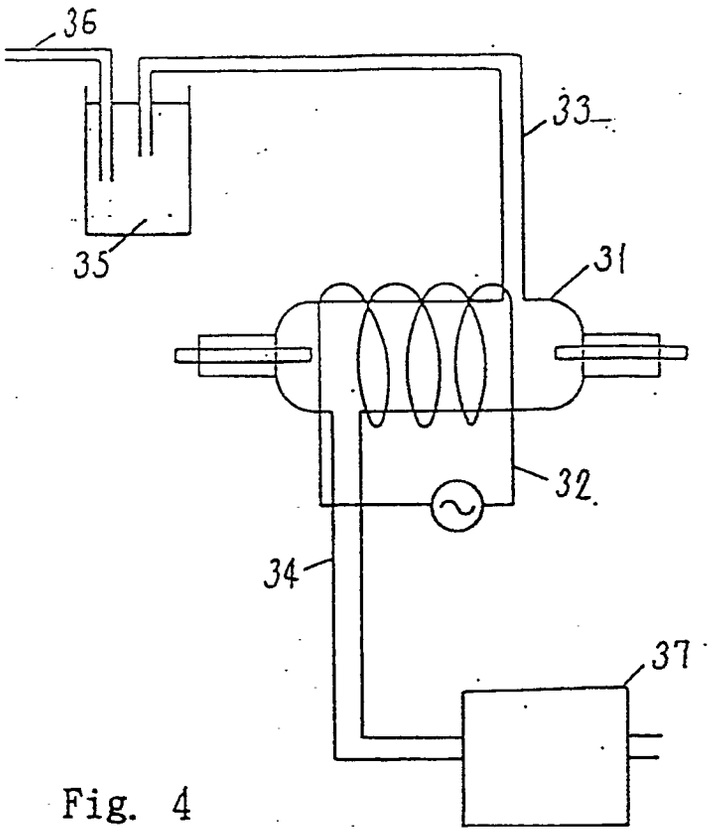

Fig. 4