

DESCRIPTION

TITLE OF INVENTION:

METHOD FOR CLEANING MASK FOR VACUUM VAPOR DEPOSITION AND
RINSING COMPOSITION

5

TECHNICAL FIELD

[0001]

The present invention relates to a method for cleaning a mask for vacuum vapor deposition and a rinsing composition.

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BACKGROUND ART

[0002]

In recent years, as a flat panel display, a liquid crystal display device or a display device provided with an organic EL device, has attracted attention. The liquid crystal display device, although low power consumption, requires an external illumination (backlight) in order to obtain a bright screen. In contrast, a display device provided with an organic EL device does not require a backlight like a liquid crystal display device, since the organic EL device is a self-luminous type device. Therefore, a display device provided with an organic EL device not only has a characteristic of being power-saving, but also has a characteristic of having a high luminance and a wide viewing angle.

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[0003]

The organic EL device has a functional layer including a light emitting layer made of an organic compound, between an anode and a cathode. As a method for forming such a functional layer, a gas phase process (also referred to as a dry process) such as a vacuum vapor deposition method, or a liquid phase process (also referred to as a wet process or coating process) of using a solution having a functional layer forming material dissolved or dispersed in a solvent, is known (see e.g. Patent Documents 1 to 3).

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[0004]

In the case of forming a functional layer by vacuum vapor deposition, a mask is placed close to a substrate, and through the mask, the respective layers of a cathode, a hole injection layer, a hole transport layer, a light emitting layer, an electron transporting

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layer and an anode, are patterned. The mask to be used at that time, in particular the vapor deposition mask for fine patterning of RGB layers, is difficult to prepare because of the high definition, and further, it is very expensive. However, in the patterning of an organic layer in the organic EL device, when vapor-deposition is conducted by using the same mask several times, organic substances will be deposited on the mask, whereby it becomes impossible to accurately transfer the pattern of the high-definition mask onto the substrate. Therefore, in order to realize a high definition mask pattern, it is inevitable to discard the expensive mask used several times, such being a reason for making mass production difficult from the viewpoint of the production cost.

10 [0005]

Under the circumstances, attempts have been made to try to lower the cost by repeated use of the mask, and a cleaning liquid composition for cleaning various organic substances attached to the mask in a vacuum vapor deposition process for the production of an organic EL device, has been proposed (see e.g. Patent Document 4).

15 [0006]

In Patent Document 4, it is disclosed that after cleaning the mask with a cleaning liquid composition, the mask is rinsed with a hydrofluoroether. However, "Novec HFE7100" ($\text{C}_4\text{F}_9\text{OCH}_3$) used as a rinsing liquid in Patent Document 4, is likely to be decomposed, for example, in the presence of N-methyl-2-pyrrolidinone and N,N-dimethylformamide, and to form fluorine ions (see e.g. Patent Document 5). Therefore, in the above method, there was a case where the mask surface was not cleaned.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

25 [0007]

Patent Document 1: JP-A-2002-110345

Patent Document 2: JP-A-2002-305079

Patent Document 3: JP-A-2002-313564

Patent Document 4: JP-A-2005-162947

30 Patent Document 5: JP-A-2009-518857

DISCLOSURE OF INVENTION

TECHNICAL PROBLEM

[0008]

The present invention was made to solve the above-mentioned problem, and it is an object of the present invention to provide, for example, a method for cleaning a mask used in a vacuum vapor deposition step at the time of producing an organic EL device, whereby at the time of rinsing the mask cleaned with a cleaning composition, with a rinsing composition, it is possible to clean the mask to be very clean without accompanying decomposition of the active ingredient of the rinsing composition, and to provide such a rinsing composition.

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SOLUTION TO PROBLEM

[0009]

The cleaning method in an embodiment is a method for cleaning a mask for vacuum vapor deposition, characterized by cleaning the mask with a cleaning composition containing at least one member selected from N-methyl-2-pyrrolidinone (NMP) and N,N-dimethylformamide (DMF), and rinsing the mask after cleaning, with a rinsing composition containing at least one hydrofluoroether selected from $\text{CF}_3\text{CH}_2\text{-O-CF}_2\text{CHF}_2$ (HFE-347pc-f), $\text{CHF}_2\text{CF}_2\text{-O-CH}_3$ (HFE-254pc), $\text{CHF}_2\text{-O-CH}_2\text{CF}_2\text{CHF}_2$ (HFE-356pcf) and $\text{CF}_3\text{CHFCF}_2\text{-O-CH}_2\text{CF}_3$ (HFE-449mec-f).

20 [0010]

In the cleaning method in the embodiment, the proportion of the content of the hydrofluoroether in the rinsing composition is preferably at least 80 mass% and at most 100 mass%.

[0011]

25 In the cleaning method in the embodiment, the cleaning composition preferably contains N-methyl-2-pyrrolidinone.

[0012]

In the cleaning method in the embodiment, the rinsing composition preferably contains $\text{CF}_3\text{CH}_2\text{-O-CF}_2\text{CHF}_2$.

30 [0013]

In the cleaning method in the embodiment, each of the cleaning and rinsing of the mask is conducted at a temperature of preferably at least 10°C and at most 40°C, more

preferably at least 20°C and at most 30°C.

[0014]

In the cleaning method in the embodiment, the vacuum vapor deposition is preferably carried out in the production of a low-molecular type organic EL device.

5 [0015]

In the cleaning method in the embodiment, the mask after being rinsed with the rinsing composition is preferably dried.

[0016]

The rinsing composition in the embodiment is a rinsing composition for rinsing a
10 mask for vacuum deposition, cleaned with a cleaning composition containing at least one member selected from N-methyl-2-pyrrolidinone and N,N-dimethylformamide, characterized by containing at least one hydrofluoroether selected from $\text{CF}_3\text{CH}_2\text{-O-CH}_2\text{CHF}_2$, $\text{CHF}_2\text{CF}_2\text{-O-CH}_3$, $\text{CHF}_2\text{-O-CH}_2\text{CF}_2\text{CHF}_2$ and $\text{CF}_3\text{CHFCH}_2\text{-O-CH}_2\text{CF}_3$.

[0017]

15 The proportion of the content of the hydrofluoroether in the rinsing composition in the embodiment is preferably at least 80 mass% and at most 100 mass%.

[0018]

In this specification, in parentheses after a compound name, an abbreviation of the compound may sometimes be shown, and as the case requires such an
20 abbreviation is used in place of the compound name. Further, in this specification, symbol " to " represents a range of at least the numerical value indicated before it and at most the numerical value indicated after it.

ADVANTAGEOUS EFFECTS OF INVENTION

25 [0019]

According to the cleaning method and the rinsing composition of the present embodiment, for example, in cleaning of a mask used in a vacuum vapor deposition step at the time of producing an organic EL device, at the time of rinsing the mask cleaned with the cleaning composition, with a rinsing composition, it is possible to clean
30 the mask very clean without accompanying decomposition of the active ingredient of the rinsing composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Fig. 1 is a diagram for illustrating a method for producing an organic EL display device.

5 Fig. 2 is a diagram schematically showing a mode for forming a light-emitting layer via a mask.

DESCRIPTION OF EMBODIMENT

[0021]

10 Hereinafter, an embodiment of the present invention will be described in detail with reference to the drawings.

The cleaning method in this embodiment is, for example, a method of cleaning a mask used in a vacuum vapor deposition step at the time of producing an organic EL device, and comprises a cleaning step, a rinsing step and a drying step. In the
15 cleaning method in this embodiment, in the cleaning step, the mask is cleaned with a cleaning composition containing at least one member selected from N-methyl-2-pyrrolidinone and N,N-dimethylformamide. Then, in the rinsing step, the mask after being cleaned with the cleaning composition, is rinsed with a rinsing composition containing at least one hydrofluoroether selected from HFE-347pc-f, HFE-254pc, HFE-
20 356pcf and HFE-449mec-f. Thereafter, as the case requires, a drying step is conducted to dry the mask.

[0022]

In the cleaning method in this embodiment, the specific hydrofluoroether contained in the rinsing composition is hardly decomposed even in the presence of N-
25 methyl-2-pyrrolidinone or N,N-dimethylformamide in the cleaning composition. Therefore, even when the cleaning composition remains on the mask after cleaning, the above specific hydrofluoroether in the rinsing composition will not be decomposed by the cleaning composition, and no fluorine ions will be formed. Therefore, it is possible to clean the mask surface extremely clean.

30 [0023]

The mask to be cleaned in the cleaning method in this embodiment is, for example, one used in a vacuum vapor deposition step in the process for producing an organic EL

display device which will be described below.

[0024]

In the following, with respect to a method for producing an organic EL display device, a vacuum vapor deposition step using a mask, will be outlined with reference to
5 Figs. 1 and 2. On a glass substrate, TFT (thin film transistor) and transparent electrodes will be formed, and further, a hole transport layer will be formed. The glass substrate 1 having such TFT, transparent electrodes and hole transport layer formed, is introduced into vacuum chambers, with the surface to be treated, of the glass substrate 1 facing downward. In the vacuum chambers, on the glass substrate 1, light emitting
10 layers corresponding to the respective primary colors R, G and B as a color display device, will be formed. This step is carried out in separate chambers corresponding to the respective primary colors R, G and B as a color display device. That is, the glass substrate 1 will be transported sequentially to a vacuum chamber for forming a light-emitting layer corresponding to primary color R, a vacuum chamber for forming a light-
15 emitting layer corresponding to primary color G and a vacuum chamber for forming a light-emitting layer corresponding to primary color B.

[0025]

In each vacuum chamber, in a manner shown in Fig. 1, a mask 20 having openings to preliminarily meet with the shape of the light emitting layer is disposed.
20 This mask 20 is fixed by a mask frame 21 disposed on a holding table 24.

[0026]

In each vacuum chamber, as the mask 20, in order to correspond to one of the primary colors R, G and B, a mask opened only at portions corresponding to transparent electrodes (anodes) 11 to be used for light emission of the predetermined
25 primary color is provided. Thus, in the respective chambers, it is possible to form the light-emitting layers corresponding to the respective primary colors at predetermined positions.

[0027]

In Fig. 1, by heating and evaporating a material (organic EL material) for a light
30 emitting layer, from a vapor deposition source (source) 30 which is disposed below the holding table 24, the same material will be vapor-deposited on the surface of a glass substrate 1 via openings of the mask. The mode of formation of the light-emitting layer

via the mask 20 is shown schematically in Fig. 2. As shown in Fig. 2, among transparent electrodes (anodes) 11, other than the formation region of the transparent electrodes corresponding to the pertinent primary color in each chamber, is covered by the mask 20. Then, the organic EL material corresponding to the pertinent primary color is heated and vaporized in the source 30, and via openings 20h of the mask 20, vapor deposited on a glass substrate 1 (more precisely, its hole-transport layer). Here, as the material of the mask, stainless steel such as SUS, Ni alone, a Ni alloy (e.g. Fe-Ni alloy or Mg-Ni alloy), or a semiconductor such as silicon may be mentioned.

[0028]

In this vapor deposition step, on the mask, various organic substances made of vapor deposition materials will adhere. The vapor deposition materials may be, in addition to the above-mentioned organic EL material, a hole injection material, hole transport material, electron transport material, etc. to be used at the time of producing an organic EL device. The hole injection material may be copper phthalocyanine (CuPC), a complex (PEDOT/PSS) of poly(3,4-ethylenedioxythiophene) (PEDOT) and polystyrene sulfonate (PSS), 4,4',4''-tris[phenyl(m-tolyl)amino] triphenylamine (m-MTDATA), etc. The hole transport material may be a triphenylamine (TPD), diphenyl naphthyldiamine (α -NPD), tris(4-carbazolyl-9-yl-phenyl)amine (TCTA), etc. The organic EL material may be a bisstyrylbenzene derivative, tris(8-quinolinolato) aluminum (Alq₃), bis[2-(2-benzoxazolyl)phenolato] zinc (II) (Zn-PBO), rubrene, dimethyl quinacridone, N,N'-dimethyl quinacridone (DMQ), 4-(dicyanomethylene)-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo [ij] quinolizin-9-yl) vinyl]-4H-pyran (DCM2), etc. The electron transport material may be Alq₃, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (PBD), a silole derivative, etc.

[0029]

In the cleaning step of the cleaning method in the present embodiment, the organic substances attached to this mask, are cleaned with a cleaning composition containing at least one member selected from N-methyl-2-pyrrolidinone and N,N-dimethylformamide. The cleaning method may be a method of immersing the mask in the cleaning composition, or a method of blowing the cleaning composition to the mask by water jet. Further, at the time of cleaning the mask, ultrasonic cleaning may be used in combination, whereby the dissolving ability will be improved, and it is possible to

shorten the cleaning time. From the viewpoint of the cleaning ability, it is preferred that the cleaning composition to be used in the cleaning step contains N-methyl-2-pyrrolidinone.

[0030]

5 The content proportion of N-methyl-2-pyrrolidinone or N,N-dimethylformamide in the cleaning composition to be used in the cleaning step, is preferably from 80 to 100 mass%, more preferably from 95 to 100 mass%, further preferably from 98 to 100 mass%, from such a viewpoint that the mask can be thereby sufficiently cleaned. In a case where the cleaning composition contains both N-methyl-2-pyrrolidinone and N,N-
10 dimethylformamide, it is preferred that their total content proportion is within the above preferred ranges in that the mask can be thereby sufficiently cleaned.

[0031]

The cleaning composition may contain components other than N-methyl-2-pyrrolidinone and N,N-dimethylformamide, so long as they do not impair the effects of
15 the present embodiment. Such components may, for example, be saturated hydrocarbons such as heptane, hexane, heptane, octane, nonane, cyclobutane, cyclopentane, cyclohexane, cyclohexane, etc., unsaturated hydrocarbons such as 1-butene, 2-butene, 2-methylpropene, 1-pentene, 2-pentene, 1-butyne, 2-butyne, pentyne, cyclopropene, cyclobutene, cyclopentene, cyclohexene, etc., alcohols such as methanol,
20 ethanol, normal propyl alcohol, isopropyl alcohol, normal butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, etc., ethers such as dimethyl ether, ethyl methyl ether, diethyl ether, diisopropyl ether, methyl-tert-butyl ether, tetrafluoroethanol, etc., ketones such as acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, etc., esters such as methyl
25 formate, ethyl formate, propyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl butyrate, ethyl butyrate, γ -butyrolactone, etc., amines such as monomethylamine, dimethylamine, trimethylamine, etc., chlorohydrocarbons such as dichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, 1,1-dichloroethylene, cis-1,2-
30 dichloroethylene, trans-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, 1,2-dichloropropane, etc., HFC (hydrofluorocarbons) such as 1,1,1,3,3-pentafluorobutane, 1,1,1,2,2,3,4,5,5,5-decafluoropentane, 1,1,2,2,3,3,4-heptafluorocyclopentane, 1,1,1,2,

2,3,3,4,4-nonafluorohexane, 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexane, 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorooctane, etc., PFC (perfluorocarbons) such as decafluorobutane, dodecafluoropentane, tetradecafluorohexane, hexadecafluoroheptane, octadecafluorooctane, etc., HCFC (hydrochlorofluorocarbons) such as dichloropentafluoropropane, 1,1-dichloro-1-fluoroethane, 1-chloro-1,1-difluoroethane, 2,2-dichloro-1,1,1-trifluoroethane, etc., but, they are not limited thereto. Further, one of such components may be contained alone, or a plurality of them may be contained in combination.

[0032]

10 In a case where the cleaning composition contains components other than N-methyl-2-pyrrolidinone and N,N-dimethylformamide, their content proportion is preferably at most 20 mass%, more preferably at most 5 mass%, further preferably at most 2 mass%. Components other than N-methyl-2-pyrrolidinone and N,N-dimethylformamide contained in the cleaning composition, may be components not exhibiting cleaning effects, among those listed above. Further, if the cleaning composition contains water, the water adheres to the mask, to cause stains, or the detergency of the cleaning composition may be deteriorated, and therefore, the content of water in the cleaning composition is preferably at most 5 mass%, more preferably at most 3 mass%, further preferably at most 1 mass%. It is particularly preferred that the cleaning composition contains no water.

[0033]

The time for the cleaning step may be, for example, from 5 to 15 minutes, although it may depend on the size of the mask or the types and amounts of adhered organic substances. The temperature of the cleaning composition in the cleaning step may be a normal temperature without conducting a temperature control and is preferably from 10 to 40°C, more preferably from 20 to 30°C. Thus, by conducting the cleaning within the above temperature range by means of a cleaning composition containing at least one member selected from N-methyl-2-pyrrolidinone and N,N-dimethylformamide, the cleanability will be excellent, and there will be no deformation or distortion of the mask by a heat during the cleaning.

[0034]

Further, in the cleaning step, it is possible to sufficiently remove one or more types

of organic substances adhered to a variety of mask surface only by the above-described cleaning composition. Therefore, cleaning tanks different in types of the cleaning liquids are not required, whereby the cleaning process becomes very simple.

[0035]

5 Further, the cleaning composition can be reused by distilling the used cleaning liquid composition. Also in a case where the cleaning composition contains components other than N-methyl-2-pyrrolidinone and N,N-dimethylformamide, it may be reused by distilling the used cleaning liquid composition and adjusting the composition of the recovered liquid.

10 [0036]

In the rinsing step of the cleaning method in the present embodiment, a mask that has been cleaned by the cleaning composition, is rinsed by a rinsing composition. In this specification, rinsing means to remove the cleaning composition adhered to the mask cleaned by the cleaning composition.

15 [0037]

As a method for rinsing the mask after cleaning, a method of immersing the mask after cleaning in a rinsing composition, or a method of flowing a rinsing composition on the mask after cleaning may be mentioned. By either method, the cleaning composition adhered to the mask surface after cleaning can be easily removed, and it is possible to rinse the mask surface to be extremely clean. The time for conducting the rinsing step may be, for example, from 5 to 15 minutes, although it may depend on the size of the mask, etc. The temperature of the rinsing composition in the rinsing step may be at a normal temperature without conducting a temperature control, and is preferably from 10 to 40°C, more preferably from 20 to 30°C. Thus, the rinsing can be conducted at a relatively low temperature, whereby deformation, distortion, etc. of the mask due to a heat will not occur.

[0038]

The rinsing composition contains, as an active ingredient, at least one hydrofluoroether selected from HFE-347pc-f, HFE-254pc, HFE-356pcf and HFE-449mec-f. Each of HFE-347pc-f, HFE-254pc, HFE-356pcf and HFE-449mec-f has a low boiling point of at most 74°C, thus is excellent drying properties and easily evaporates even at room temperature. Further, even when boiled to become a vapor,

each of them is less likely to present adverse effects to a member susceptible to an influence by a heat, such as a resin member. For the rinsing composition, one of the above hydrofluoroethers may be used alone, or two or more of them may be used in combination.

5 [0039]

HFE-347pc-f has an ozone depleting potential being zero, whereby the global warming potential is small. HFE-347pc-f has a boiling point of about 56°C. HFE-347pc-f may be produced, for example, by a method of reacting 2,2,2-trifluoroethanol and tetrafluoroethylene in the presence of an aprotic polar solvent and a catalyst (an
10 alkali metal alkoxide or an alkali metal hydroxide) (see WO2004/108644).

A commercially available product of HFE-347pc-f may, for example, be "ASAHIKLIN (registered trademark) AE-3000" (manufactured by Asahi Glass Co., Ltd.).

[0040]

HFE-254pc has an ozone depleting potential being zero, whereby the global
15 warming potential is small. The boiling point of the HFE-254pc is 37°C. HFE-254pc may be produced, for example, by a method of adding tetrafluoroethylene to methanol in the presence of a strong alkali (e.g. potassium hydroxide).

[0041]

HFE-356pcf has an ozone depleting potential being zero, whereby the global
20 warming potential is small. The boiling point of HFE-356pcf is 74°C. HFE-356pcf may be produced, for example, by a method of adding chlorodifluoromethane (HCFC-22) to tetrafluoropropanol (TFPO) in the presence of a strong alkali (e.g. potassium hydroxide).

[0042]

HFE-449mec-f has an ozone depleting potential being zero, whereby the global
25 warming potential is small. The boiling point of the HFE-449mec-f is 73°C. HFE-449mec-f may be produced, for example, by a method of reacting 2,2,2-trifluoroethanol and hexafluoropropene in the presence of an aprotic polar solvent and a catalyst (an alkali metal alkoxide or an alkali metal hydroxide) (see JP-A-H9-263559).

30 [0043]

N-methyl-2-pyrrolidinone and N,N-dimethylformamide in the cleaning composition have excellent solubility in any hydrofluoroether in the rinsing composition. Therefore,

the cleaning composition can be very readily removed by the rinsing composition.

Further, the above hydrofluoroether is not decomposed by either N-methyl-2-pyrrolidinone or N,N-dimethylformamide contained in the cleaning composition.

Therefore, on the mask surface after the rinsing, fluorine ions will not remain, and it is possible to clean the mask to be very clean.

[0044]

Here, the reason as to why the hydrofluoroether used in the rinsing composition is not be decomposed by N-methyl-2-pyrrolidinone and N,N-dimethylformamide contained in the cleaning compositions, is assumed to be as follows.

[0045]

For example, like methyl-perfluoro-n-butyl ether ($C_4F_9OCH_3$, HFE-449sl), a hydrofluoroether having a strongly electron withdrawing CF_3 - group is in such a state that the carbon bonded to the CF_3 - group is electron-deficient. In a case where an easily removable atomic group or atom such as a halogen atom is bonded to the carbon bonded to the CF_3 - group, it is susceptible to a nucleophilic attack by N-methyl-2-pyrrolidinone or N,N-dimethylformamide, and becomes to be easily decomposed. In contrast, the hydrofluoroether in the rinsing composition used in the present embodiment, does not have a CF_3 - group, or even if it has a CF_3 - group, an easily removable atom or atomic group is not bonded to the carbon to which the CF_3 - group is bonded. Therefore, unbalance of intramolecular charge is less likely to occur, and it is less susceptible to nucleophilic attack from N-methyl-2-pyrrolidinone or N,N-dimethylformamide.

[0046]

As the rinsing composition to be used in the cleaning method in the present embodiment, it is preferred to contain HFE-347pc-f, from such a viewpoint that it is thereby possible to sufficiently remove the cleaning composition, and it is excellent in drying properties.

[0047]

The content proportion of the hydrofluoroether in the rinsing composition to be used in the cleaning method in the present embodiment is preferably from 80 to 100 mass%, more preferably from 95 to 100 mass%, further preferably from 98 to 100 mass%, from such a viewpoint that the mask can thereby be sufficiently rinsed. In a

case where the rinsing composition contains two or more types of the above hydrofluoroethers, their total content proportion is preferably within the above preferred ranges, from such a viewpoint that the mask can thereby be sufficiently rinsed.

[0048]

5 The rinsing composition may contain components other than the above hydrofluoroethers so long as they do not impair the effects of the present invention. Such components other than the above hydrofluoroethers may, for example, be the same components as components other than N-methyl-2-pyrrolidinone and N,N-dimethylformamide in the above cleaning composition, but they are not limited thereto.

10 Further, one of these components may be contained alone, or a plurality of them may be contained in combination.

[0049]

 In a case where the rinsing composition contains components other than the hydrofluoroethers, the content proportion of such components is preferably at most 20

15 mass%, more preferably at most 5 mass%, further preferably at most 2 mass%.

[0050]

 As described above, if the cleaning composition contains water, there may be a case where the water adheres to the mask surface, to form stains. In a case where the rinsing composition contains at least one alcohol selected from methyl alcohol, ethyl

20 alcohol, normal propyl alcohol and isopropyl alcohol, even if water is contained in the cleaning composition, it is possible to dissolve and remove such water, such being preferred. In a case where the rinsing composition contains said alcohol, from such a viewpoint that water can be sufficiently removed, the proportion of the content of the alcohol in the rinsing composition is preferably at most 10 mass%, more preferably from

25 1 to 8 mass%, further preferably from 2 to 5 mass%.

[0051]

 In the drying step of the cleaning method in the present embodiment, the mask after the rinsing in the rinsing step, is dried. As the drying method, it is possible to use a method of drying the mask after the rinsing, by natural drying, a method of drying it by

30 air blowing, or a method for drying it under reduced pressure. Among them, from such viewpoint that the mask can be more efficiently dried, a method of drying it under reduced pressure is preferred.

[0052]

In the method of drying the mask by air blowing, it is possible to dry it by blowing dried air at a temperature of, for example, preferably from 10 to 40°C, more preferably from 20 to 30°C. Thus, since the drying can be done at a relatively low temperature, deformation, distortion or the like of the mask due to a heat, does not occur.

[0053]

With respect to the pressure at the time of drying the mask under a reduced pressure, since it takes time to reduce the pressure, the degree of the pressure reduction should better be small. However, if the amount of deposition of the rinsing composition to the mask is less, it can be dried in the process of pressure reduction, and therefore, the pressure can be suitably set by the size of the mask or the adhesion amount of the rinsing composition to the mask, and it is preferably set, for example, within a range of at least the vapor pressure at 20°C of the rinsing composition and at most 101.3 kPa. For example, in a case where the rinsing composition is made of HFE-347pc-f, it is preferred to reduce the pressure to a level of from 25 to 101.3 kPa in the drying step.

[0054]

According to the cleaning method in the embodiment as described above, by using a specific hydrofluoroether as a rinsing composition, the hydrofluoroether will not be decomposed by either N-methyl-2-pyrrolidinone or N,N-dimethylformamide in the cleaning composition adhered to the mask during the cleaning, and no fluorine ions will be formed. Therefore, it is possible to clean the mask to be very clean. The cleaning method in the present embodiment is useful as a method for cleaning a mask at the time of producing an organic EL device by a vacuum vapor deposition method, and is preferably used in the vacuum vapor deposition step at the time of producing a low molecular weight type EL device.

EXAMPLES

[0055]

Now, Test Examples and Working Example will be described. The present invention is not limited to these Test Examples and Working Example.

[0056]

(Test Example 1)

In this Test Example, decomposability of a rinsing composition by NMP and DMF when heated for a predetermined time, was investigated. 5 mass% of NMP or DMF was added to HFE-347pc-f (manufactured by Asahi Glass Company, AE-3000), and in the same manner, 5 mass% of NMP or DMF was added to HFE-449sl (manufactured by 3M Company, Novec 7100), to prepare sample liquids. Each sample liquid was left to stand for 3 days in a thermostatic bath at 55°C. The fluorine ion concentration in each solvent sample liquid after being left to stand, was measured by a fluorine ion meter (IM-55G manufactured by DKK-TOA Corporation, fluorine ion electrode: F-2021 manufactured by DKK-TOA Corporation). Here, the detection limit of the fluorine ion concentration was 0.5 ppm. The results are shown in Table 1.

[0057]

[Table 1]

Sample liquid		Fluorine ion concentration before the test (ppm)	Fluorine ion concentration after 3 days (ppm)
NMP	HFE-347pc-f	Not detected	Not detected
DMF	HFE-347pc-f	Not detected	Not detected
NMP	HFE-449sl	Not detected	18.2
DMF	HFE-449sl	Not detected	20

[0058]

(Test Example 2)

In this Test Example, decomposability of a rinsing composition by NMP when a sample liquid containing HFE-347pc-f or HFE-449sl and NMP, cleaned and refluxed as an accelerated test, was investigated. 250 g of a sample liquid having 5 mass% of NMP added to the same HFE-347pc-f (manufactured by Asahi Glass Company, AE-3000) as mentioned above, was put into a flask, heated by a heater so as to become a boiled state, and refluxed for 4 hours. Thereafter, in 80 minutes, 175 g of the distillate was collected, and the pH of the remaining still residue, the fluorine ion concentration and the acid content were measured. The results are shown in Table 2.

[0059]

Further, 250 g of a sample liquid having 5 mass% of NMP added to the same

HFE-449sl (manufactured by 3M Company, Novec 7100) as mentioned above, was put into a flask, boiled by heating by a heater, and refluxed for 4 hours. Thereafter, in 80 minutes, 175 g of the distillate was collected, and the pH of the remaining still residue, the fluorine ion concentration, and the acid content were measured. Here, the measurement of the pH was conducted by a pH meter (HM-25R manufactured by DKK-TOA Corporation, electrodes: GST-5741C manufactured by DKK-TOA Corporation); the measurement of the fluorine ion concentration was conducted by a fluorine ion meter (IM-55G manufactured by DKK-TOA Corporation, fluorine ion electrodes: F-2021 manufactured by DKK-TOA Corporation); and the measurement of the acid content was conducted by titration using phenolphthalein as an indicator. The detection limit was 0.5 ppm for both of the fluorine ion concentration and the acid content. The results are shown in Table 2.

[0060]

[Table 2]

Sample liquid		Before the test			Still residue		
		pH	Fluorine ion concentration [ppm]	Acid content [ppm]	pH	Fluorine ion concentration [ppm]	Acid content [ppm]
NMP	HFE-347pc-f	6.7	Not detected	Not detected	6.8	Not detected	Not detected
NMP	HFE-449sl	6.6	Not detected	Not detected	3.8	20	9.5

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[0061]

From Table 1 and Table 2, it is evident that even by heating for 3-days or by heating and refluxing for 80 minutes, HFE-347pc-f in the rinsing composition was not decomposed by NMP or DMF, whereby no fluorine ions were formed, while HFE-449sl was decomposed by NMP or DMF, to form fluorine ions.

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[0062]

(Working Example)

Cleanability of a metallic mask in the case of using HFE-347pc-f as a rinsing composition was investigated. A metal (SUS) piece to which low molecular type

organic EL material is adhered, is immersed in NMP at room temperature (25°C) for 1 minute. Thereafter, the metal piece is rinsed by being immersed in HFE-347pc-f (manufactured by Asahi Glass Company, AE-3000) at room temperature (25°C) for one minute, and pulled up. This metal piece is naturally dried and then immersed in pure water, whereupon the extracted fluorine ion concentration is measured by a fluorine ion meter (IM-55G manufactured by DKK-TOA Corporation, fluorine ion electrodes: F-2021 manufactured by DKK-TOA Corporation). The detection limit of the fluorine ion concentration is set to be 0.5 ppm. The results are shown in Table 3 by identifying a case where fluorine ions are detected, as "detected", and identifying a case where fluorine ions are not detected, as "not detected".

[0063]

(Comparative Example)

Cleanability of a metallic mask in the case of using HFE-449sl as a rinsing composition was investigated. A metal (SUS) piece on which low-molecular type organic EL material is adhered, is immersed in NMP at room temperature (25°C) for 1 minute, and then rinsed by being immersed in HFE-449sl (manufactured by 3M Company, Novec 7100) at room temperature (25°C) for one minute, and pulled up. This metal piece is naturally dried and then immersed in pure water, whereupon the presence or absence of the extracted fluorine ions is investigated. The results are shown in Table 3.

[0064]

[Table 3]

	Rinsing composition	Evaluation result
Example	HFE-347pc-f	Not detected
Comparative Example	HFE-449sl	Detected

[0065]

From Table 3, it is evident that by using HFE-347pc-f as a rinsing composition, it is possible to clean the mask to be clean. In contrast, when HFE-449sl is used, it is evident that fluorine ions are adhered on the mask surface, and the mask has not been cleaned.

REFERENCE SYMBOLS

[0066]

1: glass substrate, 11: transparent electrode, 20: mask, 20h: opening, 21: mask frame, 24: holding table, 30: source.

CLAIMS

1. A method for cleaning a mask for vacuum vapor deposition, characterized by cleaning the mask with a cleaning composition containing at least one member selected from N-methyl-2-pyrrolidinone and N,N-dimethylformamide, and
5 rinsing the mask after cleaning, with a rinsing composition containing at least one hydrofluoroether selected from $\text{CF}_3\text{CH}_2\text{-O-CF}_2\text{CHF}_2$, $\text{CHF}_2\text{CF}_2\text{-O-CH}_3$, $\text{CHF}_2\text{-O-CH}_2\text{CF}_2\text{CHF}_2$ and $\text{CF}_3\text{CHFCH}_2\text{-O-CH}_2\text{CF}_3$.
2. The cleaning method according to Claim 1, wherein the proportion of the content of the hydrofluoroether in the rinsing composition is at least 80 mass% and at most 100
10 mass%.
3. The cleaning method according to Claim 1 or 2, wherein the cleaning composition contains N-methyl-2-pyrrolidinone.
4. The cleaning method according to any one of Claims 1 to 3, wherein the rinsing composition contains $\text{CF}_3\text{CH}_2\text{-O-CF}_2\text{CHF}_2$.
- 15 5. The cleaning method according to any one of Claims 1 to 4, wherein each of the cleaning and rinsing of the mask is conducted at a temperature of at least 10°C and at most 40°C.
6. The cleaning method according to any one of Claims 1 to 5, wherein each of the cleaning and rinsing of the mask is conducted at a temperature of at least 20°C and at
20 most 30°C.
7. The cleaning method according to any one of Claims 1 to 6, wherein said vacuum vapor deposition is carried out in the production of a low-molecular type organic EL device.
8. The cleaning method according to any one of Claims 1 to 7, wherein the mask
25 after being rinsed with the rinsing composition, is dried.
9. A rinsing composition for rinsing a mask for vacuum vapor deposition cleaned with a cleaning composition containing at least one member selected from N-methyl-2-pyrrolidinone and N,N-dimethylformamide, characterized by containing at least one hydrofluoroether selected from $\text{CF}_3\text{CH}_2\text{-O-CF}_2\text{CHF}_2$, $\text{CHF}_2\text{CF}_2\text{-O-CH}_3$, $\text{CHF}_2\text{-O-CH}_2\text{CF}_2\text{CHF}_2$ and $\text{CF}_3\text{CHFCH}_2\text{-O-CH}_2\text{CF}_3$.
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10. The rinsing composition according to Claim 9, wherein the proportion of the content of the hydrofluoroether in the rinsing composition is at least 80 mass% and at

most 100 mass%.