Patent Literature 4: JP 2018-137435 A

SUMMARY

- Technical Problem

[0010]

However, Patent Literature 1, in which a predetermined pattern is formed on a substrate of a single material using an atomic layer deposition-inhibiting material, does not disclose a method of forming an atomic layer deposition-inhibiting layer selectively on a desired surface region on a substrate including multiple surface regions of different materials.

[0011]

The organosilane-based self-assembled monolayer used in Patent Literature 2 can be deposited selectively on a silicon-containing surface but cannot be deposited selectively on a metal or metal oxide.

[0012]

The methods of selectively forming an organic thin film described in Patent Literature 3 and Patent Literature 4 involve repeating multiple times a deposition cycle including shifting raw materials and temperatures, and thus require considerable time and effort to form an organic thin film.

[0013]

In light of the above problems, the present disclosure aims to provide a selective film deposition method which can deposit a film of an organic substance on a surface region containing a metal element selectively over a surface region containing a nonmetal inorganic material on a substrate by a simple procedure, as well as an organic substance deposited film deposited by the method, the organic substance, etc.

- Solution to Problem

[0014]

As a result of extensive studies, the present inventors have found that the use of at least one organic substance represented by the formula (1) described below allows a film of the organic substance to be deposited on a surface region containing a metal element selectively over a surface region containing a nonmetal inorganic material on a substrate. This finding has led to the completion of the present disclosure.

[0015]

A selective film deposition method according to examples of the present disclosure includes exposing a substrate having a structure on which a first surface region containing a metal element and a second surface region containing a nonmetal inorganic material are both exposed, to a solution containing an organic substance represented by formula (1) shown below and a solvent to deposit a film of the organic substance on the first surface region selectively over the second surface region:

$R^1(X)_m$ (1)

wherein R^1 is a C4-C100 hydrocarbon group optionally containing a heteroatom or a halogen atom, and m hydrogen atoms of the hydrocarbon group are replaced with X; X is $-PO_3(R^2)_2$, $-O-PO_3(R^2)_2$, $-CO_2R^2$, $-SR^2$, or $-SSR^1$; each R^2 is a hydrogen atom or a C1-C6 alkyl group; and m is a positive integer, and m/r is 0.01 to 0.25 where r is the number of carbons of the hydrocarbon group.

[0016]

According to the specified selective film deposition method, it is possible with the use of the organic substance of formula (1) to provide a method which can deposit a film of an organic substance on a first surface region containing a metal element exposed on a substrate selectively over a second surface region containing a nonmetal inorganic material exposed on the substrate by a

simple procedure. Herein, a film made of an organic substance is also referred to as a film of an organic substance or an organic substance deposited film.

[0016a]

In one aspect, the present disclosure provides a selective film deposition method, comprising exposing a substrate having a structure on which a first surface region containing a metal element and a second surface region containing a nonmetal inorganic material are both exposed, to a solution consisting of an organic substance represented by formula (1) shown below and a solvent to deposit a film of the organic substance on the first surface region selectively over the second surface region:

$R^1(X)_m$ (1)

wherein R^1 is a C4-C100 hydrocarbon group optionally containing a heteroatom or a halogen atom, and m hydrogen atoms of the hydrocarbon group are replaced with X; X is $-PO_3(R^2)_2$, $-O-PO_3(R^2)_2$, $-CO_2R^2$, $-SR^2$, or $-SSR^1$; each R^2 is a hydrogen atom or a C1-C6 alkyl group; and m is a positive integer, and m/r is 0.01 to 0.25 where r is the number of carbons of the hydrocarbon group;

wherein the solvent is at least one selected from the group consisting of esters, ethers, ketones, sulfoxide-based solvents, sulfone-based solvents, lactone-based solvents, carbonate-based solvents, alcohol-based solvents, polyhydric alcohol derivatives, nitrogen-containing solvents, and silicone solvents, and wherein the alcohol-based solvent is at least one selected from the group consisting of methanol, ethanol, propanol, pentanol, hexanol, heptanol, octanol, ethylene glycol, diethylene glycol, 1,3-propanediol, 1,2-propanediol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, triethylene glycol, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol, and glycerol, and the polyhydric alcohol derivatives are ethylene glycol

monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monobutyl ether, tetraethylene glycol monomethyl ether, tetraethylene glycol monoethyl ether, tetraethylene glycol monopropyl ether, tetraethylene glycol monobutyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monoethyl ether, tripropylene glycol monopropyl ether, tripropylene glycol monobutyl ether, tetrapropylene glycol monomethyl ether, butylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol diacetate, diethylene glycol dimethyl ether, diethylene glycol ethyl methyl ether, diethylene glycol diethyl ether, diethylene glycol butyl methyl ether, diethylene glycol dibutyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol diacetate, triethylene glycol dimethyl ether, triethylene glycol diethyl ether, triethylene glycol dibutyl ether, triethylene glycol butyl methyl ether, triethylene glycol monomethyl ether acetate, triethylene glycol monoethyl ether acetate, triethylene glycol monobutyl ether acetate, triethylene glycol diacetate, tetraethylene glycol dimethyl ether, tetraethylene glycol

diethyl ether, tetraethylene glycol dibutyl ether, tetraethylene glycol monomethyl ether acetate, tetraethylene glycol monoethyl ether acetate, tetraethylene glycol monobutyl ether acetate, tetraethylene glycol diacetate, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dibutyl ether, propylene glycol monomethyl ether acetate (propylene glycol 1-monomethyl ether 2-acetate), propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether acetate, propylene glycol diacetate, dipropylene glycol dimethyl ether, dipropylene glycol methyl propyl ether, dipropylene glycol diethyl ether, dipropylene glycol dibutyl ether, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, dipropylene glycol monobutyl ether acetate, dipropylene glycol diacetate, tripropylene glycol dimethyl ether, tripropylene glycol diethyl ether, tripropylene glycol dibutyl ether, tripropylene glycol monomethyl ether acetate, tripropylene glycol monoethyl ether acetate, tripropylene glycol monobutyl ether acetate, tripropylene glycol diacetate, tetrapropylene glycol dimethyl ether, tetrapropylene glycol monomethyl ether acetate, tetrapropylene glycol diacetate, butylene glycol dimethyl ether, butylene glycol monomethyl ether acetate, butylene glycol diacetate, glycerin triacetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, and 3-methyl-3-methoxybutyl propionate;
wherein the substrate is exposed to the solution to obtain a substrate in which a contact angle with water is higher by at least 10° in the first surface region than in the second surface region.

[0017]

A substrate according to examples of the present disclosure is a substrate including a first surface region containing a metal element and a second surface region

containing a nonmetal inorganic material, wherein the first surface region includes a film of the organic substance of formula (1), and the second surface region includes no film of the organic substance or a film of the organic substance on the second surface region has a thickness t_2 smaller than a thickness t_1 of the film of the organic substance on the first surface region.

[0018]

According to the specified substrate, it is possible to provide a substrate on which a film of the organic substance is deposited on a first surface region containing a metal element selectively over a second surface region containing a nonmetal inorganic material.

[0019]

An organic substance deposited film according to examples of the present disclosure is an organic substance deposited film formed by the specified selective film deposition method, wherein the deposited film includes the organic substance of formula (1) deposited on a substrate.

[0020]

An organic substance according to examples of the present disclosure is the organic substance of formula (1) for use in the specified selective film deposition method.

[0021]

With the use of the specified organic substance, it is possible to deposit a film of an organic substance on a first surface region containing a metal element exposed on

a substrate selectively over a second surface region containing a nonmetal inorganic material exposed on the substrate by a simple procedure.

[0022]

A solution according to examples of the present disclosure is a solution for use in the specified selective film deposition method, wherein the solution contains the organic substance of formula (1) and a solvent.

[0023]

With the use of the specified solution, it is possible to deposit a film of the organic substance on a first surface region containing a metal element exposed on a substrate selectively over a second surface region containing a nonmetal inorganic material exposed on the substrate by a simple procedure.

- Advantageous Effects

[0024]

According to the selective film deposition method according to examples of the present disclosure, it is possible with the use of the organic substance of formula (1) to provide a method which can deposit a film of the organic substance on a first surface region containing a metal element exposed on a substrate selectively over a second surface region containing a nonmetal inorganic material exposed on the substrate by a simple procedure.

[0025]

According to the substrate according to examples of the present disclosure, it is possible to provide a substrate on which a film of the organic substance of formula (1) is deposited on a first surface region containing a metal element exposed on the substrate selectively over a second surface region containing a nonmetal inorganic material exposed on the substrate.

CLAIMS

Claim 1. A selective film deposition method, comprising:

exposing a substrate having a structure on which a first surface region containing a metal element and a second surface region containing a nonmetal inorganic material are both exposed, to a solution consisting of an organic substance represented by formula (1) shown below and a solvent to deposit a film of the organic substance on the first surface region selectively over the second surface region:

$R^1(X)_m$ (1)

wherein R^1 is a C4-C100 hydrocarbon group optionally containing a heteroatom or a halogen atom, and m hydrogen atoms of the hydrocarbon group are replaced with X; X is $-PO_3(R^2)_2$, $-O-PO_3(R^2)_2$, $-CO_2R^2$, $-SR^2$, or $-SSR^1$; each R^2 is a hydrogen atom or a C1-C6 alkyl group; and m is a positive integer, and m/r is 0.01 to 0.25 where r is the number of carbons of the hydrocarbon group;

wherein the solvent is at least one selected from the group consisting of esters, ethers, ketones, sulfoxide-based solvents, sulfone-based solvents, lactone-based solvents, carbonate-based solvents, alcohol-based solvents, polyhydric alcohol derivatives, nitrogen-containing solvents, and silicone solvents, and wherein

the alcohol-based solvent is at least one selected from the group consisting of methanol, ethanol, propanol, pentanol, hexanol, heptanol, octanol, ethylene glycol, diethylene glycol, 1,3-propanediol, 1,2-propanediol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, triethylene glycol, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol, and glycerol, and

the polyhydric alcohol derivatives are ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monobutyl ether, tetraethylene glycol monomethyl ether, tetraethylene glycol monoethyl ether, tetraethylene glycol monopropyl ether, tetraethylene glycol monobutyl ether, propylene glycol monoethyl ether, propylene glycol monopropyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monoethyl ether, tripropylene glycol monopropyl ether, tripropylene glycol monobutyl ether, tetrapropylene glycol monomethyl ether, butylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol diacetate, diethylene glycol dimethyl ether, diethylene glycol ethyl methyl ether, diethylene glycol diethyl ether, diethylene glycol butyl methyl ether, diethylene glycol dibutyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, diethylene glycol diacetate, triethylene glycol dimethyl ether, triethylene glycol diethyl ether, triethylene glycol dibutyl ether, triethylene glycol

butyl methyl ether, triethylene glycol monomethyl ether acetate, triethylene glycol monoethyl ether acetate, triethylene glycol monobutyl ether acetate, triethylene glycol diacetate, tetraethylene glycol dimethyl ether, tetraethylene glycol diethyl ether, tetraethylene glycol dibutyl ether, tetraethylene glycol monomethyl ether acetate, tetraethylene glycol monoethyl ether acetate, tetraethylene glycol monobutyl ether acetate, tetraethylene glycol diacetate, propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dibutyl ether, propylene glycol monomethyl ether acetate (propylene glycol 1-monomethyl ether 2-acetate), propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether acetate, propylene glycol diacetate, dipropylene glycol dimethyl ether, dipropylene glycol methyl propyl ether, dipropylene glycol diethyl ether, dipropylene glycol dibutyl ether, dipropylene glycol monomethyl ether acetate, dipropylene glycol monoethyl ether acetate, dipropylene glycol monobutyl ether acetate, dipropylene glycol diacetate, tripropylene glycol dimethyl ether, tripropylene glycol diethyl ether, tripropylene glycol dibutyl ether, tripropylene glycol monomethyl ether acetate, tripropylene glycol monoethyl ether acetate, tripropylene glycol monobutyl ether acetate, tripropylene glycol diacetate, tetrapropylene glycol dimethyl ether, tetrapropylene glycol monomethyl ether acetate, tetrapropylene glycol diacetate, butylene glycol dimethyl ether, butylene glycol monomethyl ether acetate, butylene glycol diacetate, glycerin triacetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, and 3-methyl-3-methoxybutyl propionate;

wherein the substrate is exposed to the solution to

obtain a substrate in which a contact angle with water is higher by at least 10° in the first surface region than in the second surface region.

Claim 2. The selective film deposition method according to claim 1,

wherein the organic substance of formula (1) comprises at least one organic substance represented by at least one selected from the group consisting of the following formulas (2) to (5):

$R^3(PO_3(R^4)_2)_n$ (2)

wherein R^3 is a C4-C100 hydrocarbon group optionally containing a heteroatom or a halogen atom, and n hydrogen atoms of the hydrocarbon group are replaced with $(PO_3(R^4)_2)$; n is 1 or 2; R^4 is a hydrogen atom or a C1-C6 alkyl group; and each R^4 may be the same or different;

$R^5(O\text{-}PO_3(R^6)_2)_n$ (3)

wherein R^5 is a C4-C100 hydrocarbon group optionally containing a heteroatom or a halogen atom, and n hydrogen atoms of the hydrocarbon group are replaced with $(O\text{-}PO_3(R^6)_2)$; n is 1 or 2; R^6 is a hydrogen atom or a C1-C6 alkyl group; and each R^6 may be the same or different;

$R^7(CO_2R^8)_n$ (4)

wherein R^7 is a C4-C100 hydrocarbon group optionally containing a heteroatom or a halogen atom, and n hydrogen atoms of the hydrocarbon group are replaced with (CO_2R^8); n is 1 or 2; R^8 is a hydrogen atom or a C1-C6 alkyl group; and each R^8 may be the same or different; and

$R^9(SR^{10})_n$ (5)

wherein R^9 is a C4-C100 hydrocarbon group optionally containing a heteroatom or a halogen atom, and n hydrogen atoms of the hydrocarbon group are replaced with (SR^{10}); n is 1 or 2; R^{10} is a hydrogen atom, a C1-C6 alkyl group, or $-S-R^9$; and each R^{10} may be the same or different.

Claim 3. The selective film deposition method according to claim 2,

wherein R^4, R^6, R^8, and R^{10} in formulas (2) to (5) are hydrogen atoms.

Claim 4. The selective film deposition method according to any one of claims 1 to 3,

wherein the metal element is contained in the form of a metal or a metal oxide, and

the metal is at least one selected from the group consisting of Cu, Co, Ru, Ni, Pt, Al, Ta, Ti, and Hf, and the metal oxide is at least one oxide of at least one metal selected from the group consisting of Cu, Co, Ru, Ni, Pt, Al, Ta, Ti, and Hf.

Claim 5. The selective film deposition method according to any one of claims 1 to 4,

wherein the nonmetal inorganic material is at least one selected from the group consisting of silicon, silicon oxide, silicon nitride, and silicon oxynitride.

Claim 6. The selective film deposition method according to any one of claims 1 to 5,

wherein a concentration of the organic substance of formula (1) in the solution is at least 0.01 mass% but not more than 20 mass% based on 100 mass% of a total amount of the solution.

Claim 7. The selective film deposition method according to any one of claims 1 to 6,

wherein the organic solvent comprises ethanol or isopropyl alcohol.

Claim 8. The selective film deposition method according to any one of claims 1 to 7,

wherein the organic substance of formula (1) comprises at least one organic substance represented by at least one selected from the group consisting of the following formulas (6) to (9):

$R^{11}-PO_3H_2$ (6)

wherein R^{11} is a C6-C100 monovalent hydrocarbon group optionally containing a heteroatom or a halogen atom;

$R^{12}-O-PO_3H_2$ (7)

wherein R^{12} is a C6-C100 monovalent hydrocarbon group optionally containing a heteroatom or a halogen atom;

$R^{13}-CO_2H$ (8)

wherein R^{13} is a C6-C100 monovalent hydrocarbon group optionally containing a heteroatom or a halogen atom; and

$R^{14}-SH$ (9)

wherein R^{14} is a C6-C100 monovalent hydrocarbon group optionally containing a heteroatom or a halogen atom.

Claim 9. The selective film deposition method according to claim 8,

wherein the organic substance of formula (1) comprises at least one organic substance represented by at least one selected from the group consisting of formula (6) and formula (7).

Claim 10. The selective film deposition method according to claim 8,

wherein the organic substance of formula (1) comprises an organic substance of formula (8).

Claim 11. The selective film deposition method according to claim 8,

wherein the organic substance of formula (1) comprises an organic substance of formula (9).

Claim 12. The selective film deposition method

according to any one of claims 8 to 11,

wherein R^{11}, R^{12}, R^{13}, and R^{14} are each a hydrocarbon group whose hydrogen atoms are partially or fully replaced with fluorine atoms.

Claim 13. The selective film deposition method according to any one of claims 8 to 11,

wherein R^{11}, R^{12}, R^{13}, and R^{14} are each a monovalent organic group represented by the following formula (10):

$$R^{15}-(CH_2)_n- \quad (10)$$

wherein R^{15} is a hydrogen atom or a monovalent hydrocarbon group optionally containing a heteroatom or a halogen atom; and n is an integer of 2 to 20, and the total number of carbons in formula (10) is 6 to 100.

Claim 14. The selective film deposition method according to any one of claims 8 to 11,

wherein R^{11}, R^{12}, R^{13}, and R^{14} are each a monovalent organic group represented by the following formula (11):

$$R^{16}-O-Y-((CH_2)_pO)_q-Z-(CH_2)_r- \quad (11)$$

wherein R^{16} is a hydrogen atom, a methyl group, or a phenyl group; Y and Z are each any divalent group or a direct bond; p is an integer of 1 to 4, and q and r are positive integers; the total number of carbons in formula (11) is 6 to 100; and the repeating units $(CH_2)_pO$ and CH_2 may be present in any order in the formula.

Claim 15. The selective film deposition method according to any one of claims 1 to 14,

wherein the substrate is washed with a solvent after the film of the organic substance of formula (1) is selectively deposited on the substrate.

Claim 16. The selective film deposition method according to any one of claims 1 to 15,

wherein two or more solutions are provided as the solution, and the substrate is sequentially exposed to the solutions.

Claim 17. The selective film deposition method according to claim 16,

wherein the number of carbons of R^1 for the organic substance in the second or subsequent solution to which the substrate is exposed is greater than or equal to the number of carbons of R^1 for the organic substance in the first solution to which the substrate is exposed.