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DESCRIPTION



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ETCHING COMPOSITION

5 Technical Field

The present invention relates to an etching composition, in particular, which is capable of etching a transparent conductive layer under mild conditions without generating etching residue.

10 Background Art

A transparent conductive layer including ITO (Indium-Tin Oxide) layer has been widely used in the field of electronic devices such as an antistatic layer, a thermal reflection layer, a photoelectric transfer element, and a transparent electrode for various types of flat panel display. With the recent spread of notebook-size personal computer, compact TV, personal digital assistants and so forth, a demand therefor has been increased particularly in the field of liquid crystal displays (LCD). A transparent conductive layer such as ITO layer has been used as a pixel display electrode in the production of flat panel displays and has been produced by etching employed in the photolithographic technique.

In the field of a liquid crystal display (LCD), particularly of TFT-LCD, polycrystalline ITO has been utilized. However, the production of uniform polycrystalline ITO becomes difficult with increasing size of substrate. The display electrode is formed by the steps of applying a photo resist on a transparent conductive layer; exposing and developing the photo resist; etching by an etching agent using the photo resist as the mask; and removing the remaining photo resist.

As the etching agent for the transparent conductive layer such as ITO layer, an iron chloride/hydrochloric acid aqueous solution, an iodic acid aqueous solution, a phosphoric acid aqueous solution, a hydrochloric acid/nitric acid

aqueous solution (aqua regia) and the like have been conventionally used.

These wet etching agents for a transparent conductive layer corrode Al and so on during the patterning process, and, the selective etching along grain boundaries occurs, making the patterning with a good precision difficult.

5 For these reasons, the demand for an etching agent capable of providing a pixel display electrode with a good precision has been increased to meet the tendency to increase the substrate size and the TFT panel size, to ensure higher resolution, and to form wiring with aluminum. To meet the demands, it has been recently proposed to etch amorphous ITO by a weak acid,
10 particularly, an aqueous solution of oxalic acid.

However, the wet etching of amorphous ITO by an aqueous solution of oxalic acid has a problem of generating etching residue. Therefore, an etching agent generating no etching residue has been desired.

15 Disclosure of Invention

An objective of the present invention is to provide an etching agent for use in the wet etching of a transparent conductive layer by an aqueous solution of oxalic acid, which is capable of etching under mild conditions without generating etching residue, differing from the prior arts aforementioned.

20 As a result of extensive study in view of solving the above problems, the inventors have found that an aqueous solution containing oxalic acid and an aromatic hydrocarbon compound having a phenolic hydroxyl group, or an aqueous solution containing oxalic acid and a nitrogen-containing carboxylic acid and/or a salt thereof is capable of etching a transparent conductive layer
25 under mild conditions without generating etching residue. The invention has been accomplished on the basis of this finding.

Namely, the present invention provides an etching composition comprising an aqueous solution containing oxalic acid and an aromatic hydrocarbon compound having a phenolic hydroxyl group, and an etching
30 composition comprising an aqueous solution containing oxalic acid and a

nitrogen-containing carboxylic acid and/or a salt thereof.

Brief Description of Drawings

Fig. 1 shows a structure after forming on a glass substrate a SiN insulation layer and an amorphous ITO layer, applying a photo resist on the amorphous ITO layer, and developing the photo resist.

Fig. 2 shows a structure after etching the substrate of Fig. 1 by a conventional etching agent, and removing the photo resist.

Best Mode for Carrying Out the Invention

The present invention is explained in details as follows.

The concentration of oxalic acid being used in the present invention is preferably 0.01 to 10% by weight. If the concentration is less than 0.01% by weight, the etching rate is low. A concentration larger than 10 % by weight is not advantageous because no enhancement of the etching rate is obtained.

As the aromatic hydrocarbon compound having a phenolic hydroxyl group, the following compounds are illustrated specifically. However, the aromatic hydrocarbon compound is not restricted thereto as far as it has a phenolic hydroxyl group directly bonded to aromatic hydrocarbon in its molecule.

(1) Aromatic hydrocarbon compound having only one hydroxyl group

Phenol, cresol, ethylphenol, tert-ethylphenol, tert-buthylphenol, methoxyphenol, salicyl alcohol, chlorophenol, aminophenol, aminocresol, amidol, p-(2-aminoethyl)phenol, salicylic acid, o-salicylanilide, naphthol, naphtholsulfonic acid, and 7-amino-4-hydroxy-2-naphthalene disulfonic acid.

(2) Aromatic hydrocarbon compound having two or more hydroxyl groups

Catechol, resorcinol, hydroquinone, 4-methylpyrocatechol, 2-methylhydroquinone, pyrogallol, 1,2,5-benzenetriol, 1,3,5-benzenetriol, 2-methylphloroglucinol, 2,4,6-phloroglucinol, 1,2,3,5-benzenetetraol, benzenehexaol, Tiron, aminoresorcinol, dihydroxycinnamic acid, 2,3-dihydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 2,5-

- dihydroxybenzaldehyde, 2,6-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 3,5-dihydroxybenzaldehyde, 2,3-dihydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid,
- 5 dihydroxyacetophenone, gallic acid, 2,3,4-trihydroxybenzoic acid, 2,4-dihydroxy-6-methylbenzoic acid, naphthalenediol, naphthalenetriol, nitronaphthol, naphthalenetetraol, binaphthyldiol, 4,5-dihydroxy-2,7-naphthalenedisulfonic acid, 1,8-dihydroxy-3,6-naphthalenedisulfonic acid, dihydroxybenzotriazole, and 1,2,3-anthracenetriol.
- 10 (3) Hydroxybenzophenones
 Dihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 2,6-dihydroxy-4-methoxybenzophenone, 2,2',5,6'-tetrahydroxybenzophenone, and 2,3',4,4',6-pentahydroxybenzophenone.
- (4) Hydroxybenzanilides
 15 o-Hydroxybenzanilide.
- (5) Hydroxyanils
 Glyoxal bis(2-hydroxyanil).
- (6) Hydroxybiphenyls
 Biphenyldiol, biphenyltriol, and biphenyltetraol.
- 20 (7) Hydroxyquinones and its derivatives
 2,3-Hydroxy-1,4-naphthoquinone, 5-hydroxy-1,4-naphthoquinone, dihydroxyanthraquinone, 1,2-dihydroxy-3-(aminomethyl)anthraquinone-N,N'-diacetic acid (common name: Alizarine Complexon), and trihydroxyanthraquinone.
- 25 (8) Diphenyl or triphenyl alkane derivatives
 Diphenylmethane-2,2'-diol, 4,4',4''-triphenylmethanetriol, 4,4'-dihydroxyfuchsone, 4,4'-dihydroxy-3-methylfuchsone, and pyrocatechol violet (common name: PV).
- (9) Phenol derivatives of alkylamine
 30 Ethylenediamine di-o-hydroxyphenylacetic acid (common name: EDDHA)

and N,N-bis(2-hydroxybenzyl)ethylenediamine-N,N-diacetic acid (common name: HBED).

(10) Phenol derivatives of alkylether

3,3-Ethylenedioxydiphenol.

5 (11) Phenols having azo group and its derivatives

Diammonium 4,4'-bis(3,4-dihydroxyphenylazo)-2,2-stilbenedisulfonate (common name: Stilbazo), 2,8-dihydroxy-1-(8-hydroxy-3, 6-disulfo-1-naphthylazo)-3,6-naphtalenedisulfonic acid, o-o'-dihydroxyazobenzene, 2-hydroxy-1-(2-hydroxy-5-methylphenylazo)-4-naphtalenesulfonic acid (common
10 name: Calmagite), chlorohydroxyphenylazonaphthol, 1,2' -dihydroxy-6-nitro-1,2'-azonaphthalene-4-sulfonic acid (common name: Eriochrom Black T), 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3,6-naphtalenedisulfonic acid, 5-chloro-2-hydroxy-3-(2,4-dihydroxyphenylazo)benzenesulfonic acid (common name: Lumogallion), 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphtalenesulfonic acid [common name: NN], 1,8-dihydroxy-2-(4-sulfophenylazo)-3,6-naphtalenedisulfonic acid, 1,8-dihydroxy-2,7-bis(5-chloro-2-hydroxy-3-sulfophenylazo)-3,6-naphtalenedisulfonic acid, 1,8-dihydroxy-2,7-bis(2-sulfophenylazo)-3,6-naphtalenedisulfonic acid, 2-[3-(2,4-dimethylphenylaminocarboxy)-2-hydroxy-1-naphthylazo]-3-dihydroxybenzenesulfonic acid, and 2-[3-(2,4-dimethylphenylaminocarboxy)-2-hydroxy-1-naphthylazo]phenol.

(12) Heterocyclic compound having a hydroxy group and its derivatives

8-Quinolinol, 2-methyl-8-quinolinol, quinolinediol, 1-(2-pyridylazo)-2-naphthol, 2-amino-4,6,7-pteridinetriol, 5,7,3',4'-tetrahydroxyflavone (common
25 name: Luteolin), 3,3-bis[N,N-bis(carboxymethyl)aminomethyl]fluoresceine (common name: Calcein), and 2,3-hydroxypyridine.

(13) Alicyclic compounds having a hydroxy group and its derivatives

Cyclopentanol, croconic acid, cyclohexanol, cyclohexanediol, dihydroxydiquinoyl, tropolone, and 6-isopropyltropolone.

30 As the aromatic hydrocarbon compound having a hydroxy group, those

having two or more phenolic hydroxy groups are preferable.

Of the above compounds, preferred are 2,3-dihydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 2,3-dihydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 2,6-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, and 3,5-dihydroxybenzaldehyde.

The above aromatic hydrocarbon compounds may be used alone or in combination of two or more, preferably in a concentration of 0.0001 to 5% by weight based on the total etching composition. If the concentration is less than 0.0001% by weight, the etching residue is generated. If more than 5% by weight, the etching rate of ITO layer is unfavorably lowered or the dissolution thereof becomes inadequate.

The following compounds are illustrated, not a limitation, as the nitrogen-containing carboxylic acids and salts thereof:

- (1) N-containing carboxylic acid having one carboxyl group and its salts
Aminoacetic acid, dihydroxyethylglycin, and salts thereof.
- (2) N-containing carboxylic acid having two carboxyl groups and its salts
Iminodiacetic acid, hydroxyethyliminodiacetic acid, ethylenediaminediacetic acid, ethylenediaminedipropionic acid, and salts thereof.
- (3) N-containing carboxylic acid having three carboxyl groups and its salts
Nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, nitrilotripropionic acid, and salts thereof.
- (4) N-containing carboxylic acid having four carboxyl groups and its salts
Ethylenediaminetetraacetic acid, trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid, diaminopropanoltetraacetic acid, glycol ether diaminetetraacetic acid, hexamethylenediamine-N,N,N',N'-tetraacetic acid, diaminopropanetetraacetic acid, and salts thereof.
- (5) N-containing carboxylic acids having five carboxyl groups and its salts

Diethylenetriaminepentaacetic acid and salts thereof.

(6) N-containing carboxylic acids having six carboxyl groups and its salts
Triethylenetetraminehexaacetic acid and salts thereof.

(7) Other related compounds

5 Complex-forming amine compounds such as triethanolamine and salts thereof.

10 The above N-containing carboxylic acids and salts thereof may be used alone or in combination of two or more, preferably in a concentration of 0.0001 to 5% by weight based on the total etching composition. The N-containing carboxylic acids and salts thereof having four or less carboxyl groups are preferably used. If the concentration is less than 0.0001 % by weight, the etching residue is generated. If more than 5% by weight, the etching rate of ITO layer is unfavorably lowered or the dissolution thereof becomes inadequate.

15 The etching composition of the present invention is used in conventional means at a temperature from ordinary temperature to 90°C for 0.1 to 30 min. Further, the etching composition of the present invention is suitably applied, in addition to amorphous ITO, to the wet etching of a transparent conductive layer such as IZO (Indium-Zinc Oxide) and to the wet etching in the production
20 of various semiconductors.

The following examples are provided as illustrations, not a limitation, of the present invention:

EXAMPLE 1

25 In Fig. 1, is shown a substrate obtained by: forming a SiN_2 insulation layer on a glass substrate 1; forming an amorphous ITO_3 layer thereon; applying a photo resist thereon; and developing the photo resist. The substrate shown in Fig. 1 was etched for 2 h at 40°C by a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.1% by weight of 2,3-dihydroxybenzoic acid), and washed with water. After removing the
30 photo resist 4 by a basic resist remover, the processed substrate was washed

with water and dried. The results of observing the surface thereof under SEM (electron microscope) showed that the amorphous ITO was etched successfully and no residue was noticed.

COMPARATIVE EXAMPLE 1

5 The substrate used in Example 1 was etched for 2 h at 40°C by a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid), washed with water and dried. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched, but many residues 5 remained as shown in Fig. 2.

COMPARATIVE EXAMPLE 2

By using a washing liquid (aqueous solution containing 0.1% by weight of 2,3-dihydroxybenzoic acid), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a
15 basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO remained nearly unetched.

EXAMPLE 2

By using a washing liquid (aqueous solution containing 3.4% by weight of
20 oxalic acid and 0.01% by weight of 2,3-dihydroxybenzaldehyde), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched
25 successfully and no residue was noticed.

EXAMPLE 3

By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.3% by weight of 2,3-dihydroxybenzaldehyde), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After
30 removing the photo resist 4 by using a basic resist remover, the processed

substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 4

5 By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.01% by weight of 2,3-dihydroxybenzoic acid), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the
10 surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 5

By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.3% by weight of 2,3-dihydroxybenzoic acid, the substrate used
15 in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

20 EXAMPLE 6

By using a washing liquid (aqueous solution containing 1.0% by weight of oxalic acid and 0.1% by weight of 2,3-dihydroxybenzoic acid, the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed
25 substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 7

By using a washing liquid (aqueous solution containing 5.5% by weight of
30 oxalic acid and 0.1% by weight of 2,3-dihydroxybenzoic acid), the substrate used

in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

COMPARATIVE EXAMPLE 3

By using a washing liquid (aqueous solution containing 5.5% by weight of acetic acid and 0.1% by weight of 2,3-dihydroxybenzoic acid), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO remained nearly unetched.

EXAMPLE 8

By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.2% by weight of dihydroxyethylglycin), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

COMPARATIVE EXAMPLE 4

By using a washing liquid (aqueous solution containing 0.2% by weight of dihydroxyethylglycin), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO remained nearly unetched.

EXAMPLE 9

By using a washing liquid (aqueous solution containing 3.4% by weight of

oxalic acid and 0.2% by weight of iminodiacetic acid), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 10

By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.2% by weight of hydroxyethyliminodiacetic acid), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 11

By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.2% by weight of nitrilotriacetic acid), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 12

By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 0.2% by weight of ethylenediaminetetraacetic acid), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 13

By using a washing liquid (aqueous solution containing 3.4% by weight of oxalic acid and 2.0% by weight of dihydroxyethylglycin), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing
5 the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 14

10 By using a washing liquid (aqueous solution containing 1.0% by weight of oxalic acid and 0.2% by weight of dihydroxyethylglycin), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof
15 under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

EXAMPLE 15

By using a washing liquid (aqueous solution containing 5.5 % by weight of oxalic acid and 0.2 % by weight of dihydroxyethylglycin), the substrate used in
20 Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was washed with water and dried. The results of observing the surface thereof under SEM showed that the amorphous ITO was etched successfully and no residue was noticed.

25 COMPARATIVE EXAMPLE 5

By using a washing liquid (aqueous solution containing 5.5% by weight of acetic acid and 0.2% by weight of dihydroxyethylglycin), the substrate used in Example 1 was etched for 2 h at 40°C and washed with water. After removing the photo resist 4 by using a basic resist remover, the processed substrate was
30 washed with water and dried. The results of observing the surface thereof

under SEM showed that the amorphous ITO remained nearly unetched.

Industrial Applicability

5 The etching composition of the present invention is capable of etching a transparent conductive layer under mild conditions without generating etching residue.

CLAIMS

What is claimed is:

1. An etching composition comprising an aqueous solution containing oxalic acid and an aromatic hydrocarbon compound having a phenolic hydroxyl group.
- 5 2. The etching composition as defined in claim 1, wherein the aromatic hydrocarbon compound having a phenolic hydroxyl group has two or more phenolic hydroxyl groups.
3. An etching composition comprising an aqueous solution containing oxalic acid and a nitrogen-containing carboxylic acid and/or a salt thereof.
- 10 4. The etching composition as defined in claim 3, wherein the nitrogen-containing carboxylic acid has four or less carboxyl groups.
5. The etching composition as defined in claim 1, for use in a wet etching of a transparent conductive layer.
6. The etching composition as defined in claim 3, for use in a wet etching of a
- 15 transparent conductive layer.
7. The etching composition as defined claim 5, wherein the transparent conductive layer is an indium–tin oxide layer.
8. The etching composition as defined claim 6, wherein the transparent conductive layer is an indium–tin oxide layer.