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DESCRIPTION

WET ETCHING AGENT COMPOSITION

TECHNICAL FIELD

The present invention relates to a wet etching agent composition to be employed for the wet etching of a transparent electroconductive film such as ITO (Indium Tin Oxide) film to be used as a pixel electrode in a liquid crystal display and the like.

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BACKGROUND ART

A transparent electroconductive film originating from ITO film has been widely used in the field of electronic devices such as transparent electrodes for antistatic films, heat reflection films, photoelectric transfer elements and various flat panel displays. In particular, a liquid crystal display (LCD) has recently been in increasing demand along with the popularization of a notebook personal computer, a miniaturized TV set, a portable information terminal and the like. In the field of flat panel displays, the transparent electroconductive film such as ITO film is used as a display electrode for pixels, and is prepared by photolithography etching.

On the other hand, in the field of liquid crystal display (LCD), especially TFT (Thin Film Transistor)-LCD, polycrystalline ITO has heretofore been employed, but it becomes difficult to uniformize a polycrystalline ITO as a substrate is larger-sized. The aforesaid display electrode is formed by a method wherein a photoresist is applied onto a

transparent electroconductive film, subjected to exposure and development, followed by etching through the use of an etching agent along with the photoresist as the mask, and thereafter the residual photoresist is peeled off.

There have hitherto been employed an aqueous solution of ferric chloride / hydrochloric acid, an aqueous solution of iodic acid, an aqueous solution of phosphoric acid, an aqueous solution of hydrochloric acid / nitric acid (aqua regia) and the like as an etching agent for the above-mentioned transparent electroconductive film such as the polycrystalline ITO film. The aforesaid wet etching agent for the ITO and the like causes corrosion of aluminum and the like in the case of patterning, and selective etching proceeds starting from grain boundaries, thereby making it difficult to conduct patterning in high processing precision.

By the reasons mentioned above, an etching agent which is capable of etching a pixel display electrode in high processing precision has recently been in increasing demand, accompanying the larger-sized substrate, high precision and larger-sized TFT panel, aluminum made wiring and the like. In order to solve the above-mentioned problems, there is recently proposed a method wherein an amorphous ITO is used and is subjected to wet etching with a weak acid, particularly aqueous solution of oxalic acid.

Nevertheless, the problem still remains unsolved in that an etching residue is produced in the case of subjecting an amorphous ITO to wet etching by the use of aqueous solution of oxalic acid. In such circumstances, it has been eagerly desired

to develop an etching agent free from the generation of an etching residue.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a wet etching agent which is completely freed from the generation of an etching residue, and thus enables etching to be carried out under a mild working condition at the time of subjecting an amorphous ITO to wet etching by using aqueous solution of oxalic acid as is the case with the prior art.

In order to solve the above-mentioned subject, intensive, extensive research and investigation were accumulated by the present inventors. As a result, it has been found that wet etching of an amorphous ITO can be performed under a mild working condition, and is completely freed from the generation of an etching residue by the use of an aqueous solution containing oxalic acid and, as a surfactant, a poly(oxyethylene) alkyl ether sulfate and / or a poly(oxyethylene) alkylphenyl ether sulfate. Thus the present invention has been accomplished on the basis of the foregoing findings and information.

Specifically, the present invention is concerned with a wet etching agent composition for transparent electroconductive films which comprises an aqueous solution containing oxalic acid and a poly(oxyethylene) alkyl ether sulfate and / or a poly(oxyethylene) alkylphenyl ether sulfate.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a cross sectional view showing a glass substrate wherein a SiN film as an insulating film is formed thereon, further an amorphous ITO film is formed on the SiN film, and a resist is applied thereto and developed; and

FIG. 2 is a view showing the state after the substrate in FIG. 1 is etched with an etching agent described in Comparative Example 1. and thereafter the resist is peeled off with a basic peeling agent for the resist.

THE MOST PREFERRED EMBODIMENT TO CARRY OUT THE INVENTION

The concentration of the oxalic acid to be used in the present invention is in the range of 0.01 to 10% by weight. The concentration outside the above range is disadvantageous, since the concentration, when being 0.01% or less by weight, results in unreasonably low rate of etching, whereas the concentration thereof, when being 10% or more by weight, does not enhance the etching rate considering the increased dosage.

In addition, the poly(oxyethylene) alkyl ether sulfate to be used in the present invention is represented by the general formula [I]

wherein R is an alkyl group having 6 to 22 carbon atoms, n is an integer of from 1 to 500, and M is ammonia, an organic amine, a quaternary ammonium salt or an alkali metal.

Specifically, examples of favorably usable poly(oxyethylene) alkyl ether sulfate includes, as a trade name, Emarl 20C (manufactured by Kao Corporation), Hightenol 325 D

(manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), Alscorp AP-30, Alscorp LE-240 (each manufactured by Toho Chemical Industry Co., Ltd.), Sunnol 605N (manufactured by Lion Corporation) and the like.

In addition, the poly(oxyethylene) alkylphenyl ether sulfate to be used in the present invention is represented by the general formula [II]

wherein R is an alkyl group having 4 to 20 carbon atoms, n is an integer of from 1 to 500, and M is ammonia, an organic amine, a quaternary ammonium salt or an alkali metal.

Specifically, examples of favorably usable poly(oxyethylene) alkylphenyl ether sulfate includes, as a trade name, Hightenol N-08, Hightenol N-12 (each manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), Emarl NC-35 (manufactured by Kao Corporation), and the like. Any of the above-exemplified poly(oxyethylene) alkyl ether sulfate and poly(oxyethylene) alkylphenyl ether sulfate may be used alone or in combination with at least one other at a concentration being preferably in the range of 0.0001 to 5% by weight.

The concentration of any of the poly(oxyethylene) alkyl ether sulfate and poly(oxyethylene) alkylphenyl ether sulfate outside the above-mentioned range is unfavorable, since the concentration, when being 0.0001% or less by weight, causes the generation of an etching residue, whereas the concentration, when being 5% or more by weight, gives rise to a decrease in an etching rate of a transparent electroconductive film such as ITO film.

The working temperature of the wet etching agent

composition according to the present invention is in the range of room temperature to 90℃, and the working time is in the range of 1 to 30 minutes. The composition is preferably applicable to wet etching of IZO (Indium-Zinc Oxide) and the like in addition to the foregoing amorphous ITO film.

In what follows, the present invention will be described in more detail with reference to working examples, which however shall never limit the present invention thereto.

Example 1

FIG.1 is a cross sectional view showing a glass substrate 1 wherein a SiN film 2 as an insulating film is formed thereon, further an amorphous ITO film 3 is formed on the SiN film, and a resist is applied thereto and developed. By the use of an etching agent containing an aqueous solution of 3.4% by weight of oxalic acid and 0.01% by weight of poly(oxyethylene) alkylphenyl ether sulfate (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd. under the trade name Hightenol N-08), the substrate as illustrated on FIG. 1 was etched at 40℃ for 2 minutes, and washed with water. After the resist 4 was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water and dried. As a result of observation with an SEM (Electron Microscope), the amorphous ITO film was favorably etched, and no etching residue was observed at all.

Comparative Example 1

By the use of an etching agent containing an aqueous solution of 3.4% by weight of oxalic acid, the substrate same

as that used in Example 1 was etched at 40℃ for 2 minutes, and washed with water and dried. After the resist was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water. As a result of observation with an SEM, the amorphous ITO film was etched. but a large number of etching residues 5 were observed as illustrated on FIG. 2.

Comparative Example 2

By the use of an etching agent containing an aqueous solution of 1% by weight of poly(oxyethylene) alkylphenyl ether sulfate (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd. under the trade name Hightenol N-08), the substrate same as that used in Example 1 was etched at 40℃ for 2 minutes, and washed with water. After the resist was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water and dried. As a result of observation with an SEM, the amorphous ITO film was scarcely etched.

Example 2

By the use of an etching agent containing an aqueous solution of 3.4% by weight of oxalic acid and 0.1% by weight of poly(oxyethylene) alkylphenyl ether sulfate (manufactured by Dai-ichi Kogyo Seiyaku Co.. Ltd. under the trade name Hightenol N-12), the substrate same as that used in Example 1 was etched at 40℃ for 2 minutes. and washed with water. After the resist was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water and

dried. As a result of observation with an SEM, the amorphous ITO film was favorably etched, and no etching residue was observed at all.

Example 3

By the use of an etching agent containing an aqueous solution of 3.4% by weight of oxalic acid and 0.1% by weight of poly(oxyethylene) alkyl ether sulfate (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd. under the trade name Hightenol 325 D), the substrate same as that used in Example 1 was etched at 40℃ for 2 minutes, and washed with water. After the resist was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water and dried. As a result of observation with an SEM, the amorphous ITO film was favorably etched, and no etching residue was observed at all.

Example 4

By the use of an etching agent containing an aqueous solution of 1.0% by weight of oxalic acid and 0.1% by weight of poly(oxyethylene) alkylphenyl ether sulfate (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd. under the trade name Hightenol N-12), the substrate same as that used in Example 1 was etched at 40℃ for 2 minutes. and washed with water. After the resist was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water and dried. As a result of observation with an SEM, the amorphous ITO film was favorably etched. and no etching residue was observed at all.

Example 5

By the use of an etching agent containing an aqueous solution of 5.5% by weight of oxalic acid and 0.1% by weight of poly(oxyethylene) alkylphenyl ether sulfate (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd. under the trade name Hightenol N-12), the substrate same as that used in Example 1 was etched at 40℃ for 2 minutes, and washed with water. After the resist was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water and dried. As a result of observation with an SEM, the amorphous ITO film was favorably etched, and no etching residue was observed at all.

Comparative Example 3

By the use of an etching agent containing an aqueous solution of 5.5% by weight of acetic acid and 0.1% by weight of poly(oxyethylene) alkylphenyl ether sulfate (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd. under the trade name Hightenol N-12), the substrate same as that used in Example 1 was etched at 40℃ for 2 minutes, and washed with water. After the resist was peeled off with a basic peeling liquid for resist, the etched substrate was further washed with water and dried. As a result of observation with an SEM, the amorphous ITO film was scarcely etched.

INDUSTRIAL APPLICABILITY

By the use of the wet etching agent composition according to the present invention, it is made possible to etch an amorphous ITO under mild working conditions, while an etching residue is not generated at all.

CLAIMS

1. A wet etching agent composition for use in etching amorphous transparent electroconductive films which comprises an aqueous solution containing oxalic acid and a poly(oxyethylene) alkyl ether sulfate and / or a poly(oxyethylene) alkylphenyl ether sulfate.

2. A wet etching agent composition according to Claim 1, wherein the transparent electroconductive film is an Indium Tin oxide film.