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DESCRIPTION



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ETCHING METHOD FOR ALUMINUM-MOLYBDENUM LAMINATE FILM

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Technical Field

The present invention relates to a method of forming laminate wirings for use as signal wirings of liquid crystal display devices, etc., more specifically relates to a method of etching a laminate film on a substrate, which comprises
10 an aluminum-based metal film and a high-melting metal film containing molybdenum, etc., to form reliable laminate wirings.

Background Art

In active matrix-type liquid crystal display devices in which
15 transparent pixel electrodes such as ITO (indium tin oxide), etc. in matrix arrangement on a glass substrate are driven by TFT (thin film transistor), is employed a TFT panel structure in which a gate electrode to drive TFT, gate lines and data lines each extending from the gate electrode, etc. are formed on the same glass substrate.

20 The structure of the most common inverted staggered TFT panel will be outlined below with reference to a cross-sectional illustration shown in Fig. 1.

TFT is constructed of a normal-tapered gate electrode 2 formed on a glass substrate 1, and a source electrode 6 and a drain electrode 7 which are
25 disposed so as to oppose the gate electrode 2 via a gate insulating film 3, an i-type semiconductor film 4 and n-type semiconductor film 5. Generally, the i-type semiconductor film 4 is formed from a non-doped a-Si, and the n-type semiconductor film 5 is formed from an n⁺a-Si containing n-type impurity. The gate electrode 2 is formed from Al-based metal, etc., and the side surfaces

thereof are made into normal tapers so as to ensure a good step coverage with the i-type semiconductor film 4 formed thereon and enhance the insulating strength of the gate insulating film 3.

To provide normal tapers, the gate electrode 2 made of Al-based metal, etc. and gate lines extending therefrom have been conventionally formed by depositing a Al-based metal film throughout the entire surface of the glass substrate 1 by sputtering, etc., forming a resist pattern selectively on the deposited film, and isotropic and wet-etching the deposited film with the resist pattern using as a mask.

In the recent TFT panels, to ensure the contact between Al-based metal wiring and ITO film and prevent the hillock of Al-based metal wiring, the laminate wiring structures shown in Figs. 2 and 3 have come to be widely employed. The laminate wiring structure of Fig. 2 comprises a low resistance Al-based metal wiring 21 (Al gate electrode) and a metal wiring 22 (Mo gate electrode) of a high-melting metal such as molybdenum (Mo) thereon. In Fig. 3, a metal wiring 22 of a high-melting metal such as Mo is disposed on each of the upper surface and lower surface of a low resistance Al-based metal wiring 21. In these laminate wiring structures, the insulating strength can be enhanced also by making the side surfaces of the metal wiring 22 of a high-melting metal such as Mo into normal tapers.

Acid mixtures of phosphoric acid, nitric acid and acetic acid have been conventionally used as the wet-etching solution for Al-based metal films (Japanese Patent Application Laid-Open Nos. 7-176500, 7-176525, 9-127555). However, it is quite difficult to make the laminate structure of the Al-based metal film and the high-melting metal film into normal tapers simultaneously by the acid mixtures, for example, because the cell reaction occurs during the etching operation due to the difference between the standard electrode potentials of Al and the metal to be laminated.

Japanese Patent Application Laid-Open No. 6-104241 describes to

control the thickness ratio of the laminated films in the wet-etching of a Mo/Al laminate film by the acid mixtures, but the proposed method fails to solve the above problems thoroughly.

Therefore, it is demanded to provide a method capable of etching
5 laminate films as described above to have good normal tapers.

Disclosure of Invention

An object of the present invention is to solve the above problems in prior art and to provide a method of wet-etching an aluminum-based metal
10 film, particularly a laminate film of an aluminum-based metal film and a high-melting metal film containing molybdenum, etc. so as to have good normal tapers.

As a result of extensive research for achieving the above object, the inventors have found that a laminate film comprising at least one
15 aluminum-based metal film and at least one molybdenum-based high-melting metal film is etched to have good normal tapers by using an etching solution comprising an aqueous solution containing phosphoric acid, nitric acid, an organic acid and a cation-generating component, when the water content of the etching solution is maintained within a range of 10 to 30% by weight during
20 the etching treatment. The present invention has been accomplished on the basis of this finding.

Brief Description of Drawings

Fig. 1 is a schematic cross-sectional view of a common inverted
25 staggered TFT panel structure;

Fig. 2 is a schematic illustration showing a laminate structure comprising a high-melting metal wiring on a low-resistance Al-based metal wiring;

Fig. 3 is a schematic illustration showing a laminate structure

comprising a Mo-based high-melting metal wiring between upper and lower low-resistance Al-based metal wirings;

Fig. 4 is a flow diagram showing the formation of a tapered laminate structure of Al-based metal wiring/Mo-based high-melting metal wiring in normal form;

Fig. 5 is a schematic view showing a tapered laminate structure of Al-based metal wiring/Mo-based high-melting metal wiring in non-normal form;

Fig. 6 is a flow diagram showing the formation of a tapered laminate structure of Mo-based high-melting metal wiring/Al-based metal wiring/Mo-based high-melting metal wiring in normal form; and

Fig. 7 is a schematic view showing a tapered laminate structure of Mo-based high-melting metal wiring/Al-based metal wiring/Mo-based high-melting metal wiring in non-normal form.

Best Mode for Carrying Out the Invention

The wet-etching solution used in the present invention is an aqueous solution containing phosphoric acid, nitric acid, an organic acid and a cation-generating component.

The concentration of phosphoric acid is 50 to 80% by weight, preferably 60 to 75% by weight of the wet-etching solution. Phosphoric acid takes part mainly in the etching of the Al-based metal film. If less than 50% by weight, the etching rate of the Al-based metal film is lowered, whereas the etching rate undesirably becomes excessively high if the concentration exceeds 80% by weight. The term "Al-based metal film" referred to herein means aluminum film and films of aluminum alloy having an aluminum content of 80% by weight or more. The alloying metal may be Nd, Zr, Cu, Si, etc.

The concentration of nitric acid is 0.5 to 10% by weight, preferably 1 to 8% by weight of the wet-etching solution. Nitric acid takes part mainly in the

etching of the Mo-based high-melting metal film. If less than 0.5% by weight, the etching rate of the Mo-based high-melting metal film is lowered, whereas the etching rate undesirably becomes excessively high if the concentration exceeds 10% by weight. The term "Mo-based high-melting metal film"

5 referred to herein means molybdenum film and films of molybdenum alloy having a molybdenum content of 80% by weight or more. The alloying metal may be W, etc.

Examples of the organic acids include monocarboxylic acids such as formic acid, acetic acid, propionic acid and butyric acid; dicarboxylic acids such
10 as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, maleic acid, fumaric acid and phthalic acid; tricarboxylic acids such as trimellitic acid; hydroxymonocarboxylic acids such as hydroxyacetic acid, lactic acid and salicylic acid; hydroxydicarboxylic acids such as malic acid and tartaric acid; hydroxytricarboxylic acids such as citric acid; and
15 aminocarboxylic acid such as aspartic acid and glutamic acid.

The concentration of the organic acid is 0.5 to 10% by weight, preferably 5 to 8% by weight of the wet-etching solution, while suitably selected according to the concentrations of phosphoric acid and nitric acid, etching conditions, etc.

20 Examples of the cation-generating component include ammonia; ammonium salts such as ammonium hydroxide; aliphatic amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, dipropylamine, tripropylamine, butylamine, dibutylamine and tributylamine; alkanolamines such as monoethanolamine, diethanolamine and triethanolamine; polyamines such as ethylenediamine,
25 propylenediamine, trimethylenediamine and tetramethylenediamine; cyclic amines such as pyrrole, pyrrolidine, pyrrolidine and morpholine; and quaternary ammonium hydroxides such as tetramethylammonium hydroxide, tetraethylammonium hydroxide and trimethyl(2-hydroxyethyl)ammonium

hydroxide. In addition to ammonia, amines, quaternary ammonium hydroxides, etc., alkali metal salts such as sodium hydroxide and potassium hydroxide may be used as the cation-generating component. Of the above cation-generating components, ammonium salts are particularly preferred.

5 The concentration of the cation-generating component is 0.1 to 20% by weight, preferably 1 to 10% by weight of the wet-etching solution. If less than 0.1% by weight, the etching solution easily becomes ineffective, while the etching rates of the Mo-based metal film and the Al-based metal film undesirably become low if the concentration exceeds 20% by weight.

10 The optimum water content of the wet-etching solution is characteristic of the kinds of metal films and their compositions, and suitably determined according to the metal films to be actually etched. Generally, the water content is preferably 10 to 30% by weight. For example, the water content is 15 to 20% by weight, preferably 16 to 19% by weight for the wet
15 etching of Mo-based high-melting metal film/Al-based metal film, and 18 to 23% by weight, preferably 19 to 22% by weight for the wet etching of Mo-based high-melting metal film/Al-based metal film/Mo-based high-melting metal film.

 The etching may be performed under known conditions without any
20 limitation, for example, by bringing metal films into contact with the etching solution at room temperature (20 to 25°C) to 50°C for 0.5 to 3 min. The etching conditions may be suitably determined, taking the kind, thickness, etc. of the laminate film to be treated into consideration.

EXAMPLE 1

25 The present invention is described in detail with reference to Figs. 4(a) to (c). A laminate film of molybdenum alloy film 22 (750 Å)/aluminum alloy film 21 (750 Å) was formed on a TFT glass substrate 1 by sputtering aluminum alloy (99.1% by weight of Al and 0.9% by weight of Zr) and then sputtering molybdenum alloy (85% by weight of Mo and 15% by weight of W) as shown in

Fig. 4(a). Photoresist 23 applied on the molybdenum alloy/aluminum alloy laminate film was exposed through a patterned mask prepared in advance and developed to form an intended photoresist pattern (Fig. 4(b)).

The substrate of Fig. 4(b) was just-etched at 45°C by each of the following four etching solutions:

- (1) 65% by weight phosphoric acid, 9% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 19% by weight water;
- (2) 66% by weight phosphoric acid, 9% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 18% by weight water;
- (3) 67% by weight phosphoric acid, 9% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 17% by weight water; and
- (4) 68% by weight phosphoric acid, 9% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 16% by weight water,

rinsed with water and dried, and then, the photoresist 23 was removed with an amine-based stripping solution. The results of observation under scanning electron microscope (SEM) showed that the resultant molybdenum alloy/aluminum alloy laminate film had good normal tapers as shown in Fig. 4(c).

COMPARATIVE EXAMPLE 1

The substrate of Fig. 4(b) was just-etched at 45°C by each of the following two etching solutions:

- (5) 62% by weight phosphoric acid, 9% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 22% by weight water; and
- (6) 71% by weight phosphoric acid, 9% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 13% by weight water,

rinsed with water and dried, and then, the photoresist 23 was removed with the amine-based stripping solution. The results of observation under scanning electron microscope (SEM) showed that the resultant molybdenum alloy/aluminum alloy laminate film had non-normal tapers as shown in Fig. 5,

and that the normal taper as shown in Fig. 4(c) was not attained.

EXAMPLE 2

The present invention is described in detail with reference to Figs. 6(a) to (c). A laminate film of molybdenum alloy film 22 (750 Å)/aluminum alloy film 21 (1500 Å)/molybdenum alloy film 22 (750 Å) was formed on a TFT glass substrate 1 by sputtering molybdenum alloy (85% by weight of Mo and 15% by weight of W), aluminum alloy (99.1% by weight of Al and 0.9% by weight of Zr) and then sputtering molybdenum alloy (85% by weight of Mo and 15% by weight of W) as shown in Fig. 6(a). Photoresist 23 applied on the laminate film was exposed through a patterned mask prepared in advance and developed to form an intended photoresist pattern (Fig. 6(b)).

The substrate of Fig. 6(b) was just-etched at 45°C by each of the following four etching solutions:

- (7) 64% by weight phosphoric acid, 7% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 22% by weight water;
 - (8) 65% by weight phosphoric acid, 7% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 21% by weight water;
 - (9) 66% by weight phosphoric acid, 7% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 20% by weight water; and
 - (10) 67% by weight phosphoric acid, 7% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 19% by weight water,
- rinsed with water and dried, and then, the photoresist 23 was removed with the amine-based stripping solution. The results of observation under scanning electron microscope (SEM) showed that the resultant molybdenum alloy/aluminum alloy/molybdenum alloy laminate film had good normal tapers as shown in Fig. 6(c).

EXAMPLE 3

The substrate of Fig. 6(b) was just-etched at 45°C by each of the following four etching solutions:

(11) 63% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight propionic acid, 2% by weight ammonium hydroxide, and 22% by weight water;

(12) 64% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight propionic acid, 2% by weight ammonium hydroxide, and 21% by weight water;

5 (13) 65% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight propionic acid, 2% by weight ammonium hydroxide, and 20% by weight water; and

(14) 66% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight propionic acid, 2% by weight ammonium hydroxide, and 19% by weight water,

10 rinsed with water and dried, and then, the photoresist 23 was removed with the amine-based stripping solution. The results of observation under scanning electron microscope (SEM) showed that the resultant molybdenum alloy/aluminum alloy/molybdenum alloy laminate film had good normal tapers as shown in Fig. 6(c).

15 EXAMPLE 4

The substrate of Fig. 6(b) was just-etched at 45°C by each of the following four etching solutions:

(15) 62% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight acetic acid, 3% by weight sodium hydroxide, and 22% by weight water;

20 (16) 63% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight acetic acid, 3% by weight sodium hydroxide, and 21% by weight water;

(17) 64% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight acetic acid, 3% by weight sodium hydroxide, and 20% by weight water; and

25 (18) 65% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight acetic acid, 3% by weight sodium hydroxide, and 19% by weight water,

rinsed with water and dried, and then, the photoresist 23 was removed with the amine-based stripping solution. The results of observation under scanning electron microscope (SEM) showed that the resultant molybdenum alloy/aluminum alloy/molybdenum alloy laminate film had good normal tapers

as shown in Fig. 6(c).

COMPARATIVE EXAMPLE 2

The substrate of Fig. 6(b) was just-etched at 45°C by each of the following two etching solutions:

- 5 (19) 61% by weight phosphoric acid, 7% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 25% by weight water; and
(20) 70% by weight phosphoric acid, 7% by weight nitric acid, 5% by weight acetic acid, 2% by weight ammonium hydroxide, and 16% by weight water;
rinsed with water and dried, and then, the photoresist 23 was removed with
10 the amine-based stripping solution. The results of observation under scanning electron microscope (SEM) showed that the resultant molybdenum alloy/aluminum alloy/molybdenum alloy laminate film had non-normal tapers as shown in Fig. 7, and that the normal taper as shown in Fig. 6(c) was not attained.

15 COMPARATIVE EXAMPLE 3

The substrate of Fig. 6(b) was just-etched at 45°C by each of the following two etching solutions:

- (19) 60% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight propionic acid, 2% by weight ammonium hydroxide, and 25% by weight water;
20 and
(20) 69% by weight phosphoric acid, 8% by weight nitric acid, 5% by weight propionic acid, 2% by weight ammonium hydroxide, and 16% by weight water;
rinsed with water and dried, and then, the photoresist 23 was removed with the amine-based stripping solution. The results of observation under
25 scanning electron microscope (SEM) showed that the resultant molybdenum alloy/aluminum alloy/molybdenum alloy laminate film had non-normal tapers as shown in Fig. 7, and that the normal taper as shown in Fig. 6(c) was not attained.

Industrial Applicability

By the etching method of the present invention, an aluminum-based metal film, particularly a laminate film of an aluminum-based metal film and a molybdenum-based high-melting metal film is wet-etched to have good
5 normal tapers.

CLAIMS

WHAT IS CLAIMED IS:

1. An etching method comprising a step of bringing a laminate film which is formed on a substrate and comprises at least one aluminum-based metal
5 film and at least one molybdenum-based high-melting metal film into contact with a wet-etching solution comprising an aqueous solution containing phosphoric acid, nitric acid, an organic acid and a cation-generating component, while maintaining a water content of the wet-etching solution within a range of 10 to 30% by weight.
- 10 2. The etching method according to Claim 1, wherein the laminate film comprises an aluminum-based metal film on the substrate and a molybdenum-based high-melting metal film on the aluminum-based metal film.
3. The etching method according to Claim 2, wherein the water content is
15 15 to 20% by weight.
4. The etching method according to Claim 1, wherein the laminate film comprises a molybdenum-based high-melting metal film on the substrate, an aluminum-based metal film on the molybdenum-based high-melting metal film, and a molybdenum-based high-melting metal film on the aluminum-based
20 metal film.
5. The etching method according to Claim 4, wherein the water content is 18 to 23% by weight.
6. The etching method according to any one of Claims 1 to 5, wherein a concentration of phosphoric acid is 50 to 80% by weight of the wet-etching
25 solution.
7. The etching method according to any one of Claims 1 to 6, wherein a concentration of nitric acid is 0.5 to 10% by weight of the wet-etching solution.
8. The etching method according to any one of Claims 1 to 7, wherein the organic acid is at least one acid selected from the group consisting of formic

acid, acetic acid, propionic acid, butyric acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, maleic acid, fumaric acid, phthalic acid, trimellitic acid, hydroxyacetic acid, lactic acid, salicylic acid, malic acid, tartaric acid, citric acid, aspartic acid and glutamic acid.

5 9. The etching method according to any one of Claims 1 to 8, wherein a concentration of the organic acid is 0.5 to 10% by weight of the wet-etching solution.

10 10. The etching method according to any one of Claims 1 to 9, wherein the cation-generating component is at least one compound selected from the group consisting of ammonia, ammonium salts, aliphatic amines, alkanolamines, polyamines, cyclic amines, quaternary ammonium hydroxides and alkali metal salts.

15 11. The etching method according to any one of Claims 1 to 10, wherein a concentration of the cation-generating component is 0.1 to 20% by weight of the wet-etching solution.