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SPECIFICATION

TITLE OF THE INVENTION

Dry Processing Gas

Background of the Invention

1. Field of the Invention

The present invention relates to dry processing gas such as etching gas having CF_3I as an ingredient, a process for dry etching of conductive oxides such as Indium Tin Oxide (ITO) by using said gas, and a dry cleaning process for equipment interior contaminated by carrying out dry etching, vacuum deposition and other operation.

2. Description of the Related Art

The thin film of ITO has been widely used for a transparent electrode of a liquid crystal display. A transparent electrode is formed by etching the ITO thin film. This etching has conventionally been carried out by wet process.

However, the wet etching process renders the etching shape isotropic and thus it is difficult to process fine patterns. In addition, a large amount of waste water generated by the process has led to problems also in view of protectioning the environment.

In recent years, etching of the ITO thin film has been carried out by employing reactive ion etching (RIE) which uses hydrogen iodide (HI) gas or RIE which uses methane (CH_4) gas and hydrogen (H_2) gas.

The RIE process by HI has an advantage that the etching velocity is faster than the RIE process by CH_4 and H_2 . However, the process by HI has a problem of large fluctuation in the etching velocity due to properties of the ITO thin film, and in particular, leads to a defect of lowering the etching velocity in a location where the bond of tin and oxygen is segregated, as described in Japanese Patent Laid-open 251400/'93.

Japanese Patent Laid-open 251400/'93 has also described that the introduction of H_2 gas as a reduction initiator into HI gas protects the etching target surface from covering with tin-iodine bonded substance.

However, the process for introducing H_2 gas as the reduction initiator of HI gas as described in the Laid-open publication has a restriction that the etching temperature must be in the range of 80 - 250°C. At a temperature lower than this range, etching is scarcely promoted. Thus etching is difficult at room temperature.

OBJECT AND SUMMARY OF THE INVENTION

The object of the invention is to provide an etching process which can inhibit underetch formed in the

wet process, and to provide a dry etching process having a high velocity at room temperature where a system composed of HI gas and reducing gas cannot promote the etching reaction.

Another object of the invention is to provide a dry cleaning process for the contaminated equipment interior.

A further object of the invention will be made clear by the following description.

The invention is based on the present inventors' discovery that the high-velocity anisotropic etching of conductive oxide thin films of SnO_2 , ITO and ZnO at a room temperature can be attained by using the etching gas which contains CF_3I .

These objects of the invention can be accomplished by the following inventions.

1. Dry processing gas having CF_3I as an ingredient.
2. Etching gas having CF_3I as an ingredient and being suitable for etching a conductive oxide, wherein the dry processing according to 1 is an etching process.
3. Etching gas according to 2 wherein the moisture content of CF_3I is 100 ppm or less.
4. Etching gas according to 2 wherein the gas further includes a reducing ingredient.
5. Etching gas according to 4 wherein the reducing

ingredient is hydrogen.

6. Etching gas according to 2 wherein the gas further includes fluorine gas and/or nitrogen trifluoride gas.

7. A dry etching process for etching oxide in the presence of argon and/or oxygen by the etching gas according to one of 1 - 6.

8. The dry etching process according to 7 wherein the oxide is a conductive oxide selected from SnO_2 , ITO and ZnO .

9. The dry etching process according to 7 wherein etching is carried out by introducing etching gas which includes CF_3I according to one of 2 - 6 into a dry-etching equipment and by inducing discharge while holding an etching target material consisting of conductive oxide in the dry-etching equipment, the equipment being provided with at least evacuation means, electric power application means, etching target material introduction means, etching target material holding means, and etching target material discharging means.

10. Cleaning gas having CF_3I as an ingredient wherein the dry process according to 1 is a cleaning process.

11. Cleaning gas according to 10 wherein moisture content of CF_3I is 100 ppm or less.

12. A dry cleaning process comprising carrying out

cleaning by introducing the cleaning gas according to 10 and 11, which contains CF_3I , into an equipment to be cleaned which is provided with at least an evacuation means and electric power application means and by inducing discharge.

13. The dry cleaning process according to 12 wherein the equipment to be cleaned is dry etching equipment, vacuum deposition equipment, plasma CVD equipment or sputtering equipment.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration showing an etching treatment substrate. Figure 2 is a schematic illustration showing an evaluation method of an etching processed shape. In these figures, 1 is a mask (for example, composed of Inconel), 2 is a layer of conductive oxide thin film, 3 is a substrate, a is a top width of a channel in the conductive oxide layer, and b is a bottom width of a channel in the conductive oxide layer, respectively.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

CF_3I (trifluoro-iodo-methane) which is an ingredient of the dry processing gas in this invention is incombustible gas and has a molecular weight of 195.91, boiling point of -22.5°C , and density of 2.3608 g/cm^3 at

-32.5°C and 2.5485 g/cm³ at -78.5°C.

A technique for using CF₃I as etching gas and anisotropically etching a silicone substrate without undercut has been disclosed in Japanese Patent Laid-open 138834/'80. The technique utilizes the fact that silicone forms a volatile compound with fluorine.

However, there has been quite no report on the trial of dry etching ITO and other conductive oxides by using CF₃I, because these oxides do not form a volatile compound with fluorine.

As opposed to the recognition of those who are skilled in the art, the present inventors have unexpectedly found that ITO and other conductive oxides can be dry etched at room temperature by using CF₃I. In addition, the present inventors have found that moisture content is preferably at a low level because CF₃I corrodes metals in the presence of moisture. Specifically, in the case of using CF₃I for dry etching or dry cleaning, moisture content of CF₃I is preferably 100 ppm or less, more preferably 10 ppm or less, most preferably 1 ppm or less. It has been found that, by such means, pipe lines of CF₃I gas become difficult to corrode and good effect is simultaneously provided for the properties of etching and cleaning.

In the case of dry etching, the moisture contained in CF₃I corrodes pipe lines and the corroded

ingredient invades into the dry etching equipment and adheres to the etching target material. Alternatively, CF_3I containing moisture reacts with the internal wall of the equipment, electrode or the etching target material forms compounds containing iodine and the material thus formed adheres to the etching target material. As a result, the processing properties such as etching velocity and processed shape are adversely affected.

On the other hand, in the case of dry cleaning, the above formed compounds containing iodine adhere to the internal wall of etching, sputtering and other thin film forming equipment, or the electrode. Satisfactory cleaning effect becomes difficult to obtain due to such adhesion.

In this invention, as will be described below, CF_3I gas is preferably incorporated with hydrogen gas, fluorine gas, nitrogen fluoride gas and/or argon gas, when necessary. It is also desired that the moisture content of these addition gases be extremely reduced, to the extent of the moisture content of CF_3I , or preferably is less than the moisture content of CF_3I .

As described above, the present inventors have made a discovery that the layer of an ITO thin film and other conductive oxide thin films is anisotropically etched by using CF_3I gas as etching gas and exposing ITO and other conductive oxides to plasma at room temper-

ature.

In the present invention, a reducing ingredient is preferably added to the etching gas having CF_3I as an ingredient. Hydrogen gas is most preferred for the reducing ingredient. It has also been found that, in the absence of hydrogen or other reducing gas, the etching velocity is higher in the initial etching stage and gradually decreases with passage of time.

Addition of reducing gas is effective for reducing time dependence of the etching velocity. Consequently, mixing of CF_3I gas with hydrogen or other reducing gas is also found to be capable of anisotropically etching the ITO thin film at a higher velocity.

Further, the present inventors have found that a still higher etching velocity can be obtained by addition of fluorine gas and/or nitrogen trifluoride gas to the etching gas having CF_3I as an ingredient.

The present invention also provides cleaning gas which includes CF_3I as an ingredient.

Conventionally, the internal wall and/or electrode of the equipment for carrying out thin film etching or thin film forming by using dry etching equipment, vacuum deposition equipment, plasma CVD equipment and sputtering equipment are contaminated by the raw materials and products of the etching. Thus, the cleaning of the equipment (chamber) is essential in order

to supply a constant quality product. Conventionally, the cleaning has been generally carried out by dry cleaning which uses gaseous fluorocarbon compounds such as CF_4 and C_2F_6 . However, the gaseous fluorocarbon compounds such as CF_4 and C_2F_6 have a high coefficient of ozone destruction and are now targets of world regulation.

On the other hand, CF_3I used in the present invention has a ozone destruction coefficient of 0.008 or less, earth warming coefficient of 5 or less, and thus is a friendly compound for earth environment. Consequently, CF_3I can be suitably used as substituting gas for gaseous fluorocarbon compounds such as CF_4 or C_2F_6 which have been conventionally used for dry cleaning.

That is, according to the present invention which uses a cleaning gas which contains CF_3I , dry cleaning can be effectively carried out when the internal wall and electrode of the cleaning equipment is contaminated with these raw materials and products. The equipment to be cleaned in the invention refers to the dry etching equipment, vacuum deposition equipment, plasma CVD equipment or sputtering equipment.

The present invention will be specifically illustrated hereinafter by using etching of the ITO thin film as an example.

However, the present invention, which uses gas

which contains CF_3I , has a similar effect on and is similarly applied to the etching of a SnO_2 thin film and ZnO thin film in addition to the ITO thin film which will be illustrated below. Further, the inventors have found that copper can also be etched by the gas containing CF_3I in addition to the conductive oxides. The gas containing CF_3I has also been confirmed to have an effect on the cleaning of etching equipment and thin film forming equipment which are contaminated with a metal, metal oxide, metal nitride, metal carbide, organic compound or silicone base compound. The conditions which will be illustrated below for gas containing CF_3I can be equally applied to both etching and cleaning. In the specific examples below, CF_3I used has a moisture content of 1 ppm or less. The analysis is carried out by gas chromatography.

The etching gas which comprises CF_3I as an ingredient of the invention and is suited for etching the conductive oxides has a CF_3I concentration of usually 1 - 100%, preferably 30 - 100%.

The ITO thin film which is used for the target of dry etching in the invention is the ITO thin film, for example, film-formed by sputtering on a glass substrate to a thickness of 200 nm. The ITO thin film is for example, patterned by Inconel and used as a resist.

No particular limitation is generally imposed

upon the thickness of ITO thin film applied. For example, a thin film having a thickness of 10 - 500 nm is preferably used, because specific usage of the ITO thin film is a touch panel or color filter for liquid crystal. The ITO thin film which can be used in the invention is also obtained by film-forming on a silicone substrate, ceramic substrate or various plastic substrates in place of glass.

The ITO thin film formed as above is held, by using Inconel as a resist, in a chamber having parallel plate type RF electrodes and is etched by treating with plasma in a CF_3I gas flow. In the etching step, the plasma treatment is preferably carried out in a simultaneous gas flow of reducing gas such as hydrogen, argon gas and/or oxygen.

Any reducing gas which is added to the CF_3I gas can provide high etching velocity so long as the reducing gas has reducing power. Particularly preferred reducing gas is hydrogen.

Addition of argon gas to the CF_3I gas can accelerate dissociation of indium-oxygen and thus can improve etching efficiency. In addition to argon gas, oxygen gas has also been found to improve etching efficiency.

The amount of the additional gas can be arbitrarily selected and has no critical limitation. The

flow rate (flow ratio) of each gas also has no critical limitation and can be arbitrarily selected.

As described above, the etching gas which contains reducing gas provide high etching velocity. The etching velocity can be further enhanced by further addition of fluorine gas or nitrogen trifluoride gas.

In the examples described below, the above hydrogen gas, argon gas, oxygen gas, fluorine gas and nitrogen trifluoride gas which are introduced into the chamber simultaneously with CF_3I are fed independently through a separate line. However, the introduction method is not limited to such a procedure. A gas mixture obtained by previously mixing two or more kinds of the gas can of course be used.

The feed rate of the CF_3I gas and hydrogen gas or argon gas, that is, flow ratio of each gas, has a close relationship with the pressure in the chamber. No particular limitation is imposed upon the flow rate. The flow rate of hydrogen gas or argon gas is usually 10 - 80%, preferably 20 - 60%, for the total flow rate of the gas. The flow rate of fluorine gas or nitrogen trifluoride gas is preferably 2 - 25% for the total flow rate of the gas. Too small amount of fluorine gas or nitrogen trifluoride gas has no effect. On the other hand, too much amount of the gas sometimes leads to corrosion on the chamber. The flow ratio of the gas has

a close relationship with the material and hole shape of the conductive oxide to be treated and is suitably selected in view of the relationship.

In the case of practicing etching in the invention, higher power of the RF electrodes leads to higher etching velocity. The pressure in the chamber during etching gives great effect on the etching processed shape. In order to hold the processed shape anisotropic, the internal chamber pressure is preferably maintained at 0.1 torr or less. The internal chamber pressure exceeding 0.1 torr is liable to make the processed shape isotropic.

Further, the substrate including the conductive oxide layer (hereinafter referred to as base plate) can be satisfactorily treated at room temperature. Heating is not needed but can be applied when necessary. According to the present invention, even though treated at room temperature, anisotropic etching can be carried out at a velocity of several dozens nm/min or more by controlling the above etching conditions.

The present invention can employ various etching equipment other than the above parallel plate type RF plasma etching equipment. In particular, ECR (electronic cyclotron resonance etching) equipment can be suitably used.

According to the present invention, in addition

to the ITO conductive oxide, silicone thin film can also be similarly subjected to high velocity anisotropic etching at room temperature.

EXAMPLES

The present invention will hereinafter be illustrated further in detail by way of examples. However, these examples are merely practical embodiments to aid the understanding of the invention and are not to be construed to limit the scope of the invention.

Example 1

An ITO thin film was formed by sputtering on a glass substrate to a thickness of 200 nm. The base plate thus obtained was etched by using an Inconel pattern as a resist on the ITO thin film. Figure 1 illustrates the section view.

The base plate was held in the parallel plate type RF etching equipment and etching was carried out under the following conditions.

Etching condition:

Power source	high frequency	13.56 MHz
	400 W	
Internal chamber pressure		50 m Torr
Gas flow rate	CF ₃ I	100 sccm
Base plate temperature		25°C (constant)

The etching velocity and processed shape obtained in the example are summarized in Table 1.

The etching velocity was examined by observing the section of the base plate under an electron microscope.

In Table 1, the processed shape is illustrated by the ratio $[a/b]$ in Figure 2. "a" shows a channel width of the conductive oxide on the surface side and "b" shows a channel width of the conductive oxide on the substrate side.

As seen in these results, satisfactory etching velocity can be obtained even at room temperature and the processed shape is also almost completely anisotropic.

Example 2

An ITO thin film was formed by sputtering on a glass substrate to a thickness of 200 nm. The base plate thus obtained was etched by using an Inconel pattern as a resist on the ITO thin film. Figure 1 illustrates the section view.

The base plate was held in the parallel plate type RF etching equipment and etching was carried out under the following conditions.

Etching condition:

Power source high frequency 13.56 MHz

400 W

Internal chamber pressure	50 m Torr
Gas flow rate	
CF_3I	60 sccm
H_2	15 sccm
Ar	25 sccm
Base plate temperature	25°C (constant)

The etching velocity and processed shape obtained in the example are summarized in Table 1.

The evaluation of etching velocity and etching processed shape was carried out according to the procedures in Example 1.

As seen in these results, satisfactory etching velocity can be obtained even at room temperature and the processed shape is also almost completely anisotropic.

Example 3

A SnO_2 thin film was formed by sputtering on a glass substrate to a thickness of 200 nm. The base plate thus obtained was etched by using an Inconel pattern as a resist on the SnO_2 thin film. Figure 1 illustrates the section view.

The base plate was held in the parallel plate type RF etching equipment and etching was carried out under the following conditions.

Etching condition:

Power source high frequency 13.56 MHz

400 W

Internal chamber pressure	50 m Torr
Gas flow rate	
CF_3I	50 sccm
F_2	5 sccm
H_2	15 sccm
Ar	30 sccm
Base plate temperature	25°C (constant)

The etching velocity and processed shape obtained in the example are summarized in Table 1.

The evaluation of etching velocity and etching processed shape was carried out according to the procedures in Example 1.

As seen in these results, satisfactory etching velocity can be obtained even at room temperature and the processed shape is also almost completely anisotropic.

Example 4

A ZnO thin film was formed by sputtering on a glass substrate to a thickness of 200 nm. The base plate thus obtained was etched by using an Inconel pattern as a resist on the ZnO thin film. Figure 1 illustrates the section view.

The base plate was held in the parallel plate type RF etching equipment and etching was carried out under the following conditions.

Etching condition:

Power source	high frequency	13.56 MHz
	400 W	
Internal chamber pressure		50 m Torr
Gas flow rate	CF ₃ I	60 sccm
	NF ₃	5 sccm
	O ₂	35 sccm
	H ₂	10 sccm
Base plate temperature		25°C (constant)

The etching velocity and processed shape obtained in the example are summarized in Table 1.

The evaluation of etching velocity and etching processed shape was carried out according to the procedures in Example 1.

As seen in these results, satisfactory etching velocity can be obtained even at room temperature and the processed shape is also almost completely anisotropic.

Example 5

An ITO thin film was formed by sputtering on a PET substrate to a thickness of 200 nm. The base plate thus obtained was etched by using an Inconel pattern as a resist on the ITO thin film. Figure 1 illustrates the section view.

The base plate was held in the parallel plate

type RF etching equipment and etching was carried out under the following conditions.

Etching condition:

Power source	high frequency	13.56 MHz
	400 W	
Internal chamber pressure		50 m Torr
Gas flow rate	CF ₃ I	50 sccm
	H ₂	15 sccm
	NF ₃	10 sccm
	Ar	25 sccm
Base plate temperature		25°C (constant)

The etching velocity and processed shape obtained in the example are summarized in Table 1.

The evaluation of etching velocity and etching processed shape was carried out according to the procedures in Example 1.

As seen in these results, satisfactory etching velocity can be obtained even at room temperature and the processed shape is also almost completely anisotropic.

Results of Examples 1 - 5 are illustrated in Table 1.

Table 1 Etching velocity and processed shape

Example	etching velocity (nm/min)	Etched shape (a/b)
1	350	0.85
2	850	0.90
3	300	0.89
4	180	0.90
5	1100	0.90

Example 6

To the inner wall of the sputtering equipment, a thin plate composed of the same material (SUS) as the sputtering equipment was adhered with a polyimide tape, KAPTON (Trade Mark of E.I. Du Pont du Nemours & Co.). A portion of the thin plate was masked with a glass plate. While ventilating argon gas, thin film forming operations were individually carried out on ITO, SiO₂, ZnO and Al, respectively, by sputtering. By such procedures, inner wall of the equipment was contaminated. Thereafter, the tape adhering the thin plate to the inner wall of the equipment was removed. Contamination was measured with a thickness indicator. A thin film having a thickness of 92.5 nm was found. The composition of the thin film was measured by AES (Auger Electronic Spectroscopy). As a result, In, Sn, Si, Zn, Cu, C, N and O were detected in

an elemental ratio of 20, 5, 15, 5, 20, 15, 5, and 15%.

The thin film adhered plate was adhered again to the original position with the polyimide tape and cleaning was carried out under the following conditions.

Cleaning condition:

Power source	high frequency	13.56 MHz
	400 W	
Internal chamber pressure		1.0 Torr
Gas flow rate	CF ₃ I	50 sccm
	H ₂	15 sccm
	NF ₃	10 sccm
	Ar	25 sccm
Base plate temperature		25°C (constant)

After carrying out cleaning for 30 minutes under the above conditions, KAPTON tape was removed again and elementary analyses was carried out by AES. None of the above I, Sn, Si, Zn and Cu was detected because they were less than the detection limit. Some C, N, and O were detected. The cleaning effect of the gas containing CF₃I in this invention was confirmed by these results.

As described above, the present invention provides a high velocity anisotropic etching process at room temperature and an earth environment-friendly dry cleaning process for conventionally impossible conductive oxide.



WHAT IS CLAIMED IS:

1. Dry processing gas having CF_3I as an ingredient.
2. Etching gas having CF_3I as an ingredient and being suitable for etching conductive oxide, wherein the dry processing according to claim 1 is an etching process.
3. Etching gas according to claim 2 wherein CF_3I has a moisture content of 100 ppm or less.
4. Etching gas according to claim 2 wherein the gas further comprises a reducing ingredient.
5. Etching gas according to claim 4 wherein the reducing ingredient is hydrogen.
6. Etching gas according to claim 2 wherein the gas further includes fluorine gas and/or nitrogen trifluoride gas.
7. A dry etching process for etching oxide in the presence of argon and/or oxygen by the etching gas according to any one of claim 1 - claim 6.



8. The dry etching process according to claim 7 wherein the oxide is a conductive oxide selected from SnO_2 , ITO and ZnO .

9. The dry etching process according to claim 7 wherein etching is carried out by introducing the etching gas containing CF_3I according to one of claim 2 - claim 6 into a dry-etching equipment and by inducing discharge, while holding an etching target material consisting of conductive oxide in the dry etching equipment, the equipment being provided with at least evacuation means, electric power application means, etching target material introduction means, etching target material holding means and etching target material discharging means.

10. Cleaning gas having CF_3I as an ingredient wherein the dry process according to claim 1 is a cleaning process.

11. Cleaning gas according to claim 10 wherein the moisture content of CF_3I is 100 ppm or less.

12. A dry cleaning process comprising carrying out cleaning by introducing cleaning gas having CF_3I as an ingredient according to claim 10 or claim 11 into an equipment to be cleaned which is provided with at last



evacuation means and electric power application means and by inducing discharge.

13. The dry cleaning process according to claim 12 wherein the equipment to be cleaned is dry etching equipment, vacuum deposition equipment, plasma CVD equipment or sputtering equipment.