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(54) Title: OPTICAL EMISSION SPECTROSCOPY TO DETERMINE ETCH COMPLETION OF INDIUM TIN OXIDE

(57) Abstract

ITO is etched by a plasma containing CH_3• gas. The intensity characteristic of at least one optical emission line is monitored to determine etch completion.

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OPTICAL EMISSION SPECTROSCOPY TO DETERMINE ETCH COMPLETION OF INDIUM TIN OXIDE.

Reference to Co-pending Patent Applications

Reference is made to commonly assigned U.S. Patent Application Serial No. 533.232, filed June 4, 1990 to Paul Roselle, and to commonly assigned U.S. Patent Application Serial No. 520,486, filed May 7, 1990 to Paul Roselle, Gustavo Paz-Pujalt and Ronald Wexler.

Technical Field

The present invention relates to the plasma etching of indium tin oxide.

Background Art

Solid state CCD image sensors often employ a double polysilicon gate structure to form the sensor electrodes. Such a structure has the first polysilicon electrode (poly-1) separated from the second polysilicon electrode (poly-2) by a thin insulating layer of silicon dioxide. Poly-1 is slightly overlapped by poly-2. The systematic variation of the potential applied to these electrodes, referred to as clocking, permits the device to function. In the case of frame transfer CCD image sensors, light passes through the polysilicon electrodes and creates electron hole pairs in the underlying silicon. These electrons are accumulated prior to clocking the polysilicon electrodes to remove the accumulated charge. The polysilicon electrodes, through which light must pass, are not entirely transparent. This lack of transparency results in the reduction of sensitivity and spectral response of the image sensor.

Due to its transparency, it has been recognized that indium tin oxide would be an effective electrode for such a device. The use of an indium tin oxide electrode enhances the blue response

and overall sensitivity of a frame transfer image sensor. In fact, it has been recognized that if indium tin oxide were to be used in such a device the effective ASA of the device could be increased by as much as a factor of two. One reason that ITO has not been used on such devices is because it is difficult to pattern such material. Heretofore, the only practical method for etching indium tin oxide has been by immersion in a hot hydroiodic acid solution. Such an acid etches the material isotropically and is not selective to photoresist. These two reasons alone show the difficulties involved in using ITO for microelectronic applications where small features are defined by photoresist lithography.

It has also been recognized that ITO can be used as an antistatic coating on materials such as webs used in the manufacture of photosensitive materials. There again, it is difficult to use such a material because it is not practical to pattern it.

Disclosure of the Invention

It is the object of this invention to provide a new method for the etching of indium tin oxide employing optical emission spectroscopy to determine etch completion and provide process termination.

A plasma containing methyl radicals ($CH_3\bullet$) can effectively etch indium tin oxide anisotropically and with high selectivity to photoresist and silicon dioxide. The emission lines from the $CH_3\bullet$ containing plasma have been found to provide strong intensity changes at completion of the etching of an ITO layer, thereby indicating when to terminate the process.

The above object is achieved in a method of etching indium tin oxide, comprising the steps of:

forming a plasma containing $CH_3\bullet$;

etching the ITO by volatilizing the ITO by a reaction with the plasma of $CH_3^{\bullet}$; and

monitoring the intensity characteristic of at least one optical emission line of the plasma to determine etch completion and then terminate the etching process.

Brief Description of the Drawings

FIG. 1a is a schematic, in partial cross-section, of a conventional plasma etcher which uses radio frequency energy to ignite and sustain the plasma.

FIG. 2a is a plot of emission wavelength versus emission intensity for a CH_4, H_2 plasma;

FIG. 2b is a typical plot of intensity versus time for an emission line associated with the etch reactant $CH_3^{\bullet}$;

FIG. 2c is a typical plot of intensity versus time for an emission line associated with an etch product; and

FIG. 3 shows various steps in patterning an ITO layer formed on an SiO_2 insulating layer provided on a silicon substrate.

Mode of Carrying Out the Invention

With reference to FIGS. 1, 2 and 3a-3c, a process for the plasma etching of indium tin oxide is described.

A plasma is a state of matter in which the gases in a vessel with a total pressure less than atmospheric pressure are partially ionized by an electric field. As is well understood, such an electric field can be from a radio frequency generator, microwave frequency generator or DC voltage field.

The emission of light from the excited gases in a plasma is a well known phenomenon. The wavelength of the light emitted is specific to the excited species that compose the plasma. Such

excited species will include the reactants and products of any reactions occurring in the plasma. For the case where a plasma is used to etch a layer of some material, the intensity of the characteristic light emissions of the reactants will be low during etching and then increase as the layer of material being etched is cleared away. Conversely, for the emission from the product of the etch, the intensity will be high during the etch and will drop as the layer of material being etched is cleared away.

A plasma, ignited by the action of a suitable electric field on a mixture of CH_4 gas and H_2 gas, will contain methyl radicals ($CH_3\cdot$) as well as other species generated from the cracking of the molecules of CH_4 and H_2. As in any plasma, the concentrations of the various species in the plasma depend upon the power and frequency of the electric field applied, the pressure of the plasma, and the concentrations of the gases used. It should be understood that CH_4 and H_2 mixtures are not the only means of producing methyl radicals ($CH_3\cdot$) and that mixtures of ethane and hydrogen, propane and hydrogen, or other organic compounds will result in methyl radical creation in plasma and will, in so doing, etch ITO.

For an etcher as represented in FIG. 1, a wafer 18 is placed on a lower electrode 15 which is connected to an RF radiation source 28. Vacuum is achieved in the chamber by the use of an oil diffusion pump and rotary vacuum pump, not shown. The lower electrode 15 is heated by resistive heaters 16 located on the back of the electrode. The H_2 and CH_4 gases are admitted into the chamber through a diffuser 26. The flows of the gases are regulated by mass flow controllers 22 and 24. Process pressure in the vessel is controlled by a vacuum throttle valve 21. When the desired flow rates, pressure and

temperature are achieved, a plasma of CH_4 and H_2 is ignited in a space 30a between the lower electrode 15, on which the wafer 18 sits, and an upper electrode 12. The resultant $CH_3^{\bullet}$ generated in region 30 will react with the ITO on the wafer 18 volatilizing the ITO off the wafer to be pumped away by the vacuum pump. The emission of light from the CH_4 and H_2 plasma is monitored by an optical emission spectrometer (40) which detects light from the plasma through a window (41) in the side of the etcher. The spectrometer 30 monitors the intensity of specific lines associated with the reactants and products of the etch and displays the intensity versus time plot on a recorder 42, CRT or pen recorder. When the intensity of the monitored reactant emission lines goes up and levels off and, simultaneously, the intensity of the monitored product emission lines goes down and levels off, the ITO layer has been fully etched away. The process is automatically terminated by a control unit 44 which is coupled to the spectrometer 40 and shuts-off the RF radiation source 28. Alternatively, an operator can view the output of the recorder 42 and shut-off the RF radiation source 28.

Turning now to FIG. 2a, we see a plot of intensity in counts versus the intensity output of spectrometer 40 and displayed by recorder 42. Each count refers to a specific amount of energy received by the spectrometer. The light emission lines labelled (B) at about 345 nm and 375 nm are both caused by reactant $CH_3^{\bullet}$ in the plasma. These lines are present whether or not $CH_3^{\bullet}$ is etching ITO. The light emission line at about 353 nm is caused by a product produced by etching ITO with $CH_3^{\bullet}$. In FIG. 2b we see a plot of one of the emission lines labelled (B) in FIG. 2a. Also, FIG. 2c is a plot of an etch product produced when ITO is etched by $CH_3^{\bullet}$.

With reference to both FIGS. 2a and 2b, the etching process begins at time 0. At an inflection point (ep) in both plots, the ITO is beginning to clear (become exhausted). When both plots level off (cp) the etching process is completed. It is desirable to run the process a short duration after the process levels off to insure that all the ITO has been etched. The RF radiation source 28 is then shut-off at the termination point (TP).

The process can be monitored by viewing either a reaction product or a reactant emission line. However, those skilled in the art will recognize that it is desirable to simultaneously monitor both a reaction product line and the $CH_3\cdot$ emission line. The pressure of the plasma of CH_4 and H_2 must be maintained below the polymerization point of the plasma. Likewise, the ratio of CH_4 to H_2 should be less than 20% to prevent excessive polymerization of the species in the plasma. Such excessive polymerization produced by too high of a pressure and/or too high of a concentration of CH_4 in H_2 will prevent ITO from etching uniformly if at all.

FIGS. 3a-c show the process of pattern transfer for the definition of ITO where the etched ITO is to be used as a poly-1 electrode. In FIG. 3a it is seen that microlithographic photoresist mask 34 has been deposited and patterned in a conventional manner on the surface of an ITO layer 32 which has been deposited on an SiO_2 layer 30 on a silicon substrate 36. ITO is most usually deposited by RF sputter deposition.

In FIG. 3b the ITO layer 32 has been etched anisotropically by the plasma of $CH_3\cdot$ thereby transferring the photoresist pattern into the ITO and stopping on the SiO_2 layer 30. Measurements have shown that the plasma of $CH_3\cdot$ that etches the ITO

has a high selectivity to both the photoresist and the underlying SiO_2 layer.

In FIG. 3c the photoresist 34 has been stripped off of the ITO 32 and the device may proceed to further processing. The photoresist is most usually removed by O_2 plasma stripping.

Example

Without limiting the generality of this invention, the mechanism of etching of ITO is believed to be caused by methyl radicals reacting with indium and tin to create volatile organometallic compounds as shown by the following reaction:

$$CH_4+H_2 \xrightarrow{\text{plasma}} CH_3\cdot+\underbrace{In+Sn+O}_{ITO}\rightarrow In(CH_3)_3\uparrow+Sn(CH_3)_4\uparrow+CO\uparrow$$

Other starting gases can be used provided they form a plasma having $CH_3\cdot$.

An etcher similar to the one represented by FIG. 1 was used to etch ITO. The radio frequency used to ignite and sustain the plasma was 13.56 megahertz at 85 watts forward power. The wafer was heated to a temperature of 70°C. The chamber was evacuated to a base pressure of 1×10^{-6} prior to the admission of the CH_4 and H_2 gases. The flow rate for the CH_4 was 25 sccm and the flow rate the the H_2 was 150 sccm. A process pressure of 150 Mtorr was maintained during the etch. The sputter deposited ITO etched at a rate of 275 angstroms per minute and showed very high selectivity to the photoresist and the underlying silicon dioxide. The emission lines attributed to etch reactants and one emission line attributed to etch product were monitored and showed strong endpoint responses. Cross-sectional scanning electron micrographs of the etched ITO showed the etch to be highly anisotropic with no evidence of undercutting the photoresist.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

CLAIMS:

1. In a method of etching indium tin oxide, comprising the steps of:

forming a plasma containing $CH_3\bullet$;

etching the ITO by volatilizing the ITO by a reaction with the plasma of $CH_3\bullet$; and

monitoring the intensity characteristic of at least one optical emission line of the plasma to determine etch completion and then terminate the etching process.

2. In a method of etching indium tin oxide, comprising the steps of:

forming a plasma containing $CH_3\bullet$;

etching the ITO by volatilizing the ITO by a reaction with the plasma of $CH_3\bullet$; and

monitoring the intensity characteristic of the $CH_3\bullet$ optical emission line and a reaction product emission line of the plasma to determine etch completion and then terminate the etching process.

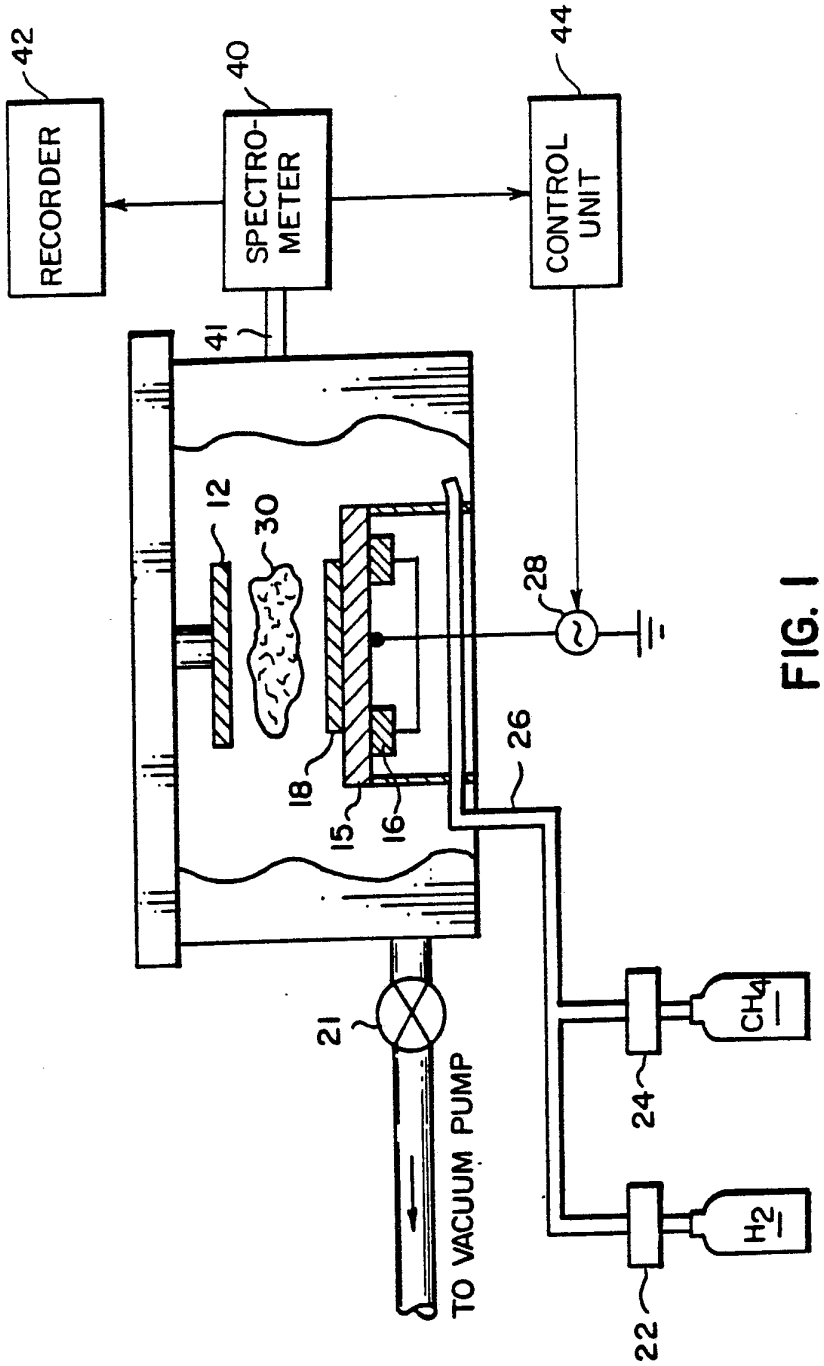

42
RECORDER
40
SPECTRO-METER
44
CONTROL UNIT
41
12
30
28
18
15
16
26
21
TO VACUUM PUMP
24
CH4
22
H2

FIG. 1

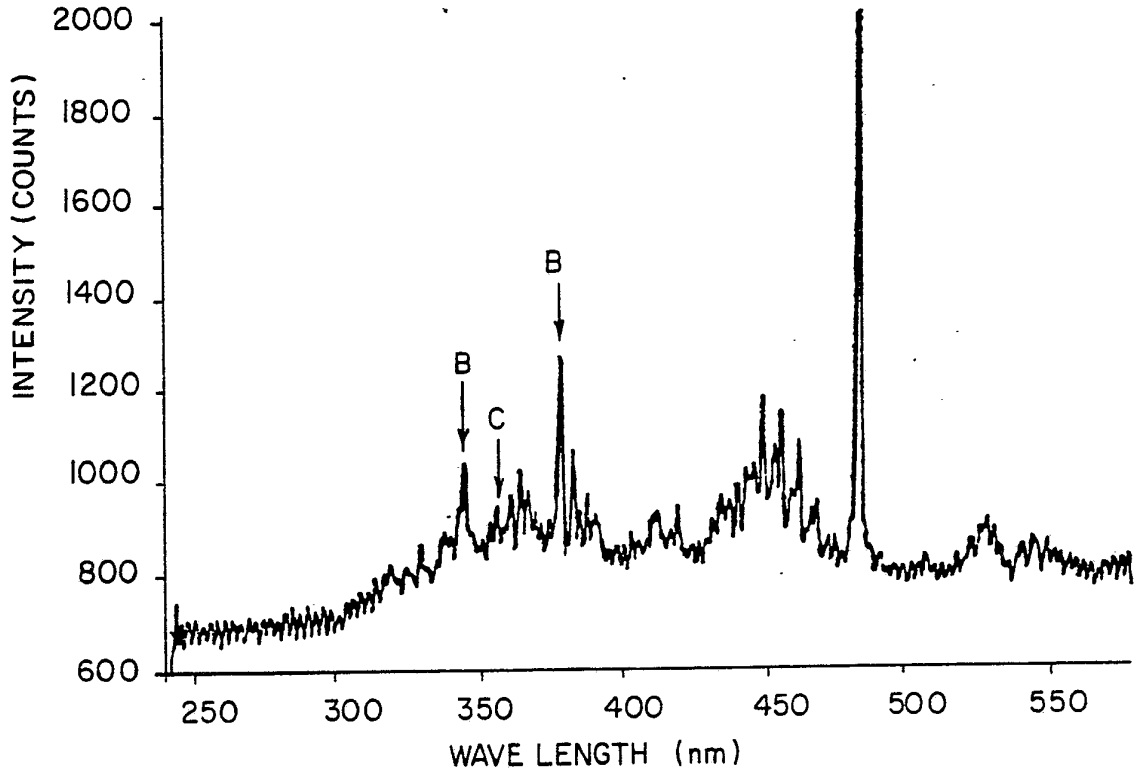
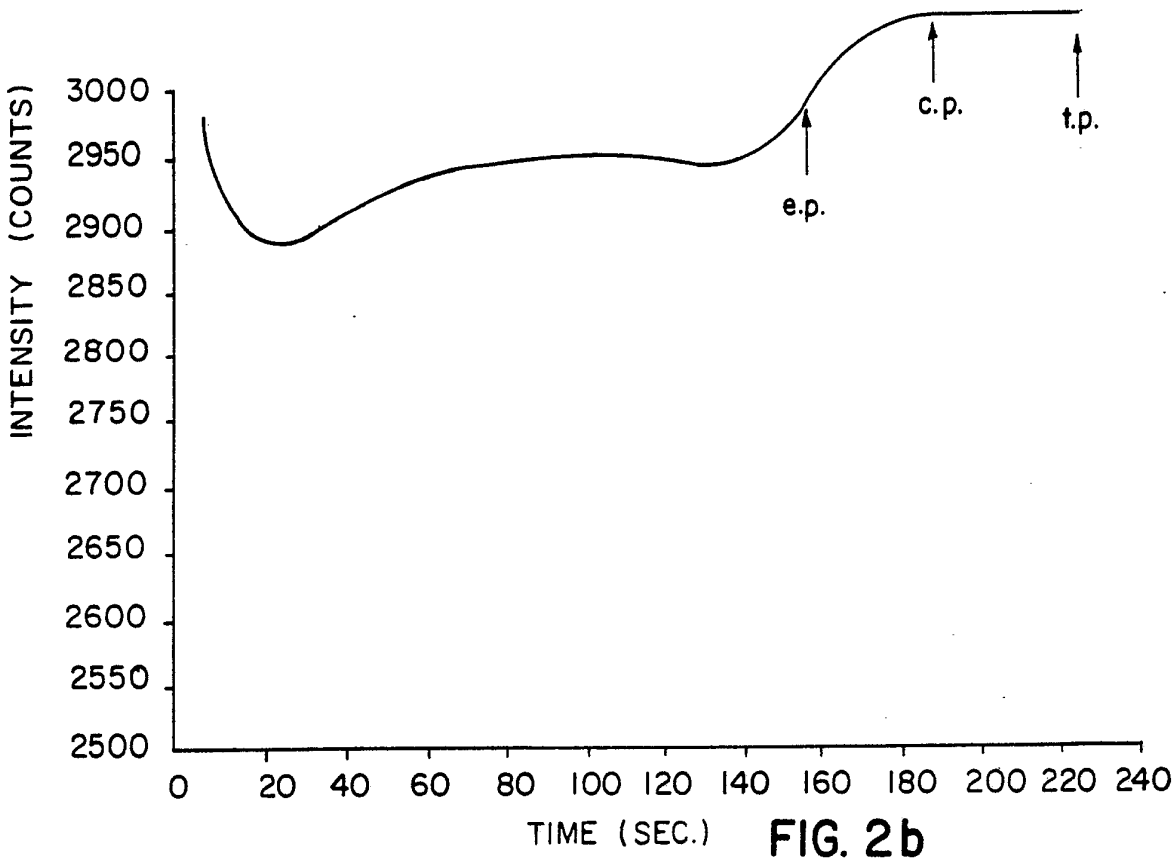

INTENSITY (COUNTS)
2000
1800
1600
1400
1200
1000
800
600
B
C
B
250
300
350
400
450
500
550
WAVE LENGTH (nm)

FIG. 2a


INTENSITY (COUNTS)
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2950
2900
2850
2800
2750
2700
2650
2600
2550
2500
e.p.
c.p.
t.p.
0 20 40 60 80 100 120 140 160 180 200 220 240
TIME (SEC.)

FIG. 2b

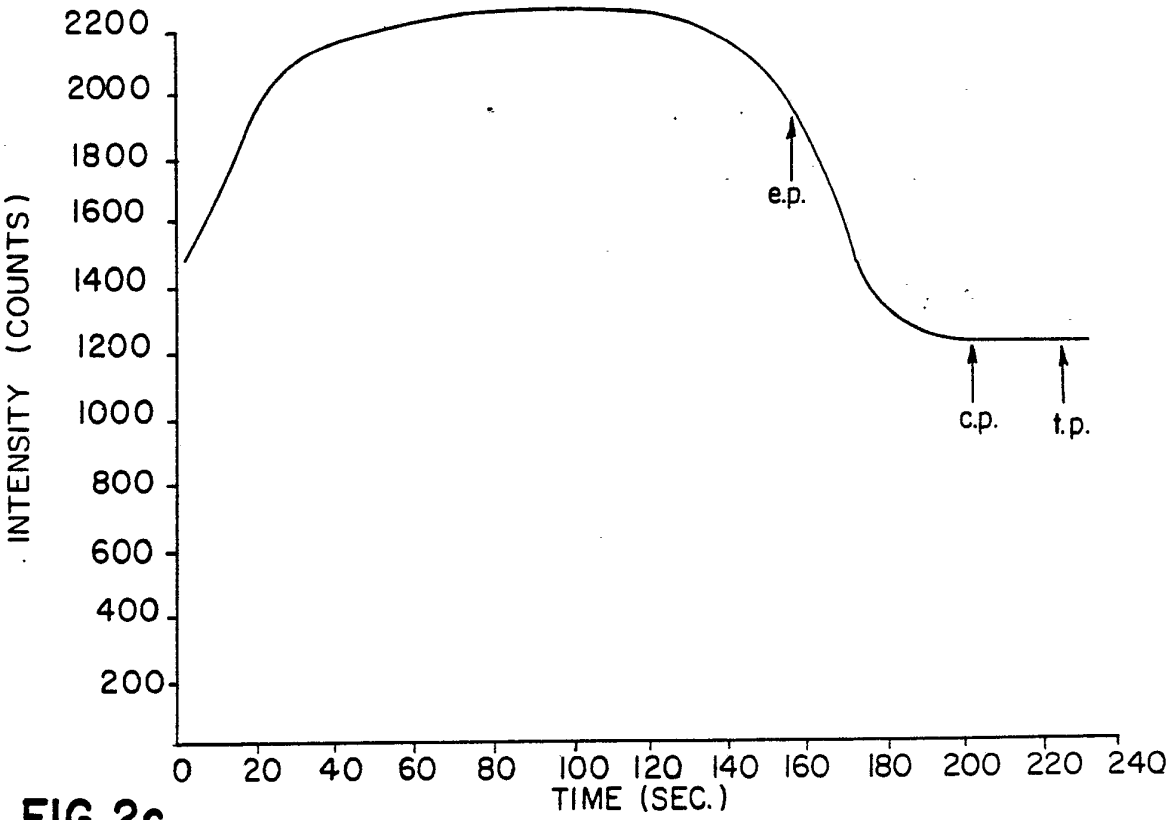

INTENSITY (COUNTS)
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
e.p.
c.p.
t.p.
0 20 40 60 80 100 120 140 160 180 200 220 240
TIME (SEC.)

FIG. 2c

FIG. 3a

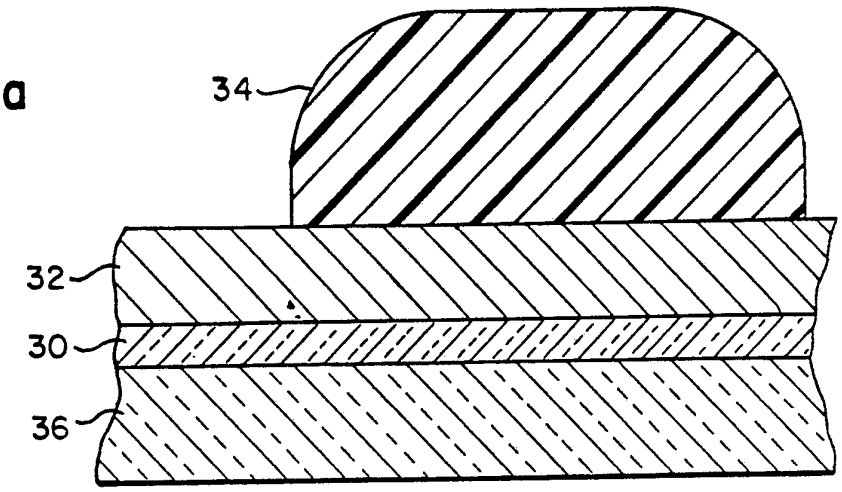


FIG. 3b

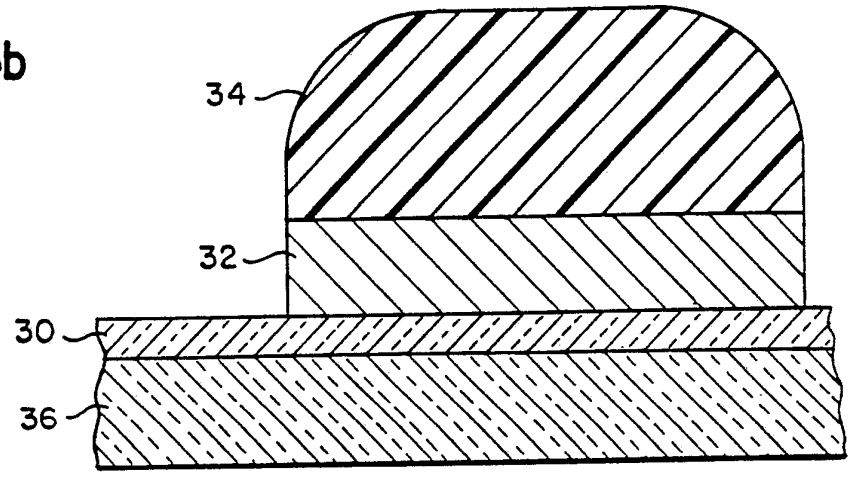
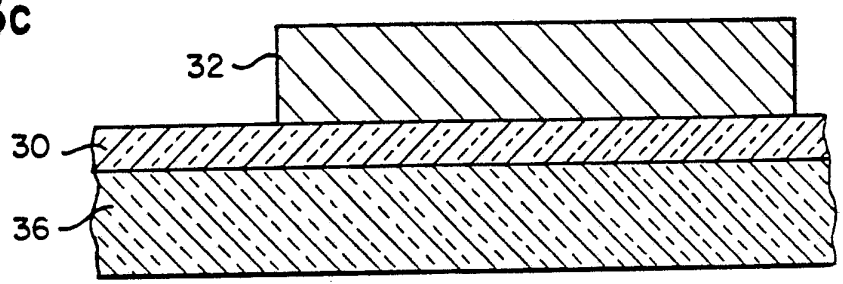


FIG. 3c



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/03664

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: H 01 L 31/185, G 02 F 1/133, H 01 J 37/32

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	H 01 L, H 01 J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	Japanese Journal of Applied Physics, vol. 27, no. 9, September 1988, T. Minami et al.: "Reactive ion etching of transparent conducting tin oxide films using electron cyclotron resonance hydrogen plasma", pages L1753-L1756 see page L1753, left-hand column, paragraphs 1,2; table 1; page L1755, right-hand column, paragraph 2 --	1,2
Y	US, A, 4528438 (POULSEN et al.) 9 July 1985 see abstract; claims 1,10 --	1,2
P,A	EP, A, 0377365 (CHOUAN et al.) 11 July 1990 see claims 1,4,9; column 3, lines 15-20, 39-44 -- ./.	1,2

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
3rd September 1991	24. 10. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Patricia Smith P.L. Smith

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	5ème Colloque International sur les Plasmas et la Pulverisation Cathodique, Antibes, Fr, 10-14 June 1985, Société Francaise du Vide Publishers, J.F. Boulineau et al.: "Etude et réalisation de couches d'oxydes d'indium et d'etain obtenues par ion plating", pages 67-71 see page 67, paragraph 4 - page 68, paragraph 1 --	1
A	Solid State Technology, vol. 24, no. 4, April 1981, (Washington, US) P.J. Marcoux et al.: "Methods of end point detection for plasma etching", pages 115-122 see whole page 116 ----------	1,2

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9103664 SA 48644

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 18/10/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4528438	09-07-85	None	
EP-A- 0377365	11-07-90	FR-A- 2640809	22-06-90
		CA-A- 2005758	19-06-90
		JP-A- 3136249	11-06-91