(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 610 121 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
15.03.2017 Bulletin 2017/11

(21) Application number: **04723347.3**

(22) Date of filing: **25.03.2004**

(51) Int Cl.:
G01N 27/414 *(2006.01)* ***H01L 29/80*** *(2006.01)*

(86) International application number:
PCT/JP2004/004196

(87) International publication number:
WO 2004/086025 (07.10.2004 Gazette 2004/41)

(54) **p CHANNEL FILED EFFECT TRANSISTOR AND SENSOR USING THE SAME**

P-KANAL-FELDEFFEKTTRANSISTOR UND SENSOR UNTER VERWENDUNG DAVON

TRANSISTOR A EFFET DE CHAMP A CANAL P ET CAPTEUR METTANT EN OEUVRE CELUI-CI

(84) Designated Contracting States:
DE FR GB

(30) Priority: **25.03.2003 JP 2003082986**

(43) Date of publication of application:
28.12.2005 Bulletin 2005/52

(73) Proprietor: **Japan Science and Technology Agency**
Kawaguchi-shi,
Saitama 332-0012 (JP)

(72) Inventor: **KAWARADA, Hiroshi**
Yokohama-shi,
Kanagawa 224-0001 (JP)

(74) Representative: **Hoarton, Lloyd Douglas Charles et al**
Forresters
Skygarden
Erika-Mann-Strasse 11
80636 München (DE)

(56) References cited:
WO-A-02/095408
JP-A- 8 240 555
JP-A- 61 231 454
JP-A- 2001 272 372
JP-A- 2002 286 692
JP-A- 2004 109 020
US-A- 4 877 582

- **NAKAMURA YUSUKE ET AL.: 'Diamond no ISFET eno ozon shori no eikyo' HEISEI 14 NEN DAI 16 KAI DIAMOND SYMPOSIUM KOEN YOSHISHU 25 November 2002, pages 210 - 211, XP002904063**

EP 1 610 121 B1

Description

Technical Field

[0001] The present invention relates to a p channel field effect transistor and a sensor including the same. In particular, it relates to a chemical sensor and a biosensor.

Background Art

[0002] The inventor of the present invention has proposed a field effect transistor in which a liquid electrolyte has been used as a gate, and a hydrogen terminated surface of a diamond has served as a channel (refer to the following Patent Documents 1 and 2).

[0003] It is known that urea is hydrolyzed by the catalysis of urease (enzyme), ammonia is generated, and the pH is increased. In a silicon based ion-sensitive field effect transistor (ISFET), urease (enzyme) is immobilized on a silicon nitride serving as a protective-sensitive film and, thereby, a change in pH is detected. In this case, the detection accuracy depends on the immobilization density and the immobilization strength. Although there is a method in which urease (enzyme) and the ISFET are separated, in this case, a problem occurs in that the detection sensitivity is reduced.

[Patent Document 1] Japanese Patent No. 3313696 (pages 2 to 4, Fig. 1)
[Patent Document 2] Japanese Patent No. 3390756 (pages 2 to 4, Fig. 1)

Disclosure of Invention

[0004] In consideration of the above-described circumstances, it is an object of the present invention to provide a p channel field effect transistor in which the sensitivity of an enzyme can be enhanced by immobilizing the enzyme directly on an FET channel surface (diamond surface), as well as a sensor including the same.

[0005] In particular, it is an object of the present invention to provide a p channel field effect transistor in which the sensitivity to urea concentration can be enhanced by immobilizing urease directly on an FET channel surface (diamond surface), as well as a sensor including the same.

[0006] The present invention was made in order to achieve the above-described object.

[1] In a p channel field effect transistor, a liquid electrolyte is used as a gate, and a polycrystalline or monocrystalline diamond surface having mixed hydrogen terminals, oxygen terminals and amino terminals serves as a channel.
[2] A sensor is characterized by including the p channel field effect transistor described in the above item [1] and exhibiting a pH sensitivity through the use of a shift of threshold voltage in the positive direction on the above-described surface having mixed amino terminals and oxygen terminals in response to an increase in pH of the above-described liquid electrolyte.
[3] The sensor described in the above item [2] is characterized in that the above-described increase in pH is 2 to 12.
[4] The sensor described in the above item [2] or [3] is characterized in that urease is immobilized to the amino terminal on the above-described surface with glutaraldehyde (divalent aldehyde) therebetween, the threshold voltage shifts in the positive direction in response to an increase in urea concentration and, thereby, the sensitivity to urea is exhibited.
[5] The sensor described in the above item [4] is characterized in that the above-described increase in urea concentration is 10^{-6} M to 10^{-2} M.

Brief Description of the Drawings

[0007]

Fig. 1 is a perspective view of a diamond FET with an electrolytic solution gate, according to the present invention.
Fig. 2 is a sectional view of a diamond FET with an electrolytic solution gate, according to an embodiment of the present invention.
Fig. 3 is a diagram showing the XPS measurement results of an aminated substrate according to the present invention.
Fig. 4 is a schematic diagram of an enzyme biosensor with an electrolytic solution gate, according to an embodiment of the present invention.
Fig. 5 is a diagram (No. 1) showing the pH sensitivity of a hydrogen-terminated diamond substrate which is partially amino-terminated and oxygen-terminated.
Fig. 6 is a diagram (No. 2) showing the pH sensitivity of a hydrogen-terminated diamond substrate which is partially amino-terminated and oxygen-terminated.
Fig. 7 is a schematic diagram of an enzyme biosensor with a solution gate, wherein urease is immobilized on an amino-terminated diamond surface, according to an embodiment of the present invention.
Fig. 8 is a schematic diagram showing the action of urease on an amino-terminated diamond surface according to an embodiment of the present invention.
Fig. 9 is an urea concentration characteristic diagram (No. 1) of a diamond urea sensor according to an embodiment of the present invention.
Fig. 10 is an urea concentration characteristic diagram (No. 2) of a diamond urea sensor according to an embodiment of the present invention.

Best Mode for Carrying Out the Invention

[0008] The embodiments of the present invention will be described below in detail.

[0009] Fig. 1 is a perspective view of a diamond FET with an electrolytic solution gate, according to the present invention. Fig. 2 is a sectional view of the diamond FET with an electrolytic solution gate.

[0010] In these drawings, reference numeral 1 denotes a polycrystalline CVD diamond substrate, reference numeral 2 denotes a P-type surface conductive layer, reference numeral 3 denotes a source electrode (Au), reference numeral 4 denotes a drain electrode (Au), reference numeral 5 denotes an epoxy resin covering the source electrode (Au) 3, reference numeral 6 denotes an epoxy resin covering the drain electrode (Au) 4, reference numeral 7 denotes an electrolytic solution, and reference numeral 8 denotes a gate electrode (Ag/AgCl reference electrode).

[0011] This diamond biosensor with an electrolytic solution gate includes the inexpensive polycrystalline CVD diamond substrate and, therefore, cost reduction can be achieved as compared with a known silicon biosensor having a source-drain on a silicon substrate.

[0012] In the silicon biosensor, signals are detected through silicon nitride and silicon dioxide. However, in the diamond sensor including no protective film nor sensitive film, signals can be directly detected. Consequently, the diamond sensor can detect signals with no noise.

[0013] In the present invention, a hydrogen-terminated diamond surface is modified by using an ultraviolet ray.

[0014] That is, when oxygen is introduced and the ultraviolet ray is applied, the hydrogen-terminated surface is partially oxidized by ozone and, thereby, is oxygen-terminated. When a substrate is put into an ammonia solution and is irradiated with the ultraviolet ray, the hydrogen-terminated diamond surface is partially amino-terminated. Since the oxygen-terminal and the amino-terminal have an insulating property, the conductance of the FET with an electrolytic solution gate is decreased to some extent, but an influence exerted on the device action is small.

[0015] Fig. 3 is a diagram showing the XPS measurement results of an aminated substrate according to the present invention.

[0016] These are the XPS measurement results of the amino-terminated substrate, where the substrate was put into an ammonia solution and was irradiated with an ultraviolet ray. Fig. 3(a) relates to carbon, Fig. 3(b) relates to nitrogen, and Fig. 3(c) relates to oxygen. In these drawings, a peak of nitrogen and a peak of oxygen are observed. As is clear from this, when the ultraviolet ray is applied to the substrate in the ammonia solution, a hydrogen-terminated surface is partially amino-terminated and oxygen-terminated. In these drawings, the vertical axis indicates a photoelectron detection intensity (arbitrary unit), and the horizontal axis indicates a bond energy.

[0017] Fig. 4 is a schematic diagram of an enzyme biosensor with an electrolytic solution gate, according to an embodiment of the present invention.

[0018] In this drawing, reference numeral 11 denotes a polycrystalline CVD diamond substrate, reference numeral 12 denotes a P-type surface conductive layer (hydrogen-, oxygen-, and amino-terminated substrate surface), reference numeral 13 denotes a source electrode (Au), reference numeral 14 denotes a drain electrode (Au), reference numeral 15 denotes an epoxy resin covering the source electrode (Au) 13, reference numeral 16 denotes an epoxy resin covering the drain electrode (Au) 14, reference numeral 17 denotes an electrolytic solution, reference numeral 18 denotes a gate electrode (Ag/AgCl reference electrode), reference numeral 19 denotes an enzyme, and reference numeral 20 denotes a substrate.

[0019] An FET with an electrolytic solution gate was produced on a surface channel of the hydrogen-, oxygen-, and amino-terminated polycrystalline diamond substrate 11.

[0020] As shown in Fig. 4, the enzymes 19 can be immobilized directly on the P-type surface conductive layer (substrate surface in which a part of the hydrogen-terminated surface is amino-terminated and oxygen-terminated) 12, the substrates 20 in the electrolytic solution 17 can be bonded to these enzymes 19.

[0021] Fig. 5 is a diagram (No. 1) showing the pH sensitivity of a hydrogen-terminated diamond substrate which is partially amino-terminated and oxygen-terminated, according to an embodiment of the present invention. Fig. 5(a) is a characteristic diagram showing the drain-to-source voltage V_{DS} versus the drain-to-source current I_{DS} in the case where the gate-to-source voltage V_{GS} is -0.7 V. Fig. 5(b) is a characteristic diagram showing the gate-to-source voltage V_{GS} versus the drain-to-source current I_{DS} in the case where the drain-to-source voltage V_{DS} is -0.1 V.

[0022] In these cases, the pH sensitivity was exhibited when the pH was 2 to 12.

[0023] Fig. 6 is a diagram (No. 2) showing the pH sensitivity of a hydrogen-terminated diamond substrate which is partially amino-terminated and oxygen-terminated, according to an embodiment of the present invention. In this drawing, the horizontal axis indicates the pH, and the vertical axis indicates the threshold voltage [V].

[0024] As is clear from these drawings, the hydrogen-terminated diamond substrate which is partially amino-terminated and oxygen-terminated has the pH sensitivity.

[0025] Fig. 7 is a schematic diagram of an enzyme biosensor with a solution gate in which urease is immobilized on an amino-terminated diamond surface, according to an embodiment of the present invention. Fig. 8 is a schematic diagram showing the action on the amino-terminated diamond surface.

[0026] In these drawings, reference numeral 21 denotes a polycrystalline CVD diamond substrate, reference numeral 22 denotes a diamond surface having

mixed hydrogen terminals, oxygen terminals, and amino terminals, reference numeral 23 denotes a source electrode (Au), reference numeral 24 denotes a drain electrode (Au), reference numeral 25 denotes an epoxy resin covering the source electrode (Au) 23, reference numeral 26 denotes an epoxy resin covering the drain electrode (Au) 24, reference numeral 27 denotes an urea solution, reference numeral 28 denotes a gate electrode, reference numeral 29 denotes an immobilized enzyme, reference numeral 30 denotes glutaraldehyde, and reference numeral 31 denotes an amino group.

[0027] When a diamond surface 22 having,mixed hydrogen terminals, oxygen terminals, and amino terminals is treated under the action of glutaraldehyde $OHC(CH_2)_3CHO$ 30, as shown in Fig. 8(a), the glutaraldehyde 30 is immobilized to the amino group 31 on the diamond surface 22 having mixed hydrogen terminals, oxygen terminals, and amino terminals, as shown in Fig. 8(b). When urease 29 is further applied thereto, the amino group 31 of the urease 29 is bonded to the glutaraldehyde 30, as shown in Fig. 8(c). That is, the urease 29 can be immobilized on the diamond surface 22 having mixed hydrogen terminals, oxygen terminals, and amino terminals.

[0028] Fig. 9 is an urea concentration characteristic diagram (No. 1) of a diamond urea sensor according to an embodiment of the present invention. Fig. 9(a) is a characteristic diagram showing the drain-to-source voltage V_{DS} versus the drain-to-source current I_{DS} in the case where the gate-to-source voltage V_{GS} is -0.7 V. Fig. 9(b) is a characteristic diagram showing the gate-to-source voltage V_{GS} versus the drain-to-source current I_{DS} in the case where the drain-to-source voltage V_{DS} is -0.1 V.

[0029] Fig. 10 is an urea concentration characteristic diagram (No. 2) of a diamond urea sensor according to an embodiment of the present invention. Fig. 10(a) is an explanatory diagram of a chemical action (decomposition) of the urea. Fig. 10(b) is a sensing characteristic diagram of urea, the horizontal axis indicates the urea concentration (M), and the vertical axis indicates the threshold voltage V_{th} (V).

[0030] As shown in Fig. 9, in the diamond FET with an electrolytic solution gate, where urease is immobilized, the drain current is increased and the threshold voltage shifts in the positive direction as the urea concentration is increased.

[0031] As shown in Fig. 10(a), urea is decomposed into urease in water. In the course of the decomposition, alkaline ammonia acid and acidic carbonic acid are generated. Since the alkaline ammonia acid is stronger than the acidic carbonic acid, the pH of the diamond surface is increased. The drain current of the diamond FET with an electrolytic solution gate is also increased as the pH is increased.

[0032] As described above, the diamond urea sensor of the present invention is an enzyme sensor to detect a change in pH. As shown in Fig. 10(b), the shift of the threshold voltage is about 30 mV/decade. When the urea concentration was increased from 10^{-6} M to 10^{-2} M, the threshold voltage shifted by about 0.1 V in the positive direction, and the urea concentration sensitivity of 30 mV/decade was exhibited.

[0033] As described above in detail, the following effects can be exerted according to the present invention.

(A) The sensitivity to the enzyme concentration can be enhanced by immobilizing the enzyme directly on the FET channel surface (diamond surface).
(B) A simplified measurement of the urea concentration is important in health care. In particular, it is useful for, e.g., a measurement of the urea in the blood used as an index of renal function in the clinical research.
(C) The food inspection, in particular, the inspection of urea in cow's milk can be simplified.
(D) A trace quantity of urea (μM) can be measured in a biochemical analysis.

Industrial Applicability

[0034] The p channel field effect transistor of the present invention and a sensor including the same can be used particularly in chemical sensors and biosensors.

Claims

1. A p channel field effect transistor in which:

   a liquid electrolyte is used as a gate, and;
   a hydrogen-terminated, partially amino-terminated and oxygen-terminated diamond surface (22) having mixed hydrogen terminals, oxygen terminals, and amino terminals serves as a channel.

2. A sensor comprising the p channel field effect transistor according to claim 1.

3. The transistor or sensor according to any preceding claim, wherein, in use, there is a shift of threshold voltage in the positive direction on the diamond surface (22), in response to an increase in pH of the liquid electrolyte of 2 to 12.

4. The transistor or sensor according to any preceding claim, wherein urease is immobilized on the amino terminal on the diamond surface (22) with glutaraldehyde (divalent aldehyde) therebetween, such that the threshold voltage shifts in the positive direction in response to an increase in urea concentration and, thereby, the sensitivity to urea is exhibited.

5. The transistor or sensor according to claim 4, wherein the increase in urea concentration is 10^{-6} M to 10^{-2}

M.

6. The transistor or sensor of claim 5, having a urea concentration sensitivity of 30 mV/decade.

7. A method of producing a p channel field effect transistor from a substrate (11), the transistor having a diamond surface (22) having mixed hydrogen terminals, oxygen terminals, and amino terminals, the method comprising:

modifying a hydrogen-terminated diamond surface of the substrate (11) using an ultraviolet ray; introducing oxygen and applying the ultraviolet ray to partially oxygen-terminate the hydrogen-terminated diamond surface (22); and
placing the substrate (11) in an ammonia solution and irradiating with an ultraviolet ray to partially amino-terminate the diamond surface (22).

8. The method of claim 7, further comprising:

immobilizing glutaraldehyde (divalent aldehyde) on an amino group on the diamond surface (22).

9. The method of claim 8, further comprising:

applying urease to bond the amino group of the urease to the immobilized glutaraldehyde.

10. The transistor or method of any preceding claim, wherein the diamond surface (22) is a polycrystalline or monocrystalline diamond surface (22).

Patentansprüche

1. p-Kanal-Feldeffekttransistor, bei dem:

ein flüssiger Elektrolyt als Gate verwendet wird und;
eine wasserstoffterminierte, teilweise aminoterminierte und sauerstoffterminierte Diamantoberfläche (22) aufweisend gemischte Wasserstoffterminals, Sauerstoffterminals und Aminoterminals als Kanal dient.

2. Sensor umfassend den p-Kanal-Feldeffekttransistor nach Anspruch 1.

3. Transistor oder Sensor nach einem vorhergehenden Anspruch, worin, im Gebrauch, eine Verschiebung der Schwellenspannung in positiver Richtung auf der Diamantoberfläche (22), als Reaktion auf eine pH-Zunahme des flüssigen Elektrolyts von 2 auf 12, stattfindet.

4. Transistor oder Sensor nach einem vorhergehenden Anspruch, worin Urease am Aminoterminal auf der Diamantoberfläche (22) mit Glutaraldehyd (divalentem Aldehyd) dazwischen immobilisiert ist, sodass sich die Schwellenspannung in positiver Richtung, als Reaktion auf eine Zunahme der Harnstoffkonzentration, verschiebt und dadurch die Empfindlichkeit gegenüber Harnstoff aufgezeigt wird.

5. Transistor oder Sensor nach Anspruch 4, worin die Zunahme der Harnstoffkonzentration 10^{-6} M bis 10^{-2} M beträgt.

6. Transistor oder Sensor nach Anspruch 5, aufweisend eine Harnstoffkonzentrationsempfindlichkeit von 30 mV/Dekade.

7. Verfahren zur Herstellung eines p-Kanal-Feldeffekttransistors aus einem Substrat (11), wobei der Transistor eine Diamantoberfläche (22) aufweisend gemischte Wasserstoffterminals, Sauerstoffterminals und Aminoterminals aufweist, wobei das Verfahren Folgendes umfasst:

Modifizieren einer wasserstoffterminierten Diamantoberfläche des Substrats (11) mittels eines Ultraviolettstrahls;
Einführen von Sauerstoff und Anwenden des Ultraviolettstrahls zum teilweisen Sauerstoffterminieren der wasserstoffterminierten Diamantoberfläche (22); und
Platzieren des Substrats (11) in eine Ammoniaklösung und Bestrahlen mit einem Ultraviolettstrahl zum teilweisen Aminoterminieren der Diamantoberfläche (22).

8. Verfahren nach Anspruch 7, ferner umfassend:

Immobilisieren von Glutaraldehyd (divalentem Aldehyd) an einer Aminogruppe auf der Diamantoberfläche (22).

9. Verfahren nach Anspruch 8, ferner umfassend:

Anwenden von Urease, um die Aminogruppe der Urease an das immobilisierte Glutaraldehyd zu binden.

10. Transistor oder Verfahren nach einem vorhergehenden Anspruch, worin die Diamantoberfläche (22) eine polykristalline oder monokristalline Diamantoberfläche (22) ist.

Revendications

1. Un transistor à effet de champ à canal p dans lequel :

un électrolyte liquide est utilisé comme grille, et ;

une surface de diamant à terminaison hydrogène, à terminaison amine partielle et à terminaison oxygène (22) ayant un mélange de parties terminales hydrogène, de parties terminales oxygène et de parties terminales amino, qui sert de canal.

2. Un capteur comprenant le transistor à effet de champ à canal p selon la revendication 1.

3. Le transistor ou capteur selon l'une quelconque des revendications précédentes, dans lequel, lors de l'utilisation, il y a un décalage de la tension seuil dans le sens positif sur la surface de diamant (22), en réponse à une augmentation du pH de l'électrolyte liquide de 2 à 12.

4. Le transistor ou capteur selon l'une quelconque des revendications précédentes, dans lequel l'uréase est immobilisée sur la partie terminale amino de la surface de diamant (22) avec du glutaraldéhyde (aldéhyde divalent) entre celles-ci, de telle sorte que la tension seuil se décale dans le sens positif en réponse à une augmentation de la concentration d'urée et, ainsi, la sensibilité à l'urée est exposée.

5. Le transistor ou capteur selon la revendication 4, dans lequel l'augmentation de la concentration d'urée est comprise entre 10^{-6} M et 10^{-2} M.

6. Le transistor ou capteur selon la revendication 5, ayant une sensibilité de la concentration d'urée de 30 mV/décade.

7. Un procédé de production d'un transistor à effet de champ à canal p à partir d'un substrat (11), le transistor ayant une surface de diamant (22) ayant un mélange de parties terminales hydrogène, de parties terminales oxygène et de parties terminales amino, le procédé consistant à :

modifier une surface de diamant à terminaison hydrogène du substrat (11) en utilisant un rayonnement ultraviolet ;
introduire de l'oxygène et appliquer le rayonnement ultraviolet pour effectuer partiellement une terminaison oxygène de la surface de diamant (22) à terminaison hydrogène ; et
placer le substrat (11) dans une solution d'ammoniaque et irradier avec un rayonnement ultraviolet pour effectuer partiellement une terminaison amino de la surface de diamant (22).

8. Le procédé selon la revendication 7, consistant en outre à :

immobiliser le glutaraldéhyde (aldéhyde divalent) sur un groupe amino de la surface de diamant (22).

9. Le procédé selon la revendication 8, consistant en outre à :

appliquer l'uréase pour lier le groupe amino de l'uréase au glutaraldéhyde immobilisé.

10. Le transistor ou procédé selon l'une quelconque des revendications précédentes, dans lequel la surface de diamant (22) est une surface de diamant polycristalline ou monocristalline (22).

FIG. 1

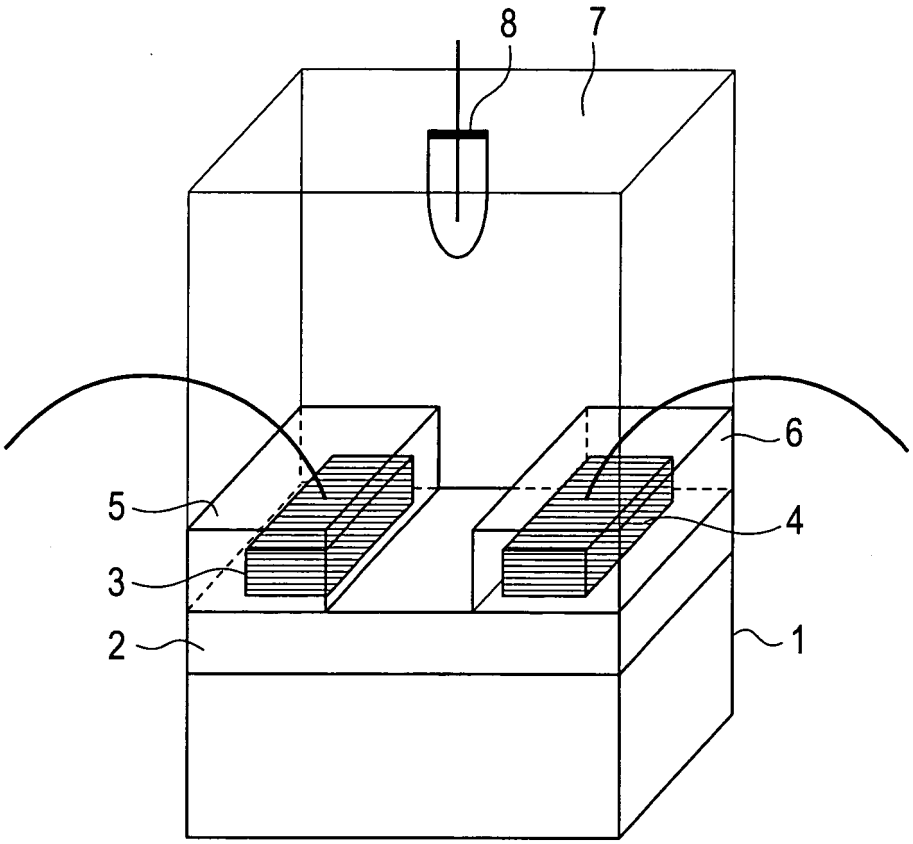


FIG. 2

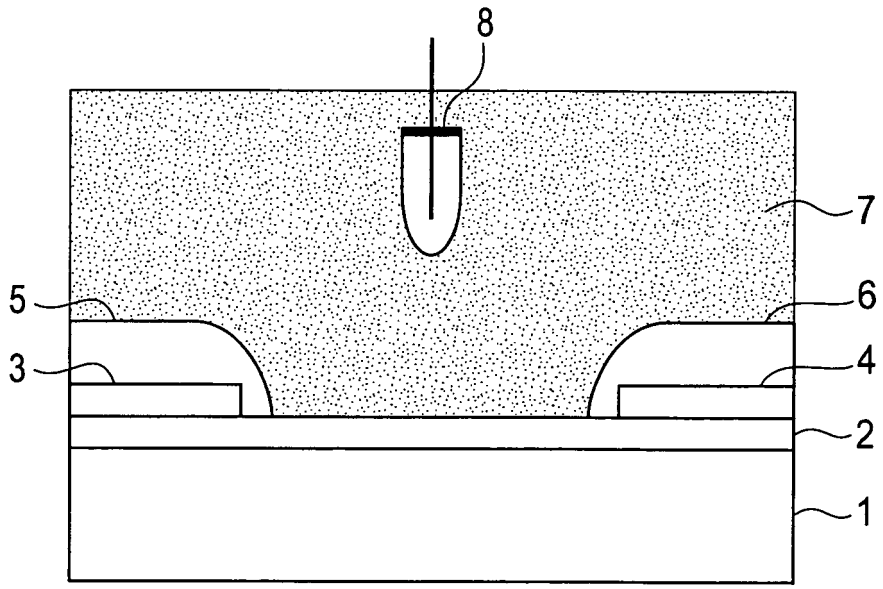
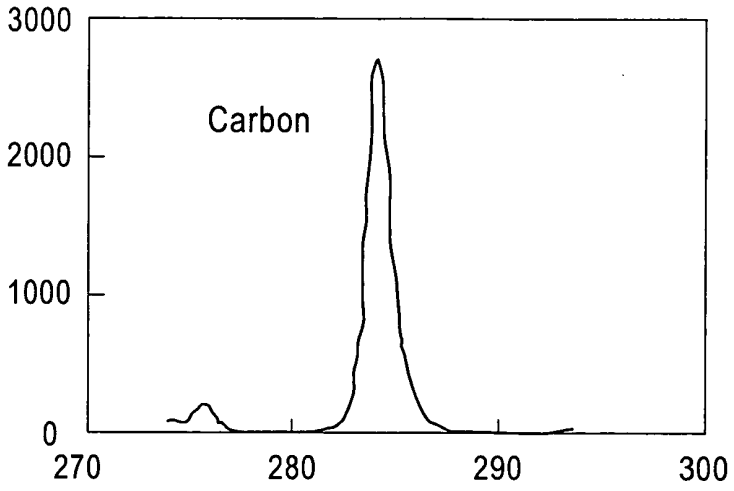
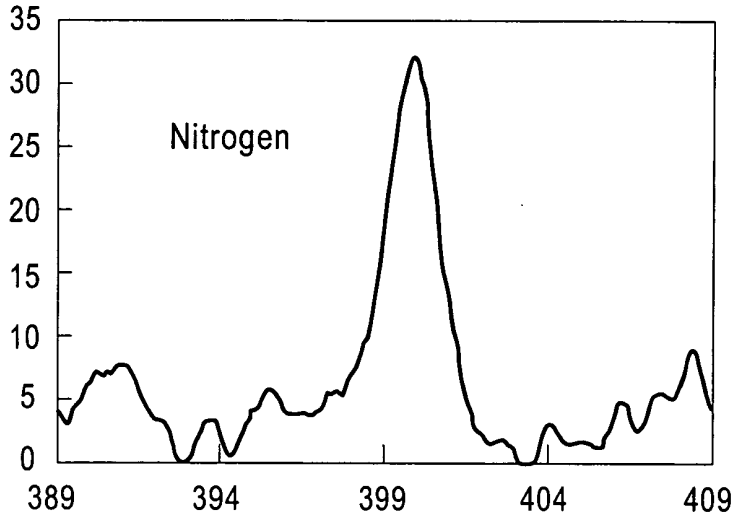


FIG. 3

(a)


3000
2000
1000
0
Carbon
270
280
290
300

(b)


35
30
25
20
15
10
5
0
Nitrogen
389
394
399
404
409

(c)

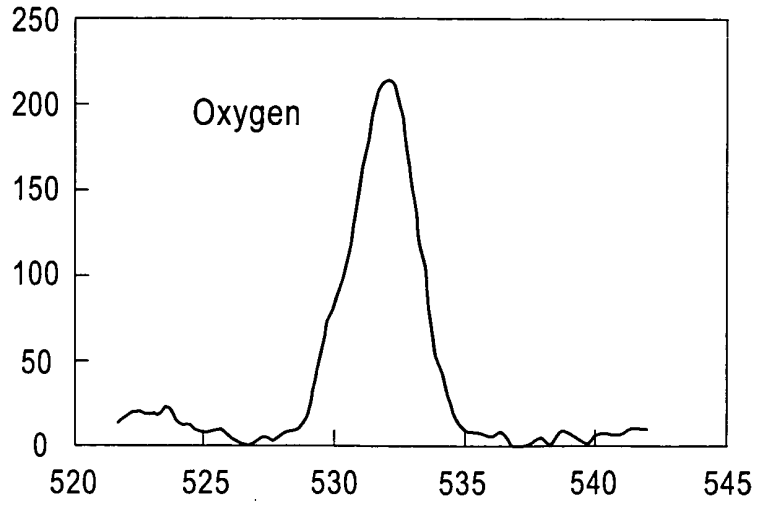

250
200
150
100
50
0
Oxygen
520
525
530
535
540
545

FIG. 4

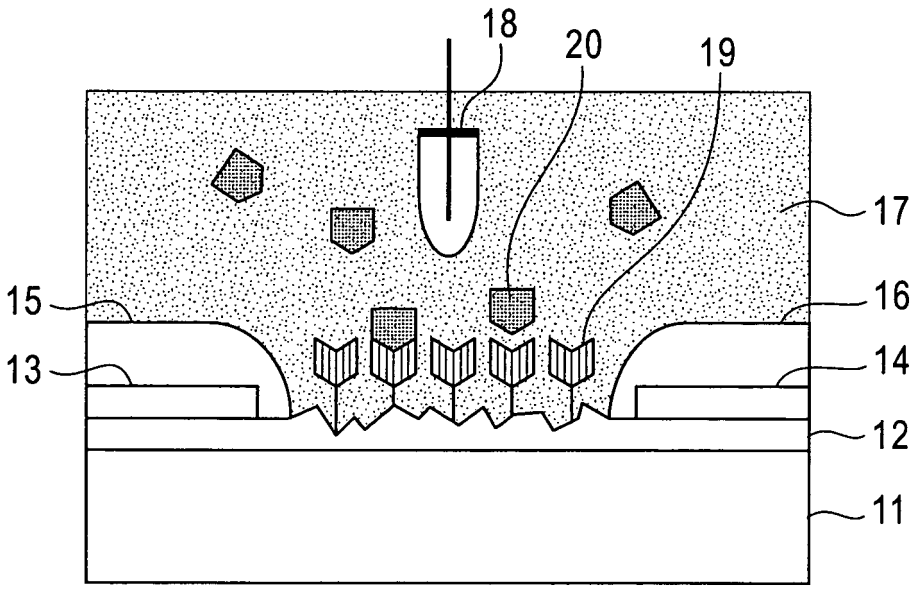


FIG. 5

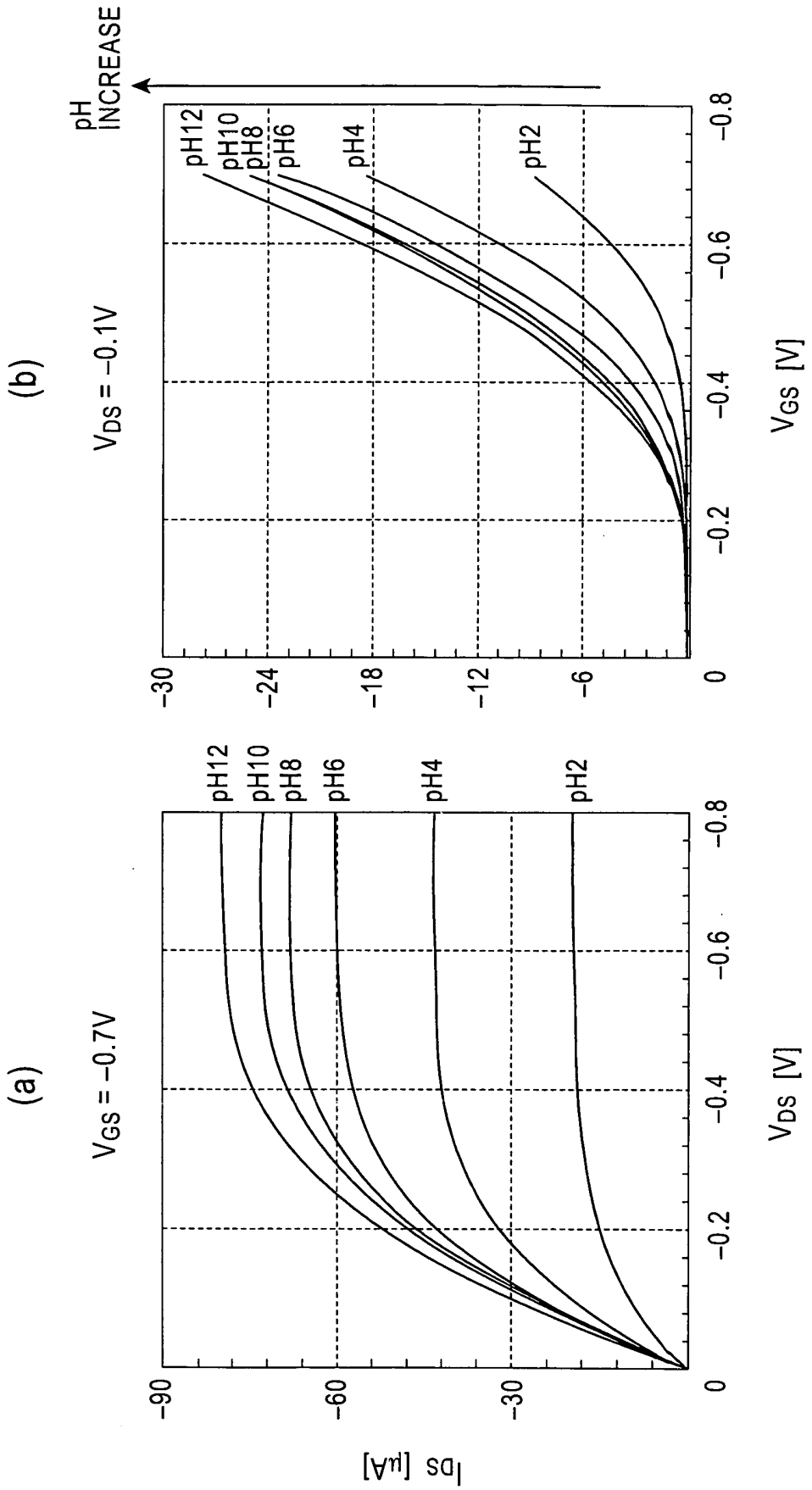

(a)
V_{GS} = −0.7V
pH12
pH10
pH8
pH6
pH4
pH2
I_{DS} [μA]
−90
−60
−30
0
−0.2
−0.4
−0.6
−0.8
V_{DS} [V]
(b)
V_{DS} = −0.1V
pH INCREASE
pH12
pH10
pH8
pH6
pH4
pH2
−30
−24
−18
−12
−6
0
−0.2
−0.4
−0.6
−0.8
V_{GS} [V]

FIG. 6

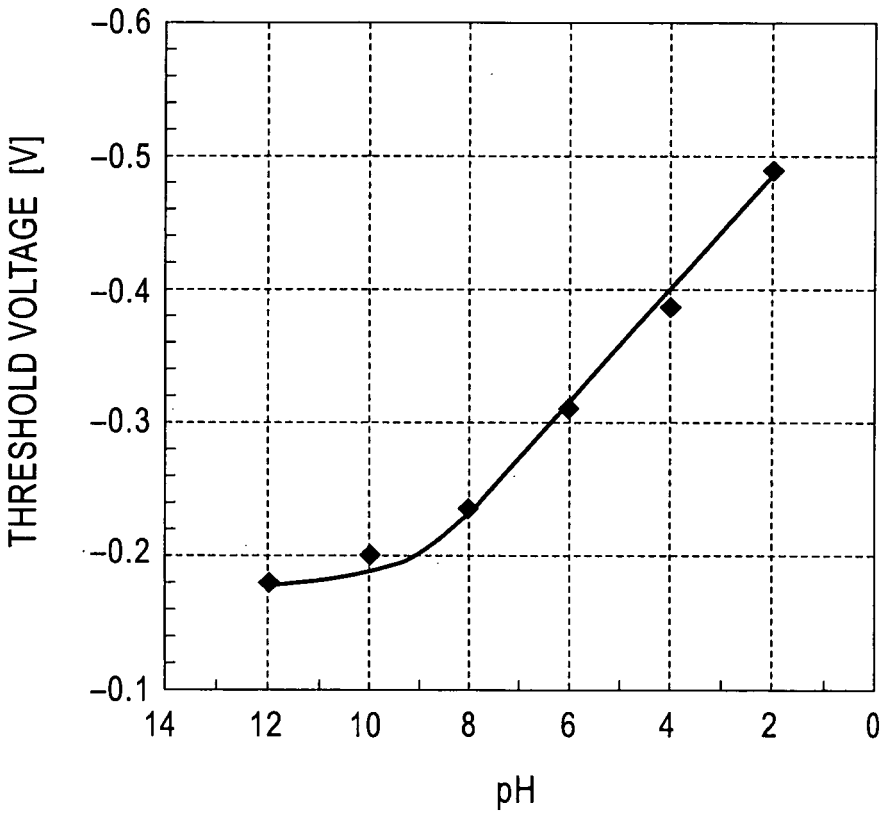


FIG. 7

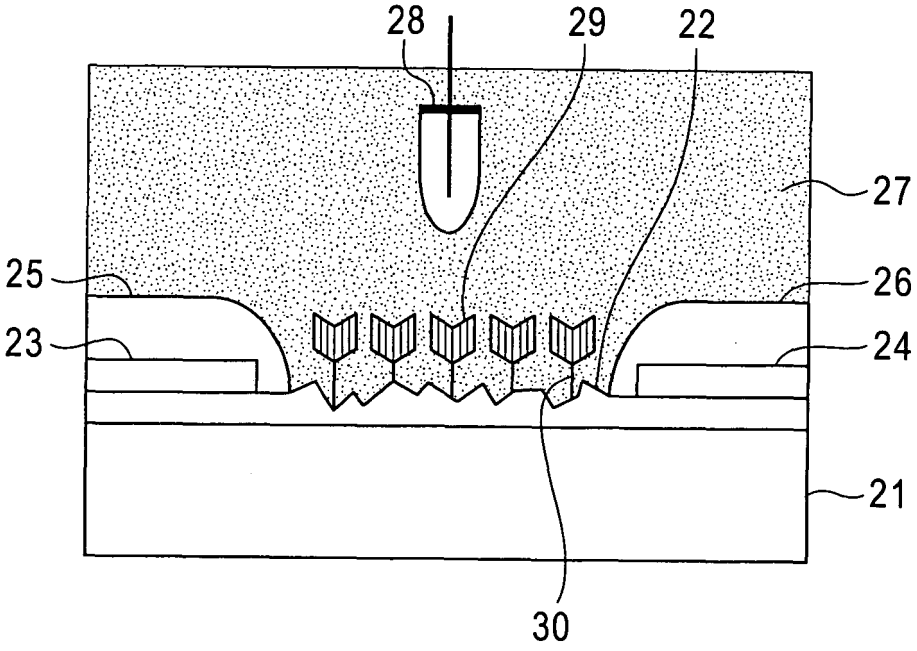


FIG. 8

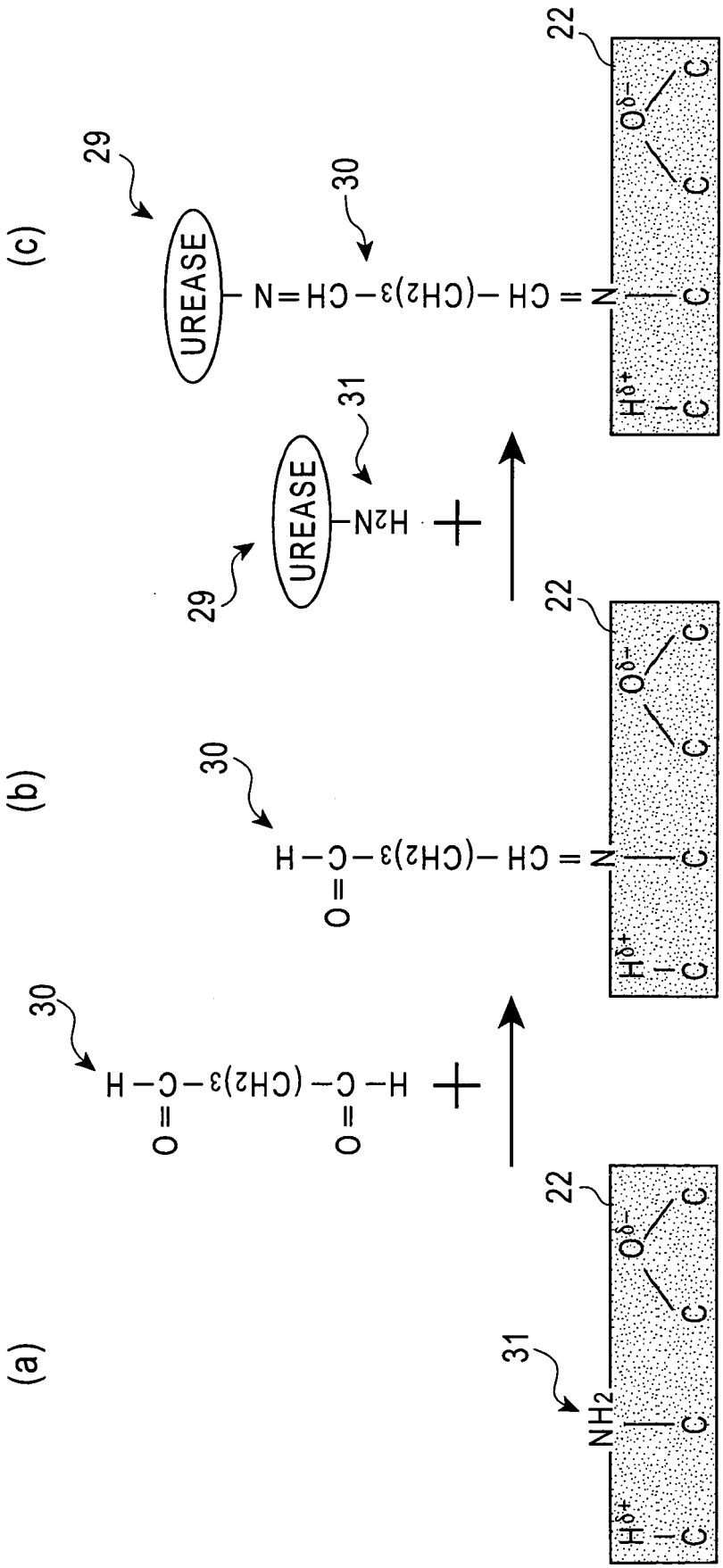


FIG. 9

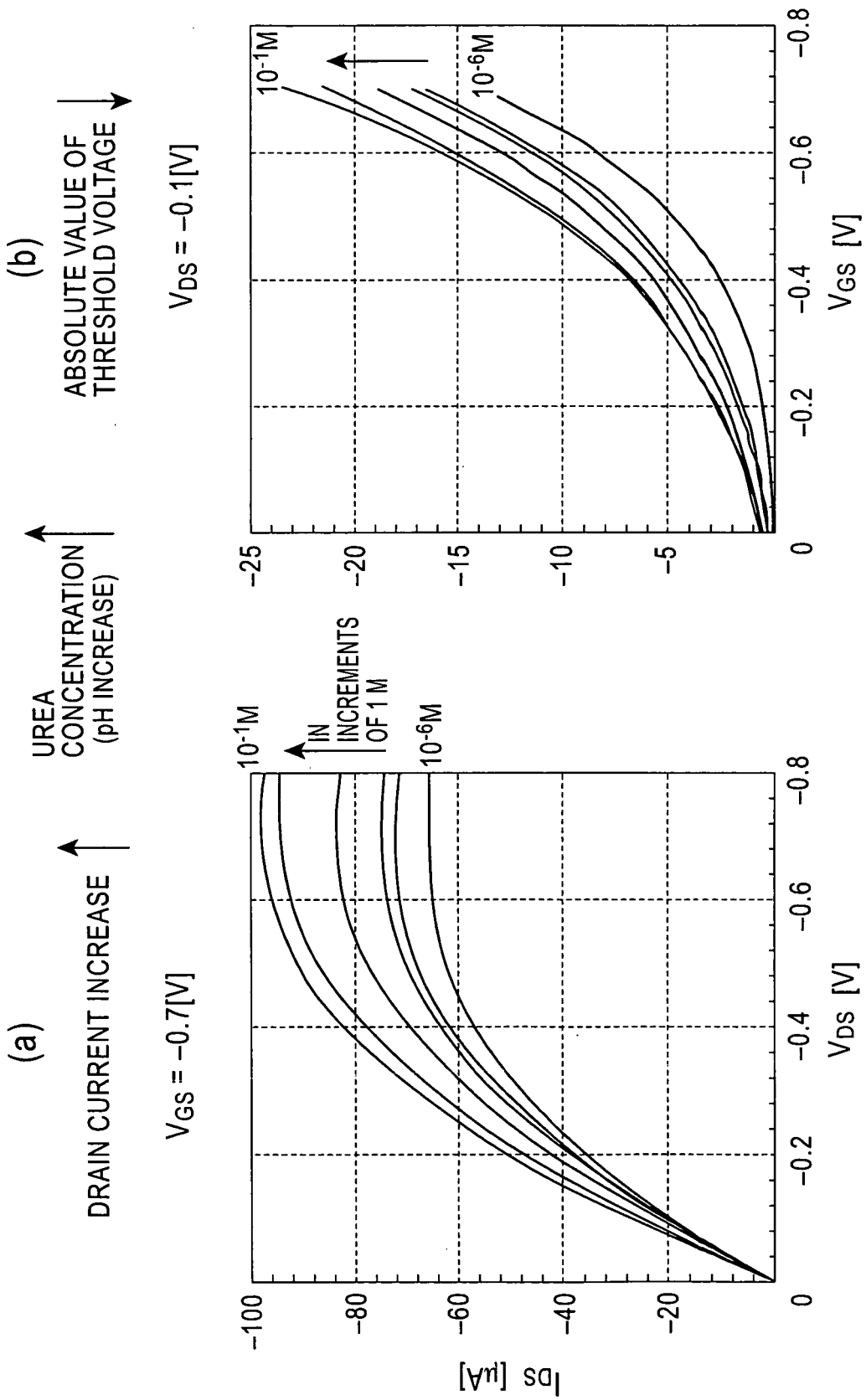
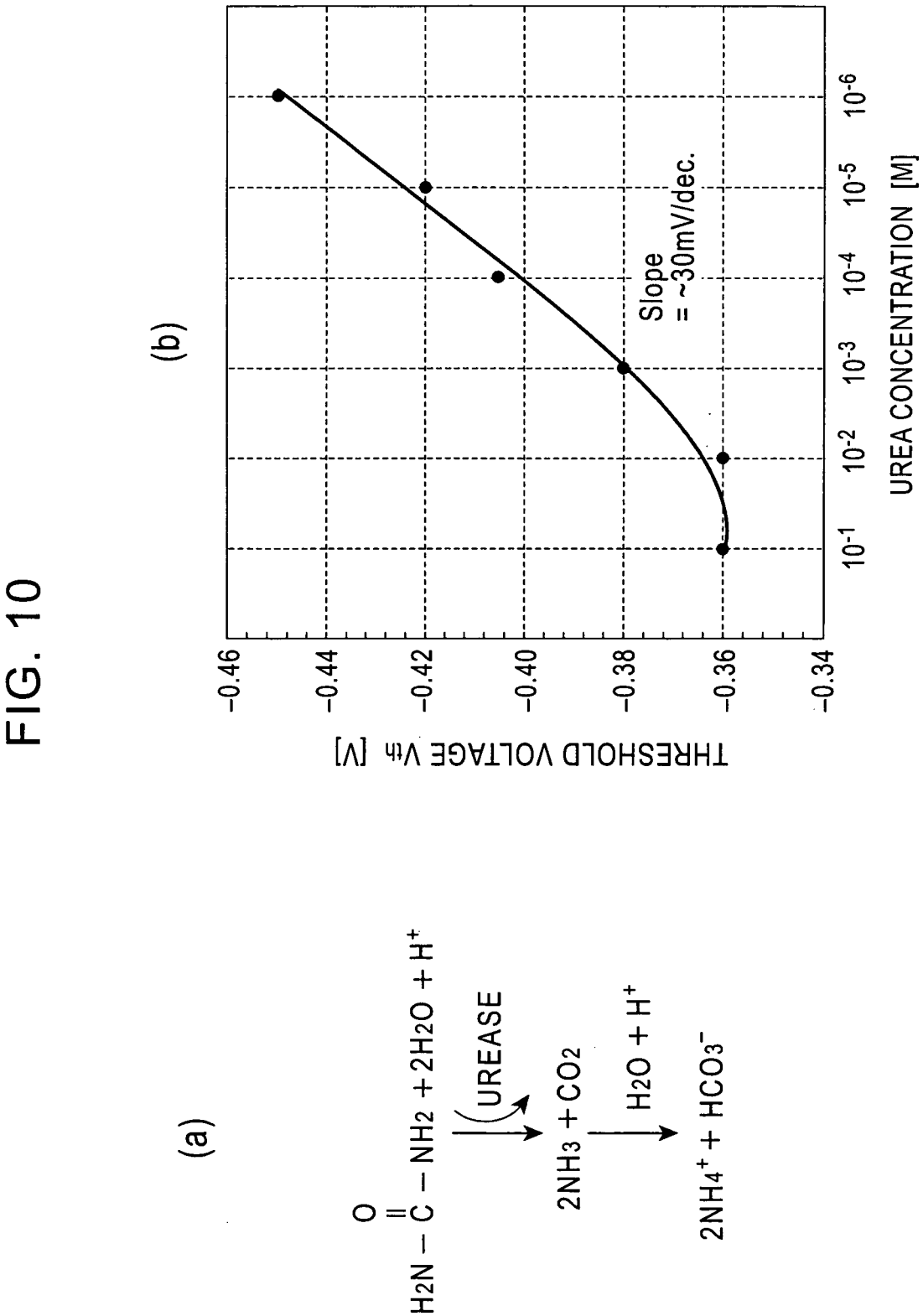

(a)
DRAIN CURRENT INCREASE
UREA CONCENTRATION (pH INCREASE)
(b)
ABSOLUTE VALUE OF THRESHOLD VOLTAGE
V_{GS} = −0.7[V]
V_{DS} = −0.1[V]
10^{-1}M
IN INCREMENTS OF 1 M
10^{-6}M
I_{DS} [μA]
V_{DS} [V]
V_{GS} [V]
−100
−80
−60
−40
−20
0
−0.2
−0.4
−0.6
−0.8
−25
−20
−15
−10
−5

FIG. 10


(a)
O
H2N – C – NH2 + 2H2O + H+
UREASE
2NH3 + CO2
H2O + H+
2NH4+ + HCO3−
(b)
THRESHOLD VOLTAGE Vth [V]
−0.46
−0.44
−0.42
−0.40
−0.38
−0.36
−0.34
Slope
= ~30mV/dec.
10-1
10-2
10-3
10-4
10-5
10-6
UREA CONCENTRATION [M]

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 3313696 B **[0003]**
- JP 3390756 B **[0003]**