

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 July 2009 (09.07.2009)

PCT

(10) International Publication Number
WO 2009/084850 A2

(51) International Patent Classification:
H01L 21/027 (2006.01)

(21) International Application Number:
PCT/KR2008/007632

(22) International Filing Date:
24 December 2008 (24.12.2008)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
10-2007-0138344
27 December 2007 (27.12.2007) KR

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE,
EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR,
LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX,
MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO,
RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

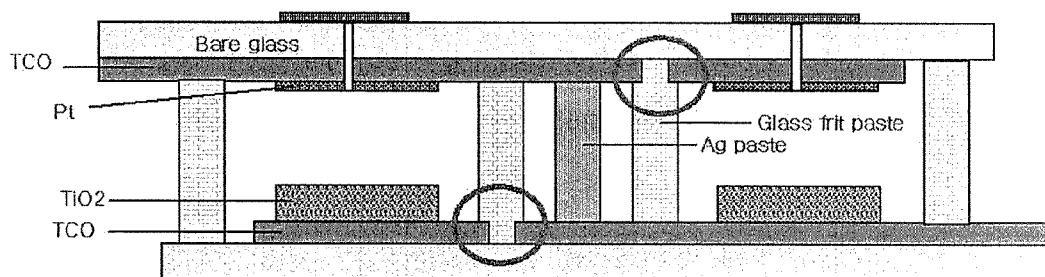
(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

(54) Title: METHOD OF PATTERNING TRANSPARENT CONDUCTIVE OXIDE OF A CONDUCTIVE GLASS AND CON-
DUCTIVE GLASS PREPARED THEREBY

[Fig. 1]



(57) Abstract: The present invention relates to a method of patterning a transparent conductive oxide film of conductive glass, and a conductive glass prepared thereby. Specifically, the present invention relates to a method of patterning a transparent conductive oxide film of a conductive glass comprising the steps of: forming a photoresist pattern on the part of the surface of a glass substrate where a transparent conductive oxide film is not to be formed; forming a transparent conductive film on the glass substrate; and removing the photoresist from the glass substrate, and a conductive glass prepared thereby. According to the present invention, a transparent conductive oxide (TCO) film can be patterned more easily and more inexpensively. Particularly, in the case of using TCO consisting of FTO, a conductive glass comprising FTO pattern formed thereon can be manufactured without using expensive laser equipment, and such conductive glass can be used as an electrode plate of a dye-sensitized solar cell.

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METHOD OF PATTERNING TRANSPARENT CONDUCTIVE OXIDE OF A CONDUCTIVE GLASS AND CONDUCTIVE GLASS PREPARED THEREBY

【Technical Field】

5 The present invention relates to a method of patterning a transparent conductive oxide film of a conductive glass and a conductive glass prepared thereby, more specifically to a method of patterning a transparent conductive oxide film of a conductive glass which can pattern a TCO(transparent conductive oxide) film more easily and more inexpensively, and particularly in the case of using TCO consisting of FTO, manufacture
10 a conductive glass having FTO pattern formed thereon without using expensive laser equipment, which can be used as an electrode plate of a dye-sensitized solar cell, and a conductive glass prepared thereby.

【Background Art】

15 In general, a transparent conductive coating is used for a transparent conductive film for display, a transparent conductive film for solar cell, etc., and the market is increasing day by day. It is generally prepared by coating conductive material on an electrical insulator glass(bare glass, soda-lime).

20 Glass is an electrical insulator with electrical conductivity of from 10^{-10} to 10^{-11} (Ωcm)⁻¹ at room temperature. In order to give electrical conductivity to the glass insulator while maintaining high transmittance, TCO(transparent conductive oxide) or metal is coated on the glass surface to form a transparent conductive coating and thus prepare a conductive glass.

25 However, the transparent conductive coating of a conductive glass is not necessarily coated on the whole glass surface. In general, suitable pattern(removing a part and maintaining the rest) is formed according to the applied field or equipment. For example, referring to dye-sensitized solar cell shown in Fig. 1, a conductive glass comprising an upper electrode(a second electrode) and a lower electrode(a first electrode)

respectively coated with TCO as transparent conductive coating is used, and the TCO is patterned so as to have cut parts as expressed by circles in Fig. 1.

For patterning transparent conductive coating on a conductive glass, typically, pattern is formed while TCO is placed on the whole substrate, and for this, images formed on a mask are exposed using PR and the PR is developed, and then, etched using an etchant to form a circuit pattern. However, in order to manufacture dye-sensitized solar cell, FTO is mainly used as TCO because it is thermally stable at high temperature of approximately 500 to 600°C and has excellent chemical resistance thus stands electrolyte, and, although photoelectric transformation efficiency is rather low, ITO is occasionally used in case of using a material that can be processed at low temperature.

In the case of using ITO, a pattern is formed by etching using the etchant. However, the chemical etching using exposure and etchant has problems in that cost increases due to the use of etchant, the process is not easy, and environmental pollution is most likely to be caused.

In the case of using FTO, since chemical etching using etchant cannot be conducted due to excellent chemical resistance of FTO, circuit pattern should be formed using laser as shown in Fig. 2, which increases equipment cost and decreases productivity.

Therefore, there is a high demand for the development of a method of patterning TCO which does not use the existing laser pattern or chemical etching using exposure for circuit patterning, when preparing a conductive glass comprising a pattern formed thereon using TCO.

【Disclosure】

【Technical Problem】

In order to solve the above problems of the prior art, it is an object of the present invention to provide a method of patterning a transparent conductive oxide film which can pattern TCO more easily and more inexpensively, and particularly in the case of using TCO consisting of FTO, manufacture a conductive glass comprising FTO pattern

formed thereon without using expensive laser equipment, said conductive glass used as an electrode plate of a dye-sensitized solar cell, and a conductive glass prepared thereby.

【Technical Solution】

5 In order to achieve the objet, the present invention provides a method of patterning a transparent conductive oxide film of conductive glass, comprising the steps of: forming a photoresist pattern on the part of the surface of a glass substrate where a transparent conductive oxide film is not to be formed; forming a transparent conductive film on the glass substrate; and removing the photoresist from the glass substrate.

10 The present invention also provides a conductive glass prepared by the method of the present invention, comprising a glass substrate and a transparent conductive oxide film pattern formed on the glass substrate.

 The present invention also provides a dye-sensitized solar cell comprising: a first electrode consisting of transparent electrode; a second electrode combined to the surface
15 opposite to the transparent electrode; and an intermediate layer comprising oxide semiconductor between the first and second electrodes, dye, and electrolyte, wherein the first electrode or the second electrode comprises the conductive glass of the present invention.

20 【Advantageous Effects】

 According to the present invention, a transparent conductive oxide(TCO) film can be patterned more easily and more inexpensively. Particularly, in the case of using TCO consisting of FTO, a conductive glass comprising FTO pattern formed thereon can be manufactured without using expensive laser equipment, and such conductive glass can
25 be used as an electrode plate of a dye-sensitized solar cell.

【Brief Description of Drawings】

Fig. 1 is a cross sectional view schematically showing a dye-sensitized solar cell

according to one embodiment of the present invention.

Fig. 2 schematically shows a patterning method of the prior art using FTO as a transparent conductive coating.

Fig. 3 schematically shows a method of patterning a transparent conductive oxide film of a conductive glass according to one embodiment of the present invention.

【Mode for Invention】

The present invention will now be explained in detail with reference to the attached drawings.

10 The present invention relates to a method of patterning a transparent conductive oxide film of a conductive glass, which comprises the steps of forming a photoresist pattern on the part of the surface of a glass substrate where a transparent conductive oxide film is not to be formed; forming a transparent conductive film on the glass substrate surface; and removing the photoresist from the glass substrate.

15 Fig. 3 shows one embodiment of the method according to the present invention using negative photoresist(PR). Referring to Fig. 3, negative PR is applied to a glass substrate, photomask which is patterned so as to conduct exposure only to a part where PR is to be remained(where a transparent conductive oxide film is not to be formed on the glass substrate) is placed thereon, and exposure is conducted to leave only exposed PR
20 after development, thus forming PR pattern(parts where a transparent conductive oxide film is not to be formed on the glass substrate). To the contrary, in the case of using positive PR, the same PR pattern can be formed by setting exposed parts contrarily. The nega-PR preferably has reverse taper shape thus facilitating the removal of PR. However, posi-PR can also have reverse taper shape according to the kinds of PR. It is
25 preferable to form a PR pattern having cross section of reverse taper shape because it facilitates the removal of PR. Any process can be used only if the PR pattern in the second step of Fig. 3 can be obtained, i.e., only if a photoresist pattern can be obtained on a part where a transparent conductive oxide film is not to be formed on the glass substrate.

Specifically, on a bare glass(soda-lime) required for forming a transparent conductive oxide(TCO) film, Nega-PR for forming a partition mainly used for display is applied, desired circuit shape is exposed using exposure mask, and then developed. The height of the partition is preferably 1 ~ 3 μm as shown in Fig. 3, because the film thickness of TCO is generally 1500 to 200 $\text{\AA}$ for ITO and 6000 to 8000 $\text{\AA}$ for FTO, thus ranging from approximately 1500 to 8000 $\text{\AA}$, and the partition should be higher than that so as to enable patterning. And, the width of the partition is determined by design value.

Next, on the glass substrate having thus formed PR pattern, a transparent conductive oxide(TCO) film is formed. Preferably, the transparent conductive oxide film is formed by anisotropical deposition where the film grows from the bottom to the top on the glass substrate, because it forms a transparent conductive oxide film only on the top as shown in Fig. 3, thus facilitating the removal of PR and TCO on the PR.. In the case where anisotropical deposition is conducted on reverse tapered PR pattern as shown in Fig. 3, deposition is conducted only on the top of the PR pattern thus facilitating the removal of PR. The anisotropical deposition includes vapor deposition such as CVD, sputtering, wet deposition such as spray coating, etc.

In the process of forming a transparent conductive oxide film, the glass substrate is preferably heated to 150 to 250 $^{\circ}\text{C}$, more preferably to 200 $^{\circ}\text{C}$. The heating to the above temperature range can simplify the process because PR does not need separate curing process, and such condition is naturally obtained during the practical process of forming a transparent conductive oxide film. Since the process of forming a TCO film using CVD, sputtering, spray, etc. is conducted at a substrate temperature of about 200 $^{\circ}\text{C}$, Nega-PR for a partition is naturally cured and hardened without separate curing process.

As the TCO, various materials can be used, and ITO or FTO is preferable in terms of process stability and easiness of manufacture. And, in the case of using ITO or FTO, it is preferable to further comprise the step of annealing the transparent conductive oxide film between the step of forming a transparent conductive oxide film and the step

of removing photoresist as shown in Fig. 3. The heat treatment by annealing after formation of a TCO film can increase crystallinity of the TCO film. Annealing is not limited to ITO and FTO, and can be selectively applied to any TCO which properties can be improved by annealing.

5 The annealing is generally conducted at a temperature of approximately 250 to 350°C for ITO, and around 500°C for FTO. In the case of FTO, since the annealing temperature is sufficiently higher than Td(decomposition temperature) of commonly applied PR, PR can be partly removed by annealing, thus enabling the subsequent PR removal within a short time.

10 Next, PR is removed from the glass substrate, by which process a transparent conductive oxide film deposited on the PR is removed together with PR thus obtaining a conductive glass having a pattern as shown in the bottom of Fig. 3. Specifically, PR is removed using rework chemical(for example, amine based organic solvent), and washing is conducted to obtain a TCO glass having a circuit shape formed thereon.

15 The present invention also provides a conductive glass having a transparent conductive oxide film pattern prepared by the method of patterning a transparent conductive oxide film of a conductive glass as explained above. The conductive glass of the present invention is prepared by the method of patterning a transparent conductive oxide film of a conductive glass as explained above, and comprises a glass substrate and a
20 transparent conductive oxide film pattern formed thereon, of which example is shown in the bottom of Fig. 3.

 The conductive glass can be used for display, solar cell, etc. The present invention also provides a dye-sensitized solar cell comprising the conductive glass, which comprises a first electrode consisting of transparent electrode; a second electrode
25 combined to the surface opposite to the transparent electrode; and, an intermediate layer comprising oxide semiconductor (for example, TiO₂) between the first electrode and the second electrode, dye and electrolyte, wherein the first electrode or the second electrode comprises the above explained conductive glass.

One embodiment of the dye-sensitized solar cell of the present invention is shown in Fig. 1. Referring to Fig. 1, both of the first electrode and the second electrode are comprised of the conductive glass of the present invention. However, only the first electrode or the second electrode can be comprised of the conductive glass of the present invention.

In general, a dye-sensitized solar cell comprises a first electrode(the lower electrode of Fig. 1), a second electrode(the upper electrode of Fig. 1), a layer comprising oxide semiconductor particles(for example, TiO_2) and dye, and, an electrolyte layer placed thereon. The first electrode can be comprised of the conductive glass of the present invention, and semiconductor oxide layer(for example, TiO_2) can be formed thereon; or, the second electrode can be comprised of the conductive glass of the present invention, and Pt can be coated on the bottom surface thereof. Specifically, on a substrate having a pattern formed according to the method of the present invention, photoelectrode(TiO_2) which is a basic structure of a dye-sensitized solar cell is formed, and counter electrode Pt is formed on the opposite substrate(a second electrode). Dye is absorbed into the photoelectrode, and the two substrates are combined, and then electrolyte is injected inside, and the inlet is sealed to obtain a dye-sensitized solar cell.

The present invention is not limited to the foregoing examples and drawings attached hereto, and various modification or alteration can be made by a person of ordinary skill in the art without departing from the aspect and scope of the present invention as described in the claims appended hereto.

【Industrial Applicability】

According to the present invention, a transparent conductive oxide(TCO) film can be patterned more easily and more inexpensively. Particularly, in the case of using TCO consisting of FTO, a conductive glass comprising FTO pattern formed thereon can be manufactured without using expensive laser equipment, and such conductive glass can

be used as an electrode plate of a dye-sensitized solar cell.

【CLAIMS】**【Claim 1】**

A method of patterning a transparent conductive oxide film of conductive glass, comprising the steps of:

- 5 forming a photoresist pattern on the part of the surface of a glass substrate where a transparent conductive oxide film is not to be formed;
 forming a transparent conductive film on the glass substrate; and
 removing the photoresist from the glass substrate.

【Claim 2】

- 10 The method according to claim 1, wherein the cross section of the photoresist pattern is of reverse taper shape, and the transparent conductive oxide film is formed by anisotropical deposition so as to grow from the bottom to the top on the glass substrate, such as vapor deposition, sputtering and spray coating.

【Claim 3】

- 15 The method according to claim 1, wherein in the step of forming a transparent conductive film, the glass substrate is heated to a temperature from 150 to 250 °C .

【Claim 4】

- The method according to claim 1, wherein the transparent conductive film is ITO or FTO, and the method further comprises the step of annealing the transparent
20 conductive oxide film between the step of forming a transparent conductive oxide film and the step of removing the photoresist.

【Claim 5】

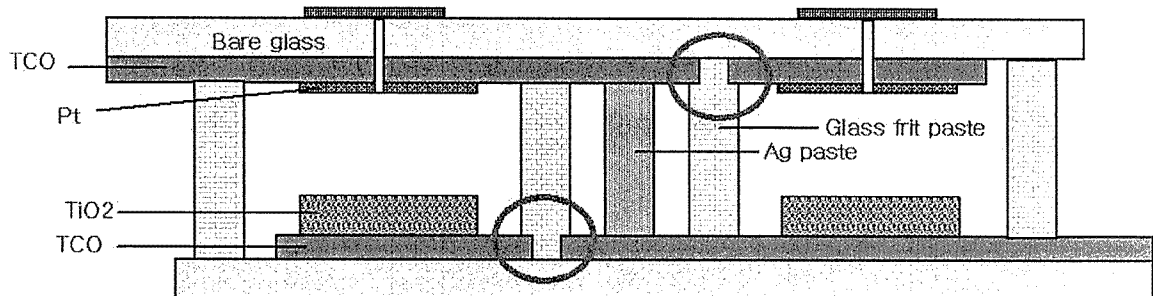
- A conductive glass prepared by the method according to anyone of claims 1 to 4, comprising a glass substrate and a transparent conductive oxide film pattern formed on
25 the glass substrate.

【Claim 6】

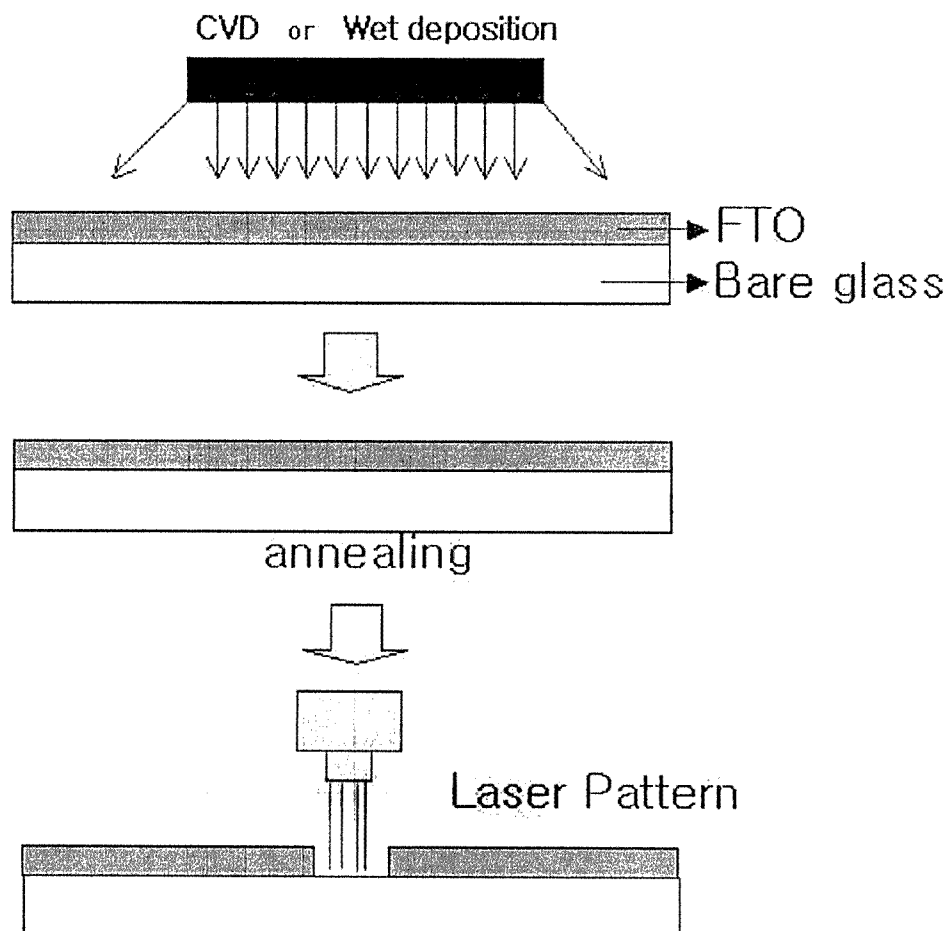
A dye-sensitized solar cell comprising: a first electrode consisting of transparent electrode; a second electrode combined to the surface opposite to the transparent electrode; and an intermediate layer comprising oxide semiconductor between the first and second electrodes, dye, and electrolyte,

5 wherein the first electrode or the second electrode comprises the conductive glass according to claim 5.

[Fig. 1]



[Fig. 2]



[Fig. 3]

