Title: A METHOD FOR TEXTURING A GLASS SURFACE

Abstract: The present invention relates to a new method of texturing a glass surface. In further aspects, the present invention relates to the resulting textured glass surface; to a photovoltaic device comprising the textured glass surface; and, to use of the textured glass surface for scattering light.
A method for texturing a glass surface

FIELD OF INVENTION

The present invention relates to a new method of texturing a glass surface.

In further aspects, the present invention relates to a textured glass surface; to a photovoltaic device; and, to use of a textured glass surface for scattering light.

BACKGROUND OF THE INVENTION

Methods of texturing glass surfaces are known in the prior art from e.g. EP 1 613 562 B1.

EP 1 613 562 B1 recites a method of texturing a glass surface, the method comprising the steps of coating the glass surface with a material film, stimulating a reaction at the interface between the glass and the material film resulting in the formation of reaction products, and removing the material film and the reaction products from the glass surface.

Examples of EP 1 613 562 B1 relate to use of aluminium as the material film. The step of stimulating a reaction comprises annealing the coated glass at a relatively high temperature of 630°C for a long period of time. This temperature is very close to the softening temperature of glass and the melting temperature of aluminium and can lead to problems with handling of the coated glass during and after annealing. The process of EP 1 613 562 B1 is also problematic in practice since during annealing it is essential that there is temperature uniformity across the surface of the coated glass.

US2012097239 (A1) recites a method for roughening a substrate surface, comprising a first step of forming a protection film on a surface of a translucent substrate, a second step of exposing the surface of the translucent substrate by forming a plurality of openings arranged regularly at a certain pitch in the protection film, a third step of forming parabolic irregularities including substantially hemispherical depressions arranged substantially periodically on the surface of the translucent substrate by performing isotropic etching by using the protection film having the openings formed as a mask and under conditions in which the protection film has resistance to the surface of the translucent substrate on which the protection film is formed, and a fourth step of removing
the protection film, wherein at the fourth step, the isotropic etching is continued after formation of the parabolic irregularities to separate the protection film from the translucent substrate and round apexes of protruded portions in the parabolic irregularities. The method may be considered as complex.

It is an object of the present invention to overcome one or more disadvantages of methods of texturing glass surfaces of the prior art.

SUMMARY OF THE INVENTION

In a first aspect, the present invention relates to a method of texturing a glass surface, the method comprising the steps of: (a) providing glass having a glass surface; (b) depositing a sacrificial zinc oxide layer on at least a portion of the glass surface; (c) contacting the sacrificial zinc oxide layer with an etching solution for etching zinc oxide and glass; and, (d) removing the sacrificial zinc oxide layer and at least a portion of the glass thereunder. In an example the present method is limited to steps a through d above, i.e. consists of steps a through d. The present invention relates to a maskless process.

The present zinc oxide is a heterogeneous material, e.g. a material comprising an amorphous phase and a crystalline phase. When the sacrificial zinc oxide layer is exposed to the etching solution, the sacrificial zinc oxide layer is etched inhomogeneously, with different etching rates over the heterogeneous material, e.g. for the amorphous and crystalline phase. Some parts of the sacrificial zinc oxide layer etch faster than other areas (e.g. at crystal boundaries). Where the sacrificial zinc oxide layer etches faster, the glass surface is exposed sooner to the etching solution. Once the etching solution contacts the glass it will begin to etch the glass. Once the entire sacrificial zinc oxide layer has been consumed by the etching solution a textured glass surface remains.

Experimentation by the inventors has revealed that the morphology of a glass surface textured according to the present invention is dependent on characteristics of the sacrificial zinc oxide layer and on the composition of the etching solution.
Whilst for certain applications a uniformly textured glass surface may be preferred, for other applications less uniformly textured glass may be more desirable.

In a first preferred embodiment, the sacrificial zinc oxide layer further comprises a dopant selected from a group consisting F, B, Al, Ga, In, and Sn and combinations thereof, such as wherein the dopant is at an amount in the range of 0.1 to 10 % w/w dopant/zinc oxide, preferably 0.2 to 5 % w/w, most preferably 0.5 to 3 % w/w.

A number of techniques may be used for applying the sacrificial zinc oxide layer such as MOCVD, LPCVD, PLD, ALD, sol-gel method, evaporation, etc.


In a second preferred embodiment, the sacrificial zinc oxide layer is deposited by sputtering, or any of the above mentioned techniques, preferably at a sputtering temperature in the range of 50 to 500°C, typically from 100-400°C. By sputtering the zinc oxide or doped zinc oxide, the thickness and physical characteristics of the resulting film can be tuned. In particular, the degree of crystallinity and size of crystals can be chosen e.g. by choosing a suitable sputtering temperature falling within the above range, taking into account the drawing of Figures 2-5.

In a third preferred embodiment the sacrificial zinc oxide layer of claim 1 step (b) has a thickness in the range of 50 nm to 1000 nm, preferably 100 nm to 900 nm, most preferably 150 nm to 600 nm. I.e. the sacrificial zinc oxide layer is deposited at- or to- a thickness falling within these ranges. When the layer is too thin, the glass surface barely becomes textured; when the layer is too thick, the surface be-
comes textured beyond that which is desirable e.g. for light scattering applications.

In a fourth preferred embodiment, the etchant is an etching solution comprising a first etching component for etching zinc oxide and a second etching component for etching glass. Thus a high degree of control over the etching process may be achieved.

In a fifth preferred embodiment, the first etching component is nitric acid and/or the second etching component is hydrofluoric acid. Nitric acid etches only zinc oxide, whereas hydrofluoric acid is also able to etch glass. Both are cheap and readily available etchants.

In a sixth preferred embodiment, the first etching component is nitric acid and the second etching component is hydrofluoric acid and the ratio of concentrations of nitric acid to hydrofluoric acid is in the range of 1:1 to 20:1, preferably 2:1 to 15:1, most preferably 4:1 to 11:1, such as 4:1 to 8:1.

In a second aspect, the present invention relates to a textured glass surface prepared according to one or more embodiments of the above method.

Scattering of light is used for incoupling into a photovoltaic device. We claim that it can also be used the other way around, so for the outcoupling of light. This may be of use in the fabrication of (O)LEDs, scattering the light generated by the device and thereby making it more diffuse.

Also for flexible opto-electronic devices scattering of light can be of interest. According to the invention it is possible to quickly make master stamps that can be used to texture the surface of a flexible substrate.

In a third aspect, the present invention relates to a photovoltaic device comprising a textured glass surface prepared according to one or more embodiments of the above method.

In a fourth aspect the present invention relates to use of a textured glass surface prepared according to one or more embodiments of the above method for scattering light, e.g. for incoupling of light into a photovoltaic device (increasing an optical light path of light within the photovolta-
ic device), or for outcoupling of light, such as from (O)LEDs (scattering the light generated by the device and thereby making it more diffuse).

In a further example a textured glass surface may be used for improving efficiency of a photovoltaic cell.

In a further example a textured glass surface may be used for modifying the out-coupling of light from a (organic) light-emitting diode.

In a further example a textured glass surface may be used as a master for making stamps for flexible opto-electronic devices.

In a further aspect the present invention relates to a method for tuning a texture of glass. It is considered important that the method allows tuning of the texture of glass. It is noted that the texture may affect material properties of a subsequent deposited film. In a solar cell these may perform less efficient, as a consequence. The present method that realizes texturing, and can be tuned, allows circumventing these problems.

The invention is further elucidated with reference to the Drawings of Figures 1-6. It is noted that the Drawings are provided to facilitate understanding of the invention and are not intended to limit its scope.

DETAILS DESCRIPTION OF THE FIGURES

Fig. 1 is a schematic representation of the method of the invention;

Fig. 2 relates to an exemplary embodiment of the present invention using aluminium doped zinc oxide as the sacrificial zinc oxide layer and shows the influence of varying sputtering temperature, sacrificial zinc oxide layer thickness and etching solution composition on the RMS roughness of the resulting textured glass surface;

Fig. 3 shows atomic force microscope images of glass surfaces textured according to the present invention with aluminium doped zinc oxide as the sacrificial zinc oxide layer.

Fig. 4 relates to a further exemplary embodiment of the present invention using intrinsic zinc oxide as the sacrificial zinc oxide layer and shows the influence of varying sputtering temperature, sacrificial zinc oxide layer thickness
and etching solution composition on the RMS roughness of the resulting textured glass surface;

Fig. 5 shows atomic force microscope images of glass surfaces textured according to the present invention with intrinsic zinc oxide as the sacrificial zinc oxide layer.

Figure 6. The influence of textured glass morphology (Rs= σRMS/1c) on the performance of single-junction hydrogenated microcrystalline silicon (μc-Si:H) solar cells with different i-layer thicknesses. Parameters shown here are the average values with standard deviation calculated from the best 10 cells out of 24 cells in each stripe. Lines are used as a guide to the eye.

With reference to Figure 1, a schematic representation of the method for texturing a glass surface of the invention is shown.

Textured glass surfaces used for the measurements whose results are shown in the drawings of Figures 2-5 were prepared according to this method. Specifically, sacrificial zinc oxide layers were deposited on Corning Eagle XG glass using a magnetron sputtering system with a ZnO:Al or ZnO ceramic target at a range of sputtering temperatures. Glass surfaces were prepared having ZnO:Al or intrinsic ZnO layers of various thicknesses. The resulting ZnO:Al- or intrinsic ZnO- covered glass surfaces were etched with etching solutions comprising hydrofluoric acid and nitric acid for 15 s to 60 s depending on the thickness of the zinc oxide layer to be etched.

The surface morphologies of the resulting textured glass surfaces were studied by atomic force microscopy (AFM, NT-MDT nTegra). The following statistical parameters extracted from AFM scans are used: root mean square roughness (σRMS), correlation length (lc), and surface angle distribution (AD). Definitions thereof are given in the article mentioned below. Further experimental data and details supporting the present invention have been published after filing the priority document in "A novel way of texturing glass for microcrystalline silicon thin film solar cells application" by Guangtao Yang et al., Prog. Photovolt.: Res. Appl. (2014), which is incorporated in the present application in its entirety by reference. Some of the details have been incorporated in the present ap-
plication. The following relates to further examples and results obtained.

The optical scattering capability of the textured glass was studied in a specific embodiment such as n-i-p μc-Si:H solar cells. For these solar cells the textured glass is covered with 250-nm thick Ag layer on the rough surface. The RMS for textured glass decreased by around 8 nm after 250-nm Ag coverage; the surface morphology changes induced by Ag coverage were determined.

In the embodiment the textured glass was used as substrate for n-i-p μc-Si:H solar cells. After surface texturing, the textured glass and flat glass (reference) are covered with 250-nm thick Ag layer as back reflector and conductive surface by thermal evaporation. Then substrate-type n-i-p μc-Si:H solar cells are deposited on these substrates, leading to the structure: textured glass/Ag/n-SiOx:H/i-μc-Si:H/p-SiOx:H/In2O3:Sn (ITO)/metal grid.

In order to find the conversion efficiency (Eff.), the open-circuit voltage ($V_{oc}$) and fill factor (FF) of the solar cells are determined from J-V measurements under 100mW/cm² illumination (AM1.5G, Pasan Flash Simulator). Typical $V_{oc}$ values found are from 0.5-0.6 V. Typical fill factors found are from 70-80. The $J_{sc}$ is calculated by convoluting the obtained AM1.5G spectrum and the external quantum efficiency spectrum in a wavelength range of interest of the photo-active layer; typical values found are 20-30 mA/cm².

Fig. 2 and 4 relate to sacrificial zinc oxide layers of ZnO:Al and to intrinsic ZnO respectively, and show the influence of sputtering conditions and the composition of the etching solution on the RMS of the resulting textured glass. Fig. 2 shows that a RMS roughness can be varied with the present method. Typical ranges are a roughness of 10-500 nm, such as 20-100 nm. Likewise Fig. 4 shows that the RMS can be varied as a function of the ratio HNO₃/HF in a similar range.

Corresponding AFM images are shown in Fig. 3 and 5 respectively.

The aforementioned texturing procedure allows producing a wide variety of morphologies. In this respect a relation between the solar cell performance and substrate morphology
(as characterized by the Rs value) was studied. The results are shown in Figure 6. Inventors find that the FF of solar cells deposited on textured glass does not seem to be affected by Rs in the investigated range for solar cells less than 3 μm thick. On the other hand, the $V_{oc}$ decreases with the increasing solar cells thickness. Inventors also observe that solar cells deposited on textured glass with higher Rs value have higher $J_{sc}$ but lower $V_{oc}$. Inventors found that there will be less difference in the density of defective regions for thick cells than that for thin cells with increasing the substrate Rs. That is, the variation of $V_{oc}$ as a function of Rs is less for 2-μm and 3-μm thick cell than for 1.5-μm thick cell series.

Maximum solar cell efficiency is considered a compromise between electrical and optical performance, because an increase of $V_{oc}$ and FF tends to be accompanied by a decrease of $J_{sc}$. This relation between solar cell electrical and optical performance is shown in Figure 6. Inventors found the best combination between these solar cell parameters for thicker solar cells deposited on a substrate with large oRMS and high Rs value. In an example the efficiency is from 9-12%.

The RMS of textured glass decreases as the ratio $[\text{HNO}_3]/[\text{HF}]$ increases i.e. increasing the amount of HF relative to HNO$_3$ results in a less uniformly textured surface. Increasing the zinc oxide film thickness increases the RMS of the glass surface after etching.

Decreasing the heater temperature during zinc oxide sputtering causes the RMS after etching to increase.

Glass with a higher roughness and lateral feature size is obtained when using intrinsic ZnO deposited and etched at the same conditions as ZnO:Al.

By choosing an appropriate combination of dopant, extent of doping, sputtering temperature, deposition thickness and etching solution composition, a predictable morphology of texturing can be arrived at that is suitable for a particular application. Therewith a simple and versatile process is provided.

Although the invention has been discussed in the foregoing with reference to an exemplary embodiment of the method and textured glass surface of the invention, the invention is not
restricted to this particular embodiment which can be varied in many ways without departing from the gist of the invention. The discussed exemplary embodiment shall therefore not be used to construe the appended claims strictly in accordance therewith. On the contrary the embodiment is merely intended to explain the wording of the appended claims without intent to limit the claims to this exemplary embodiment. The scope of protection of the invention shall therefore be construed in accordance with the appended claims only, wherein a possible ambiguity in the wording of the claims shall be resolved using this exemplary embodiment.
CLAIMS

1. A method of texturing a glass surface, said method comprising the steps of:
   (a) providing glass having a glass surface;
   (b) depositing a heterogeneous sacrificial zinc oxide layer on at least a portion of the glass surface;
   (c) contacting the sacrificial zinc oxide layer with an etchant for etching zinc oxide, with different etching rates, and glass,
   (d) removing the sacrificial zinc oxide layer and at least a portion of the glass thereunder.

2. A method according to claim 1, wherein the sacrificial zinc oxide layer further comprises a dopant selected from a group consisting F, B, Al, Ga, In, and Sn and combinations thereof, such as wherein the dopant is at an amount in the range of 0.1 to 10 % w/w dopant/zinc oxide, preferably 0.2 to 5 % w/w, most preferably 0.5 to 3 % w/w.

3. A method according to claim 1, wherein the sacrificial zinc oxide layer is deposited by sputtering at a temperature in the range of 50 to 250°C.

4. A method according to one or more of the preceding claims wherein the zinc oxide layer of claim 1 step (b) has a thickness in the range of 50 nm to 1000 nm, preferably 100 nm to 900 nm, most preferably 150 nm to 600 nm.

5. A method according to one or more of the preceding claims wherein the etchant is an etching solution comprising a first etching component for etching zinc oxide and a second etching component for etching glass.

6. A method according to claim 5, wherein the first etching component is nitric acid and/or wherein the second etching component is hydrofluoric acid.

7. A method according to claim 6, wherein the ratio of concentrations of nitric acid to hydrofluoric acid is in the range of 1:1 to 20:1, preferably 2:1 to 15:1, most preferably 4:1 to 11:1, such as 4:1 to 8:1.

8. A textured glass surface prepared according to the method of one or more of claims 1-7.
9. A photovoltaic device comprising a textured glass surface prepared according to the method of one or more of claims 1-7, such as a thin film silicon based solar cell.

10. Use of a glass surface textured according to the method of one or more of claims 1-7 for one or more of scattering light, improving efficiency of a photovoltaic cell, modifying the out-coupling of light from a (organic) light-emitting diode, and as a master for making stamps for flexible opto-electronic devices.

11. A method for tuning a texture of glass according to any of claims 1-7.
Fig. 5

Intrinsic ZnO

300 nm Sputtered at 200 °C

Intrinsic ZnO

600 nm Sputtered at 200 °C

\[
\frac{[\text{HNO}_3]}{[\text{HF}]}
\]

4.7

RMS = 198 nm

RMS = 384 nm

RMS = 100 nm

RMS = 208 nm

RMS = 40 nm

RMS = 69 nm

5 µm

5 µm

5 µm

5 µm
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

INV.  C03C15/00

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**C03C**

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C03C

**Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched**

**Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)**

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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**Further documents are listed in the continuation of Box C.**

**See patent family annex.**

* "A"* document defining the general state of the art which is not considered to be of particular relevance

* "E"* earlier application or patent but published on or after the international filing date

* "L"* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

* "O"* document referring to an oral disclosure, use, exhibition or other means

* "P"* document published prior to the international filing date but later than the priority date claimed

* "T"* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

* "X"* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

* "Y"* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

* "&"* document member of the same patent family

**Date of the actual completion of the international search**

16 March 2015

**Date of mailing of the international search report**

26/03/2015

**Name and mailing address of the ISA/**

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