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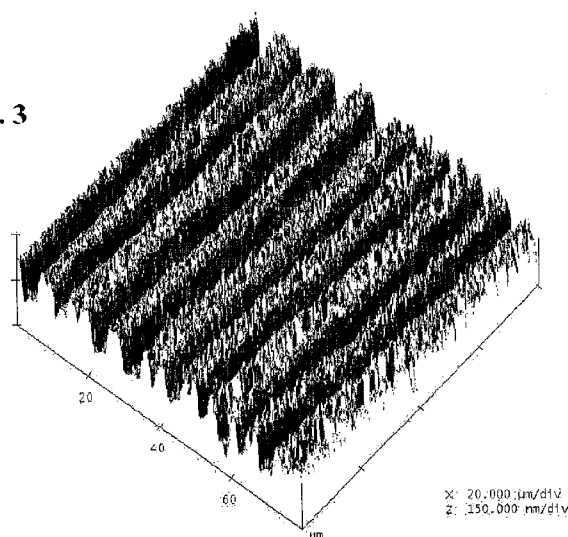
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Fig. 3



(57) Abstract: A method of texturing a surface of a selected material is provided. The method includes: a. applying a base etching component as a layer extending over the surface of the selected material; b. depositing a fluid etching component in a pattern of discrete deposition points over a predetermined area of the surface to be textured, such that the deposited fluid etching component spreads laterally after being deposited. The base etching component and the deposited fluid etching component combine to form an etching composition to etch the surface of the selected material in the areas where the deposited fluid etching component is deposited and spreads. This results in an etched pattern of texture on the surface of the selected material, which is a 2 dimensional spatial modulation of the pattern of discrete deposition points.

METHOD FOR TEXTURING SURFACES

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Technical Field of the Invention

The present invention relates generally to the field of device fabrication and, in
10 particular, to the texturing of materials such as silicon dioxide and silicon for enhanced light capture in thin film solar cell devices.

Background

Many modern photovoltaic (solar) cells are typically thin film in nature
15 whereby a thin film of some photoactive material is deposited onto a substrate which then serves as the front, or sun-side, surface of the solar cell. The most commonly used substrate is various forms of glass, or silicon dioxide, though other substrates may also be used. Because the photoactive layers of thin film solar cells are so thin (typically in the order of 1-2 μm), it is highly advantageous to trap incoming light in the device to
20 maximize its absorption. Traditionally, silicon wafer solar cells have employed textured silicon surfaces to maximize the light trapping in the cell. This texturing is achieved by immersing the silicon wafer in baths of reactive chemicals to etch the silicon preferentially in one crystal direction thus leaving the surface of the cell patterned. The patterned surface reduces reflection of light out of the cell by increasing
25 the chances of light reflected from the surface being re-directed back onto the device surface rather than into the surrounding air.

Currently there is no commonly-used method for texturing thin films of photoactive material such as crystalline silicon. It is not possible to chemically etch thin films of silicon, as is achieved with silicon wafer solar cells, due to the thinness of
30 the silicon layer. Typically, light trapping in these thin films is achieved by modifying or texturing the substrate prior to deposition of the thin film of photoactive layer. Then as the photoactive material is deposited, the resulting thin film follows the textured

profile of the underlying substrate allowing the creation of a solar cell in superstrate configuration.

Current methods for texturing substrates used by thin film solar cells include but are not limited to aluminum induced texturing, sol-gel processing, dip coating in
5 chemical etchants, and sand blasting.

Aluminum induced texturization involves the deposition of a thin aluminum layer, typically in the range of 40 to 230 nm, onto a glass substrate. This is followed by thermal annealing of the aluminum-coated glass at a temperature approximately 610°C for typically 40 minutes. During the annealing process, the aluminium is oxidized by
10 the glass resulting in the formation of aluminum oxide and silicon on the surface of the glass which is subsequently removed using wet etching techniques leaving a textured surface. Although this method is suitable for the large substrates used in thin film photovoltaic processes and is relatively simple it is considered too expensive to implement commercially.

Another process which has been developed for texturing thin film crystalline silicon solar cells involves the coating the surface of the glass with silicon dioxide particles. This additive texturing process is performed by dip coating the glass substrate into a sol-gel bath. Monospherical beads, comprising silicon dioxide particles in the range of 0.1 to 2 μm , are deposited on the substrate surface forming a textured
20 surface. In some cases, the sol-gel solutions also contain crushed quartz in the range of between 0.5-3 μm to improve the texturing result. However, this dip coating process can result in non-uniform texturing across the surface of the glass. In addition to reducing light capture, untextured regions can also create stress concentration points. Dip coating in this manner also involves a subsequent belt bake that can add to the cost
25 of the finished product.

Direct chemical etching of glass by dipping the sheets into baths of acid (such as HF) or otherwise uniformly applying the etchant is an example of a subtractive method of texturing. It is well known to be prohibitively expensive due to the large volumes of etchant material required. Additionally, disposing of the large volumes of
30 used etchant can be environmentally hazardous. Direct etching of glass also tends to result in uniform etching with insufficient surface variation for successful light trapping.

Another technique used for texturing glass is sandblasting, however this method is reported to create cracks in the glass which can adversely affect solar cell
35 performance by shunting.

Summary of the Invention

A method of texturing a surface of a selected material is provided, the method comprising:

- 5 a. applying a base etching component as a layer extending over the surface of the selected material;
- b. depositing a fluid etching component in a pattern of discrete deposition points over a predetermined area of the surface to be textured,

whereby the deposited fluid etching component spreads laterally after being deposited and the base etching component and the deposited fluid etching component
10 combine to form an etching composition to etch the surface of the selected material in the areas where the deposited fluid etching component is deposited and spreads, resulting in an etched pattern of texture on the surface of the selected material, which is a two-dimensional spatial modulation of the pattern of discrete deposition points.

Embodiments of the texturing method may etch 90% or more of the
15 predetermined area of the surface to be textured. The spatial modulation of the pattern of discrete deposition points may have a modulation amplitude of at least 50 nm. The degree of spreading of the fluid etching component may be varied by adjusting the composition, water content and thickness of the layer of base etching component. When the fluid etching component is deposited the spreading at some adjacent
20 deposition points may cause them to overlap.

The fluid etching component may be deposited using a printing method. The printing method may use deposition devices such as a screen printer; a drop-on-demand inkjet printer; a continuous printer; or an electrohydrodynamic printer in which case the pattern of discrete deposition points is a predetermined pattern. Alternatively the
25 printing method may use a deposition device such as an aerosol jet printer in which case the pattern of discrete deposition points is an arbitrary pattern (at least at the scale of the deposition points). The pattern etched on the surface may have a primary direction of orientation which is aligned with a printing direction of the printing method.

30 The thickness of the layer of base etching component may be determined by the viscosity of a solution used to form the layer of base etching component and the base etching component layer may comprise a polymer film. Further the base etching component layer may contain aligned molecular components and the alignment of the molecular components may be achieved using poling.

35 The polymer film may be formed using polymers which act as liquid crystal molecules, such as poly-n-alkyl acrylates, poly-n-alkyl methacrylates, poly-n-

alkylvinyl ethers, poly-n-alkylvinyl esters or poly-n-alkylstyrenes. Alternatively the polymer film may be formed using polymers which contain small molecule additives which act as liquid crystals in which case the additives may comprise one of poly(ethylene glycol) diacrylate, and polyethylene glycol derivatives having charged
5 side chains. The polymer film may also incorporate small molecule liquid crystals into side chains of acidic polymers to impart liquid crystal behaviour on the resulting polymer phase. The Liquid Crystals are preferably able to be poled (or aligned) in specified directions in the polymer phase by an applied electrical field. The polymer films may thus be used to impart a desired directionality on the resulting textured
10 pattern and to further reduce the resolution or pitch of the resulting texture pattern.

The pattern in which the etching component is deposited is typically a digital pattern. The fluid etching component is preferably a liquid, but may also be a gas.

In one embodiment the etching is performed to create a textured surface and the resulting textured surface is used to enhance the capture of light into a device such
15 as a photovoltaic device. The selected material may be any of a variety of materials such as silicon but in the preferred embodiment is glass (silicon dioxide). The device is preferably a photovoltaic device formed in a semiconductor such as silicon that is textured by the method or formed in a semiconductor film layer on the etched surface of a substrate such as glass.

The maximum depth of the etched pattern may be no more than 100 nm and the texture pattern that is formed may have rounded features created by immersing the textured surface in a solution which isotropically etches the substance. In the case where the substance is glass, the isotropic etchant may be a solution comprising HF or mixtures of HF and NH_4F and in a preferred example may be a solution comprising
25 10% 7:1 buffered oxide etchant.

Brief Description of the Drawings

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings in which:

30 Figure 1A is a schematic illustration showing, in cross-section, a glass substrate coated with a surface acidic polymer layer;

Figure 1B is a schematic illustration showing the deposition of two drops of a solution containing an etching component onto the acidic polymer layer, the two drops being dispensed in close proximity to each other;

35 Figure 1C is a schematic illustration showing the formation of overlapping etched regions in the surface of the glass substrate;

Figure 1D is a schematic illustration showing the glass substrate after the etch residue and acidic polymer layer have been removed;

Figure 2 shows the structure of an example acidic polymer, polyacrylic acid;

Figure 3 is an Atomic Force microscope (AFM) profile of a textured region
5 created using the preferred arrangement;

Figure 4 is a section through the AFM profile in Figure 3 with the section being recorded at an angle which is $\sim$ perpendicular to the etched grooves.

Figure 5 is a schematic illustration of a large-area aerosol spray unit which can be used to spray on fluoride-containing solution to achieve higher texturing throughput;
10 and

Figure 6 is a schematic illustration of the large-area aerosol spray unit of Figure 5 with a linear spray unit placed in-line to form a polymer layer on the surface to be textured prior to spraying with the fluoride-containing solution.

15 Detailed Description of embodiments

Typically thin film solar cells are formed on substrates such as glass to provide mechanical support for the otherwise mechanically insubstantial structure of the thin film material. Because the active layers of thin film devices are generally too thin to be directly textured, the substrate is often textured before the thin film device is formed
20 on its surface. Improved methods of applying texturing to surfaces will be described, including surfaces of substrates, such as glass, typically used for enhanced light capture in thin film solar cell devices. These methods use a fluid deposition device to deliver a pattern of a fluid to a substrate surface where it can react to cause etching of regions of the surface and thus form a textured surface on the substrate. In the case of substrates
25 for solar cells the resulting textured surface preferably has a periodic structure where the period of the texture pattern is similar in magnitude to the thickness of the thin film of photoactive material which is subsequently deposited onto the textured substrate. The periodic structure of the textured surface is achieved by fine resolution spatial distribution of the concentration of the molecular species responsible for the etching of
30 the substrate surface.

The fluid deposition device enables the delivery of small amounts of functional fluid to be deposited on the substrate in a pattern. The device can be a drop-on-demand device such as an inkjet printer or a hydrodynamic printer. Alternatively, a continuous stream device such as a continuous inkjet or an aerosol jet printer can be
35 used. For applications employing an inkjet printer, the functional fluid is formulated as a liquid with the deposition device placing specific requirements on the properties of

the deposited liquid (e.g., surface tension and viscosity). Alternatively the functional fluid can be deposited as an aerosol by a device such as an aerosol jet printer. In further variations, the functional fluid may also be delivered as a gas to the substrate, although in these cases it is more difficult to control the delivery of the fluid to precise and discrete locations on the surface of the substrate. Two component etchants may be used in which a first component is applied over the surface as a gel or more viscous fluid and a second component is applied in a pattern to create points of reaction where the second component is applied. Alternatively a pattern of a liquid or gel component may be applied and a gaseous atmosphere of a second etch component used to activate etching in the areas where the pattern has been applied.

Currently fluid deposition devices, such as described above, are limited in their ability to precisely deposit small volumes of fluid and therefore typically cannot achieve etching of features which have dimensions less than $\sim 20 \mu\text{m}$. It has been found that texturing having smaller dimensions can be achieved by deposition of overlapping fluid streams or droplets onto a functional polymer layer. Using such a method texturing patterns which have a periodicity in the order $10 \mu\text{m}$ can be achieved. By overlapping droplets or streams of a functional fluid on a reactive surface, a distinct pattern of varying regional concentration of the molecular species responsible for the etching can result on a surface thus causing the formation of an etched pattern that can have feature dimensions significantly less than the dimensions of the deposited droplets or fluid streams. Furthermore, the sequence in which droplets or streams are deposited on the surface can be used to create specific periodic features in the etched (textured) surface.

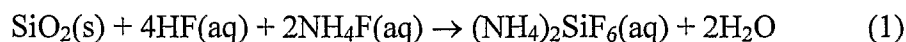
The described method of texturing a substrate is not limited to the fabrication of thin film solar cells. It can be used for other applications where a textured surface is required. Furthermore, although the preferred embodiment describes the texturing of silicon dioxide (i.e. glass) substrates, clearly the method can also be used to texture other dielectric substrates including but not limited to various forms of doped glass, silicon nitride, silicon carbide, transparent conducting oxides, organic resins and other polymers including pattern mask materials. Furthermore by varying the deposition solution from that used in the preferred arrangement, the method can also be applied to texture semiconducting materials such as silicon, germanium, gallium-arsenide, indium phosphide, or alloys such as silicon-germanium or aluminium-gallium-arsenide, indium-selenide, gallium-selenide, cadmium-telluride or copper indium gallium selenide (CIGS)) and indeed metals such as aluminium, copper, silver, gold, tin and lead or alloys.

Note however that for light trapping applications, significant flat areas are undesirable and so least 90% of the surface should be etched to some extent. If the etchant covers the entire area to be textured then there should be a significant variation of the etchant local concentration deposited over the area to achieve variable etching depths at different locations of the area to be textured.

A preferred arrangement will be described in which a glass (silicon dioxide) substrate is textured for light trapping purposes in thin film solar cells employing a photoactive layer of crystalline silicon (on glass). These solar cells typically involve the deposition of a layer of silicon which is 1.2 to 1.5 μm thick on the glass substrate. Preferably, the glass used for the substrate is borosilicate glass and is ~ 3.3 mm thick. It is textured on a single side using a texturing method described in this disclosure, and then silicon is deposited on the textured surface of the glass substrate to a thickness of 1.2 to 1.5 μm , and more ideally 1.4 μm . Preferably the silicon is deposited using Plasma Enhanced Chemical Vapour Deposition (PECVD) though other deposition techniques such as sputtering or evaporation techniques can also be used. The deposited amorphous silicon is then crystallised in a furnace where sheets (of the glass substrate carrying the silicon) are heated to a temperature of about 600°C. Further annealing is then performed by rapid thermal annealing using a belt or roller furnace to minimize the time spent at higher temperatures. If necessary each sheet may then be cut into discrete cells of a desired size by laser scribing. The rear surface is then preferably coated with a white insulating resin which acts as an optical reflector and isolates the metal contacts from rear surfaces except where contact is required. Metal contacts are then formed to both polarities of the thin film solar cell by depositing a metal through the openings in the resin layer. Finally, cells are encapsulated into modules and laminated.

Known methods for wet etching of silicon dioxide involve exposing the silicon dioxide surface to a solution containing hydrofluoric acid (HF) with the etch rate depending on the etching solution composition, type of oxide and temperature. For example, (concentrated) 49% HF solution will etch a thermal silicon dioxide layer at a rate of 2300 nm/min at room temperature. Etching of silicon dioxide can also be achieved using buffered oxide etching solutions. These solutions are mixtures of ammonium fluoride and hydrogen fluoride with the ammonium ions maintaining the etch solution at a constant pH thus resulting in a constant etch rate as etching proceeds. Different etch rates have been reported for different ratios of ammonium fluoride and hydrogen fluoride. For example, a 5:1 buffered oxide etch (which is a mixture of 5

parts of 40% NH₄F and 1 part 49% HF) has an etch rate of ~100 nm/min. The overall silicon dioxide etching reaction occurring in a buffered oxide etch is:



5

Many variations of silicon dioxide etching recipes exist in the prior art.

The method described herein for the patterned etching of silicon dioxide used in the preferred arrangement relies on providing the fluoride ion and the acid separately and bringing these two essential precursor components together at the desired etching
10 location. Preferably, the acid component is provided as acidic protons in a water-soluble acidic polymer film which is formed as a surface layer over the surface of the glass substrate to be etched. In alternative arrangements, the surface layer can comprise materials other than polymers (e.g., inorganic materials deposited by methods such as evaporation, sputtering or chemical or plasma vapour deposition.

15

The fluoride ion is preferably formulated in an aqueous solution which is then deposited according to a pattern by the fluid deposition device. At locations where the deposition fluid contacts the polymer film, the polymer is locally dissolved and the fluoride ions abstract acidic protons from the polymer to form HF. The formed HF, dissolved in the fluid at the deposition location, can then etch the exposed silicon oxide.
20 This means that corrosive etching solutions, which contain HF, are not directly handled. Although, fluoride-containing solutions are classified as toxic they are more safely handled than HF solutions. In addition, the method of the preferred arrangement uses only small quantities of fluoride ion and the fluoride ion is formulated in solutions of reasonably dilute concentration. Furthermore, the deposition method used by the
25 preferred arrangement for the fluoride-containing solution minimises operator contact with the solution. Once loaded in the fluid reservoir of, for example, an inkjet printer, the solution does not require further handling.

Direct deposition of the etching fluids containing HF is difficult to achieve because few printheads, or jetting devices more generally, can tolerate the corrosive
30 nature of the fluid. The HF will attack and corrode most ceramic, stainless steel, and silicon-based printheads. Silicon-based printheads cannot be used because they typically contain silicon dioxide components which are etched by the hydrogen fluoride. In addition to causing long-term corrosion of the printhead, the etch products quickly cause intermittent nozzle blockages which make it difficult to reliably jet the
35 solution. Furthermore, few operators would consider it safe to deposit HF-containing solutions via inkjet, or other fluid deposition methods, because of the risk of operator

contact in the event of fluid leaks. This is not a problem for the proposed methods, because the fluoride-containing solution is not corrosive. This also means the solution can be jetted using silicon and ceramic printheads.

A preferred arrangement for texturing of a glass substrate will now be described with reference to **Figures 1A to 1D**. A water-soluble acidic polymer film **110** is spin-coated over the surface of a ~ 3.3 mm glass substrate **105** as shown in **Figure 1A**. Preferably, the film is spin-coated for 30 s from a solution of 25% (w/v) polyacrylic acid (PAA) in water at a spin speed of 7000 rpm. The molecular weight of the PAA is preferably in the 20,000 to 200,000 g mol⁻¹ range, and more preferably $\sim 90,000$ g mol⁻¹. Polyacrylic acid is a homopolymer of acrylic acid. The acrylic acid monomer unit is a source of acidic protons as shown by the chemical structure in **Figure 2**. The pKa of PAA is ~ 4.3 .

The spin-coated polymer film is air dried for ~ 3 hours resulting in a film ~ 2.5 μm thick. The solid content of the solution used to form the acidic polymer film can be varied from 5% to 35% without significantly affecting the polymer film quality, however preferably the solid content is between 20% and 30%. Use of a lower solid content and/or faster spinning speeds results in a thinner film. The glass substrate **105** with the polymer film **110** is preferably stored under nitrogen until required in order to minimise uneven humidification of the polymer film.

In alternative arrangements, other water-soluble polymers or resins containing acidic groups (e.g., acidic polythiophene or polyaniline derivatives, polystyrene sulfonate, polyester or phenolic resins) can also be used. It is also possible to use polymer mixtures or blends to form the acidic film. For example, PAA can be blended with other water soluble polymers such as polyvinyl alcohol (PVA) in PAA:PVA ratios ranging from 1:1 to 1:4 depending on the extent of etching required. Polyacrylic acid can also be blended with less hydrophilic polymers, such as polymethacrylic acid to result in a dried film with a lower critical surface tension. This variation can be advantageous when smaller etched features are required because the deposited droplets spread less on the more hydrophobic surface. Copolymers of the acidic polymer (e.g., PAA) can also be used to form the polymer film. The use of copolymers or polymer blends for forming the thin film is a way in which the acidity of the formed film can be controlled. Furthermore, polymer films can contain additives which can either directly provide further acidic groups or indirectly enhance the acidity of the film. These additives can be either dissolved or dispersed (e.g., nanoparticles) in the solution used to form the acidic polymer layer. These additives can also be used to modify the surface properties of the polymer film.

The polymer film may also contain surfactants. Preferably fluorsurfactants (e.g., Novec 4200 from 3M) are used and in concentrations $< 1.0\%$. These surfactants can improve the evenness of the resulting etching by enabling the deposited solution to more evenly wet the surface to be etched. The added surfactant can also actively
5 reduce the critical surface tension of the polymer film thus enabling smaller etched features to be obtained. Other fluoropolymer additives, such as FC-4432 (also from 3M) can also be added to the film, specifically to reduce the critical surface tension of the final polymer surface. However, the longer chain fluoropolymers are less effective wetting agents than the smaller surfactant preparations like Novec 4200. Other
10 surfactants or surface tension modifying agents, which are compatible with fluoride ion chemistry, can also be used.

In further variations of the preferred arrangement, the polymer film can be formed using polymers which can either act as liquid crystal molecules (e.g., poly-n-alkyl acrylates and methacrylates, poly-n-alkylvinyl ethers and esters and poly-n-
15 alkylstyrenes) or contain small molecule additives which can act as liquid crystals [e.g., poly(ethylene glycol) diacrylate, and other polyethylene glycol derivatives having charged side chains). Alternatively, small molecule liquid crystals can be incorporated into the side chains of acidic polymers to impart liquid crystal behaviour on the resulting polymer phase. Liquid crystals can be poled (or aligned) in specified
20 directions in the polymer phase by an applied electrical field. Films so formed can be used to impart a desired directionality on the resulting textured pattern and to further reduce the resolution or pitch of the resulting texture pattern.

Patterned etching of the surface of the glass substrate **105** is achieved by deposition of a fluid, containing a source of fluoride, onto the surface according to a
25 predetermined pattern. In the preferred arrangement, the fluid is deposited by a drop-on-demand inkjet printer as a solution containing fluoride ions. The inkjet device **120**, depicted in **Figure 1B**, contains one or more printheads **125** which can eject droplets of a solution **130** from an array of nozzles. Firing of individual nozzles can be under thermal or piezoelectric control. The solution being jetted can be stored in a cartridge
30 on or close to the printhead or in a reservoir located more distant to the printhead. In the preferred arrangement, the printhead of the inkjet device **120** scans across the polymer surface depositing solution as required in the scan. The glass substrate **105** is located on a platen which moves relative to the printhead in an axis perpendicular to the scan axis. However, in alternative arrangements the platen can be maintained
35 stationary as the printhead scans in both directions, or the printhead can be maintained stationary as the substrate (i.e., the glass substrate **105**) is moved in both directions.

Preferably, the platen and thus the glass substrate **105** can be heated while printing is occurring.

In the preferred arrangement, a piezo-electrically controlled silicon printhead, manufactured by FUJIFILM™ Dimatix™, is used to deposit the fluoride-containing solution. The printhead is incorporated in a cartridge and has 16 nozzles linearly spaced at 254 microns with a drop size of 1 picoliter. Printheads able to deposit other droplet volumes can also be used, however smaller droplet volumes are preferred as they result in less etching and finer resolution texture patterns. The firing of individual nozzles is under software control thus enabling programmed deposition of droplets according to a predetermined pattern. The pattern can be provided using standard image formats such as bitmap files.

Depending on how closely droplets of the deposition pattern are positioned, multiple layers of the etching pattern may need to be deposited. It should be appreciated that the requirement to print multiple layers of the fluoride-containing solution arises from the etching stoichiometry. Six fluoride ions are required for every etched silicon atom in the silicon dioxide crystal layer. The software of the inkjet device used by the preferred arrangement enables multiple layers of a selected pattern to be printed at a selected location. The layers are printed one after another with only very short delays between the successive layers. Optionally, a delay can be inserted between the printing of successive layers. In a further alternative arrangement, rather than printing multiple layers of a pattern, multiple droplets of the deposition solution can be deposited at each location before the printhead and/or platen are moved to the next deposition location.

The inkjet device, used in the preferred arrangement, jets solutions optimally when the viscosity is between 10 and 14 cP and the surface tension is between 28 and 32 mN/m. However, it is possible to jet solutions having viscosities as low as 2 cP using the device. This is achieved by appropriately tuning the waveform applied to the piezoelectric nozzles. Variations in surface tension are harder, though also possible, to accommodate. If a solution's surface tension is too high (e.g., ~ 70 mN/m as for deionised water), it is difficult to prime the printhead (i.e., no solution can be initially ejected from the nozzles). On the other hand, if the solution's surface tension is too low then the surface which contains the nozzle orifices (nozzle plate) typically becomes flooded with the jetting solution thus causing erratic placement of droplets on the polymer surface. The nozzle plate of the inkjet device used in the preferred arrangement has a polymer non-wetting surface, however the jetting of low-surface-

tension fluids can still result in significant wetted areas on that surface and thus erratic firing.

Preferably the fluoride ion in the deposition solution is provided as an aqueous solution of ammonium fluoride, with the ammonium fluoride concentration being in the range of 10% to 15% (w/v), and more preferably ~11% (w/v). Other sources of fluoride ion can also be used (e.g., sodium fluoride, lithium fluoride, tetra alkyl ammonium fluoride compounds), however the solubility of the final etch product needs to be considered carefully. For example, the solubility of sodium fluorosilicate (~ 40 mg L⁻¹ at 20 °C) is much less than that of ammonium fluorosilicate. Thus it is preferable to jet more dilute fluoride solutions to ensure that the etching product does not precipitate on the surface to be etched and preventing further etching of the surface. Deposition of more dilute fluoride solution may necessitate larger volumes of the deposition solution to be jetted (i.e., more layers of the pattern will be printed).

In alternative arrangements, where the depth of etching is required to be very shallow, then the formation of an etch-blocking precipitate can be used to control the extent of etching. So, for example, sodium fluoride could be jetted using a high platen temperature to quickly evaporate water from the deposition solution. After the formation of relatively small amounts of fluorosilicate, a sodium fluorsilicate precipitate will form on the surface and prevent further etching. Lower fluoride concentrations can also be used to form shallow texture patterns. Shallower etched features can be advantageous as they can result in less stress in the crystalline silicon film formed on the textured surface.

In the preferred arrangement, 20% (v/v) polyethylene glycol, having a molecular weight of 400 g mol⁻¹, (PEG 400) is also added to the jetting solution to increase the viscosity to ~4 cP and thus improve the jetting performance. In alternate arrangements, the PEG 400 can be omitted from the deposition solution, or included at a lower concentration in the solution. However, lower pulse voltages, slower pulse rise times and lower jetting frequencies are required in order to reliably jet the lower-viscosity solution. In other arrangements, the PEG 400 can be replaced by other compounds which increase the solution's viscosity (e.g., glycerol, basic water-soluble polymeric compounds such as polyvinyl pyrrolidone, or other glycols).

The pH of the deposition solution may be increased to between 8-10 and more preferably 8 by addition of ammonium hydroxide. A high pH is preferred in order to avoid high concentrations of the reactive etching species, HF and HF₂⁻, in the deposition solution. In ammonium fluoride solutions, at pH values greater than 7, the concentration of both these species is effectively zero resulting in no etching of silicon

dioxide, thus protecting any silicon dioxide components in the printheads. If the solution is too alkaline (e.g., pH > 11), some etching of the silicon printhead may occur.

The surface tension of the resulting deposition solution of the preferred arrangement is ~ 46 mN/m at 28 °C. Although this exceeds the optimal surface tension range for the FUJIFILM™ Dimatix™ printheads used, the jetting waveform can be adjusted to accommodate the increased surface tension. The increased surface tension advantageously results in less spreading of the solution when it contacts a PAA surface, which has a critical surface tension of ~ 44 mN/m. Reductions in the surface tension of the deposition solution result in more spreading of the deposited droplets and thus larger etched features.

Finally, the temperature of the deposition solution is preferably maintained at around 28 °C. The use of lower temperatures can also be used, however typically the surface tension of a solution will increase at lower temperatures thus making it more difficult to jet the solution.

The jetting of a solution having a moderately high surface tension onto a polymer surface containing a surfactant, such as Novec 4200 (from 3M) is a useful strategy to achieve small, cleanly etched features. This strategy is possible because of the ability to tune the firing waveform used by the FUJIFILM™ Dimatix™ printheads.

In alternative arrangements, fluorinated surfactants, such as Novec 4200 (from 3M), can be added to the deposition solution. These surfactants can effectively reduce the surface tension to values which are in the optimal range for the FUJIFILM™ Dimatix™ printheads (see Figure 3). For the Novec 4200, a concentration of between 0.3% and 0.5% (v/v) will reduce the surface tension of the deposition solution to a surface tension range of 28-32 mN/m and thus enable it to be reliably jetted. Other surfactants, which are compatible with solutions containing fluoride ions, can also be used.

Furthermore, other additives that can vary the surface tension may also be used. For example, addition of glycols such as propylene glycol can also readily reduce the surface tension to the optimal range for the FUJIFILM™ Dimatix™ printheads. In other arrangements, which use different printheads, the surface tension and viscosity may need to be varied to meet the operating requirements of the printheads.

In the preferred arrangement, the platen and thus the glass substrate **105** is heated during the jetting of the deposition solution. Heating of the platen, results in some of the solvent of the deposition solution being evaporated during jetting causing

smaller wetted areas and therefore smaller etched openings. Preferably, the platen temperature is maintained at 55 °C for the etching of texture patterns. Excessive heating of the platen can result in too much solvent evaporation and therefore a reduced aqueous environment at the surface to be etched. This can result in less etching and possibly also the precipitation of the etch product, ammonium fluorosilicate which can cause uneven etching across the region to be textured. As mentioned previously, precipitation of etch product can be used as a way of preventing excessive etching and forming shallow etch patterns.

Returning now to **Figure 1C**, the deposited droplets **130** dissolve the polymer where they contact the surface layer **110** to form a region **150** of dissolved polymer. The fluoride ions in the deposition solution react with the dissolved polymer to form HF which can etch the underlying surface of the glass substrate **105** to form etched regions **160** and **165** in the glass substrate **105**. The shape and depth of these etched regions **160** and **165** depend on the fluoride ion concentration in the deposition solution, the properties and thickness of the polymer layer **110**, the type of glass used for the substrate **105**, the platen temperature, the volume and relative placement of adjacent droplets **130** and the speed of printing. All the above factors can be varied to achieve different texturing patterns over an area of substrate **105**.

Preferably, subsequent deposited droplets **130** in a raster scan of the deposition pattern overlap to result in a varying concentration of formed HF across the surface. More particularly, when the drops are deposited using a raster-based fluid deposition device **120**, such as the FUJIFILMTM DimatixTM printer used in the preferred arrangement, the droplets tend to merge after deposition and form highly textured narrow grooves in the surface of the glass substrate **105** as shown in **Figure 3**. An Atomic Force Microscope (AFM) profile of the pattern shown in **Figure 3** shows a periodic etching pattern results if the surface is scanned perpendicular to the formed grooves (see **Figure 4**). The distance between these regularly formed grooves can be varied by altering the drop spacing of the deposition pattern. The texture pattern shown in **Figure 3** was created using a drop spacing of 10 µm in both axes. In other words, the deposition pattern used to create the texture shown in **Figure 3** was a pixel grid with a pixel resolution of 100 pixels per mm. Smaller drop spacings result in even finer patterns however the etched depth of the texture features is typically greater because a greater amount of HF is created. Alternatively, the extent of etching can be controlled by increasing the platen temperature and/or using chemical means (e.g., reducing the fluoride ion concentration or using sodium fluoride as the fluoride source).

When texturing is used for light trapping purposes it is critical that the occurrence of flat regions are minimised. Figure 3 and Figure 4 demonstrate that there are minimal flat regions in the texture patterns formed using this technique. Even for these patterns where the raster deposition sequence has been exploited to achieve
5 shallow groove structures, there is still some texture in the surface at the base of the grooves. Ideally a texture with steeper slopes will increase the light trapping capabilities of this texture as compared to a shallow texture.

When the fluid deposition process is complete, the glass substrate **105** is removed from the platen of the fluid deposition device **120** and immersed in flowing
10 deionised water for 5-10 minutes. This final rinse step removes both etching product trapped in the etched area **150** and the water-soluble polymer film to form the final etched substrate **100** with openings **160** as shown in **Figure 1D**. Unlike existing wet etching processes, the quantity of fluorinated waste during this rinse step is very small, being only that fluoride which has been deposited by the inkjet printer. This means that
15 the waste is very dilute and not very hazardous.

For some applications, it may be desirable to form a texture pattern having more rounded features. For example, sharp edges may result in higher stresses in films deposited on top of the textured surface. Rounding of sharp edges can be simply achieved by immersing the textured surface in a solution which isotropically etches
20 glass (e.g., solutions comprising HF or mixtures of HF and NH_4F). Preferably a solution comprising 10% 7:1 buffered oxide etch is used as it etches the glass very slowly and the extent of rounding (smoothing) can be readily controlled by the duration of the immersion time.

In an alternative arrangement, higher texturing throughput can be achieved by
25 using a large-area aerosol spray unit to deposit a fine mist, or aerosol, of the fluoride-containing solution onto the polymer layer **110**. Preferably the aerosol spray unit is arranged as an essentially linear unit, approximately the same width as the sheets of glass sheets to be textured, which extends across the glass sheets as shown in Figure 5. The glass substrate **105** which is coated with a polymer layer **110** is passed under an
30 overhead linear aerosol unit **520** which is suspended on a structure **510**. The glass substrate **105** with the polymer layer **110** is positioned on a belt **505** which moves it relative to the fixed linear aerosol unit **520**. Preferably the belt **505** is heated to a temperature in the range of 30 to 60 °C and more preferably in the range of 40-50 °C.

In this way, the linear aerosol unit **520** can deliver a fine mist of aerosolised
35 fluoride solution to the polymer surface **110** of the glass substrate **105** as it moves under the fixed structure **510** containing the linear aerosol unit **520**. The linear aerosol

unit 520 preferably comprises a linear array of aerosol nozzles, however alternative arrangements in which two dimensional arrays of aerosol nozzles can also be used. The fixed overhead structure 510 is connected to units on the side of the belt 500 which house a reservoir of the liquid to be aerosolised. In the arrangement depicted in Figure 5, the aerosol housing unit, comprising components 500, 510 and 520, are structurally connected to the unit that comprises the belt drive 505 for moving the glass substrates 105. Alternatively, the aerosol housing unit can be structurally separate from the unit comprising the belt drive 505.

The reaction that occurs when the small particles from the aerosol mist contact the polymer of the polymer layer 110 is essentially as described for the preferred arrangement. The reaction rate and therefore extent of etching depends on the amount of water remaining in the aerosolised particles. Drying out the particles too much results in a very slow etching rate. Preferably the aerosol mist is generated using an ultrasonic atomiser. Other atomisers or nebulisers (e.g., pneumatic atomisers, inkjet atomisers) can also be used provided that they do not excessively reduce the water content of the particles. In order to minimise loss of aerosol particles to the ambient the output nozzles of the linear aerosol unit are placed a distance of 1 to 5 cm from the surface, and more preferably about 2 cm from the surface.

In the arrangement depicted in Figure 5, properties of the texture pattern can be varied by varying the belt speed and temperature, the concentration of fluoride ion in the solution which is aerosolised, the humidity of the aerosol (which effectively controls the individual particles size), and the thickness and properties of the polymer layer. After the glass substrate 105 passes under the linear aerosol unit 520 it continues to be transported along the belt 505 until the reaction is complete then it moves into a rinse unit where deionised water is sprayed from above to wash away the polymer layer 110 and the etch residue. The length of time required for the reaction to complete is typically very short (preferably 30 – 60 seconds), however it depends of the factors listed above which control the etching rate.

The above-described glass texturing process can process glass substrates 105 continuously by simply maintaining a minimum fluid level in the liquid reservoir used to form the aerosol. Because the concentration of fluoride in the waste from the rinse station can be controlled to be very low (< 5 ppm) in most jurisdictions there is no need to treat the effluent from the process. Therefore, the rinse unit can operate continuously with a waste effluent being continually drained to accommodate the new waste water.

In a further variation of the method depicted in Figure 5, the polymer layer 110 can also be formed by a further linear spray unit placed in-line with the linear aerosol unit 520. This variation is depicted in by the schematic cross-section in Figure 6. The additional linear spray unit 610 is positioned over the belt 505 upstream from the linear aerosol unit 520 which dispenses the aerosolised fluoride solution. Each glass substrate 105 first passes under the first linear spray unit 610 where a spray of polymer solution is dispensed onto the surface of the glass substrate 105 resulting in the polymer layer 110 forming on the surface of the glass substrate 105. The linear spray unit 610 preferably deposits a spray of polymer solution, which is substantially the same as the polymer solution which is used to spin-coat the surface of the glass substrate 105 in the preferred arrangement. The solution can be more or less dilute than the solution used to spin-coat in the preferred arrangement depending on the belt speed. Unlike the delivery of the fluoride ions to the surface of the polymer 110, it is not necessary to aerosolise the polymer solution so a simply spray unit that delivers a uniform amount of polymer solution across the glass substrate 105 can be used.

Preferably, a heating unit 630 is then positioned over the belt 505 to effect drying of the polymer layer in a short time. Alternatively, the polymer layer 110 can be dried by passing a gas or air flow over the surface of the deposited polymer. Preferably, the dried polymer layer 110 has a final dried thickness of 2-3 μm , and more preferably $\sim 2.5 \mu\text{m}$. However, thinner polymer layers may be employed to enable very high-throughput processing.

The glass substrate 105 with the drying polymer layer 110 is then moved by the belt 505 to the position of the linear aerosol unit 520 where an aerosol containing fluoride ions 550 is deposited in a linear manner over the surface of the moving substrate 100 as described previously.

It will also be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Claims:

1. A method of texturing a surface of a selected material, the method comprising:
 - a. applying a base etching component as a layer extending over the surface of the selected material;
 - b. depositing a fluid etching component in a pattern of discrete deposition points over a predetermined area of the surface to be textured,whereby the deposited fluid etching component spreads laterally after being deposited and the base etching component and the deposited fluid etching component combine to form an etching composition to etch the surface of the selected material in the areas where the deposited fluid etching component is deposited and spreads, resulting in an etched pattern of texture on the surface of the selected material, which is a 2 dimensional spatial modulation of the pattern of discrete deposition points.
2. The method of claim 1 wherein at least 90% of the predetermined area of the surface to be textured is etched.
3. The method of claim 1 or 2 wherein the spatial modulation of the pattern of discrete deposition points has a modulation amplitude of at least 50 nm.
4. The method of claim 1, 2 or 3 wherein the composition, water content and thickness of the layer of base etching component are selected to determine the degree of spreading that the fluid etching component will exhibit when it is deposited on the base etching component.
5. The method of claim 4 wherein the fluid etching component is deposited using a printing method.
6. A method of claim 5 wherein the pattern of discrete deposition points is predetermined.
7. The method of in claim 6 wherein the fluid etching component is deposited using a deposition device selected as one of a screen printer; a drop-on-demand inkjet printer; a continuous printer; or an electrohydrodynamic printer.
8. The method of claim 5 wherein the fluid etching component is an aerosol and the pattern of discrete deposition points is an arbitrary pattern.
9. The method of claim 8 wherein the fluid etching component is deposited using an aerosol printer or aerosol spraying device.
10. The method of claim 7 or 9, wherein the pattern etched on the surface has a primary direction of orientation which is aligned with a printing direction of the printing method.

11. The method as claimed in any one of claims 4 to 10 wherein the thickness of the layer of base etching component is determined by the viscosity of a solution used to form the layer of base etching component.
12. The method as claimed in any one of claims 1 to 11 wherein the base etching
5 component layer comprises a polymer film.
13. The method of claim 12 wherein the base etching component layer contains aligned molecular components.
14. The method of claim 13 wherein alignment of the molecular components is achieved using poling.
- 10 15. The method as claimed in any one of claims 12 to 14 wherein the polymer film is formed using polymers which act as liquid crystal molecules.
16. The method of claim 15 wherein the polymer film comprises one of poly-n-alkyl acrylates, poly-n-alkyl methacrylates, poly-n-alkylvinyl ethers, poly-n-alkylvinyl esters and poly-n-alkylstyrenes.
- 15 17. The method of claim 14 wherein the polymer film is formed using polymers which contain small molecule additives which act as liquid crystals.
18. The method of claim 17 wherein the additives comprise one of poly(ethylene glycol) diacrylate, and polyethylene glycol derivatives having charged side chains.
19. The method of claim 14 wherein the polymer film incorporates small molecule
20 liquid crystals into side chains of acidic polymers to impart liquid crystal behaviour on the resulting polymer phase.
20. The method as claimed in any one of claims 15 to 19 wherein the Liquid Crystals are able to be poled (or aligned) in specified directions in the polymer phase by an applied electrical field.
- 25 21. The method as claimed in any one of claims 14 to 20 wherein the polymer films are used to impart a desired directionality on the resulting textured pattern and to further reduce the resolution or pitch of the resulting texture pattern.
22. The method as claimed in any one of claims 1 to 21 wherein after the fluid etching component is deposited the spreading at some adjacent deposition points causes
30 them to overlap.
23. The method as claimed in any one of claims 1 to 22 wherein the pattern in which the etching component is deposited is a digital pattern.
24. The method as claimed in any one of claims 1 to 23 wherein the fluid etching component is a liquid.
- 35 25. The method as claimed in any one of claims 1 to 23 wherein the fluid etching component is a gas.

26. The method as claimed in any one of claims 1 to 25 wherein the etching is performed to create a textured surface and the resulting textured surface is used to enhance the capture of light into a device.

27. The method as claimed in any one of claims 1 to 26 wherein the selected
5 material is silicon.

28. The method of claim 27 wherein the device is a photovoltaic device formed in the silicon.

29. The method as claimed in any one of claims 1 to 26 wherein the selected material is a glass.

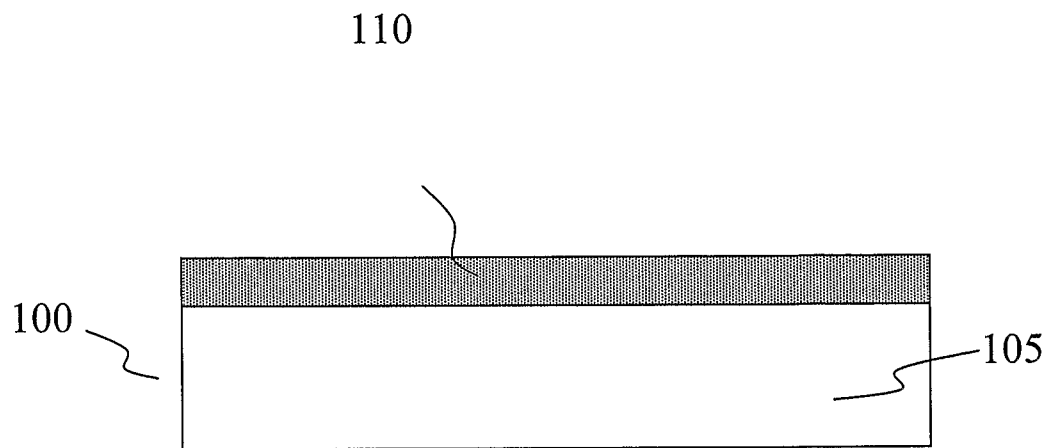
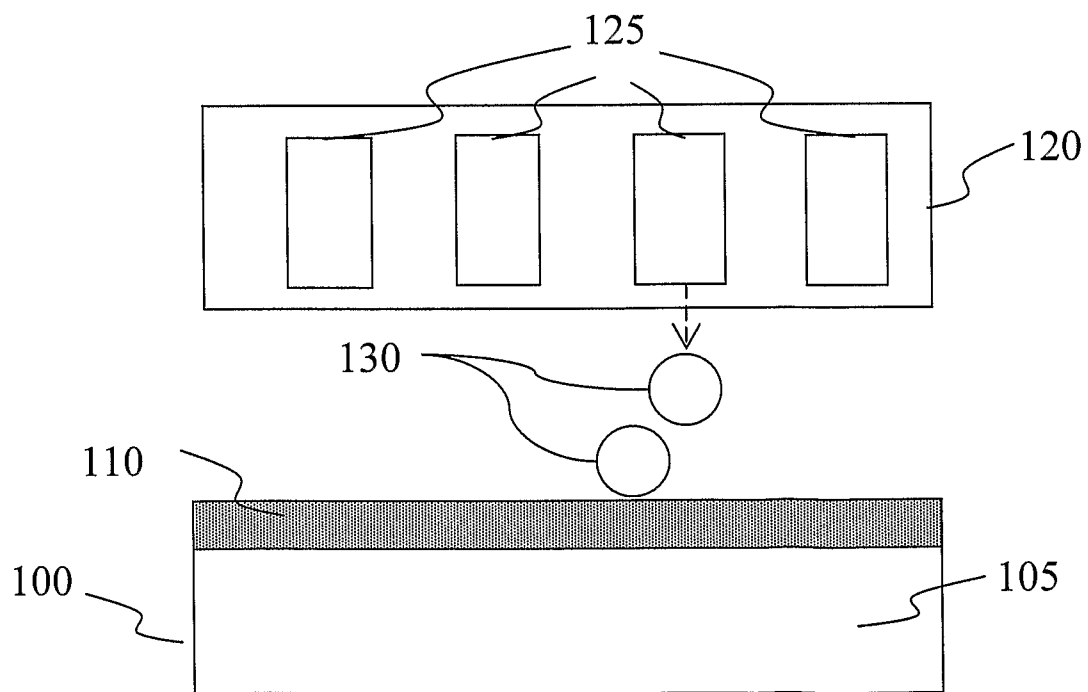
10 30. The method of claim 29 wherein the device is a photovoltaic device formed in a semiconductor film layer on the etched surface.

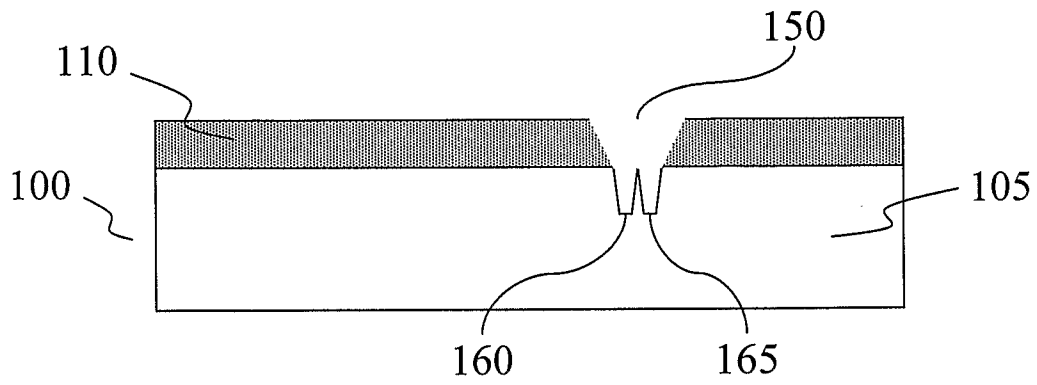
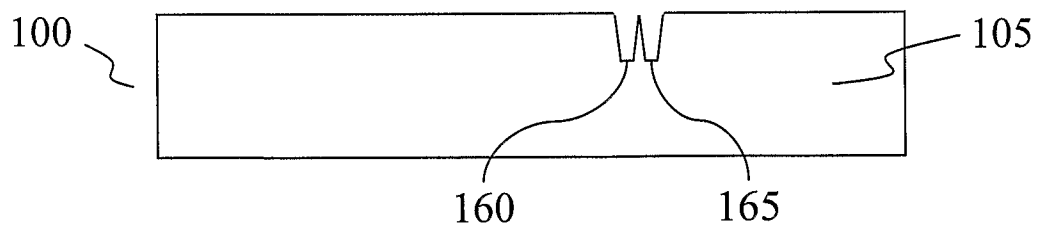
31. The method as claimed in any one of claims 1 to 30 wherein the maximum depth of the etched pattern is no more than 100 nm.

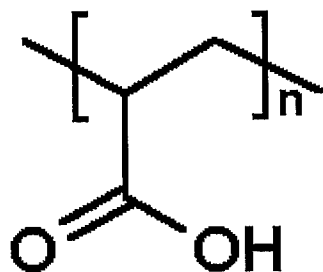
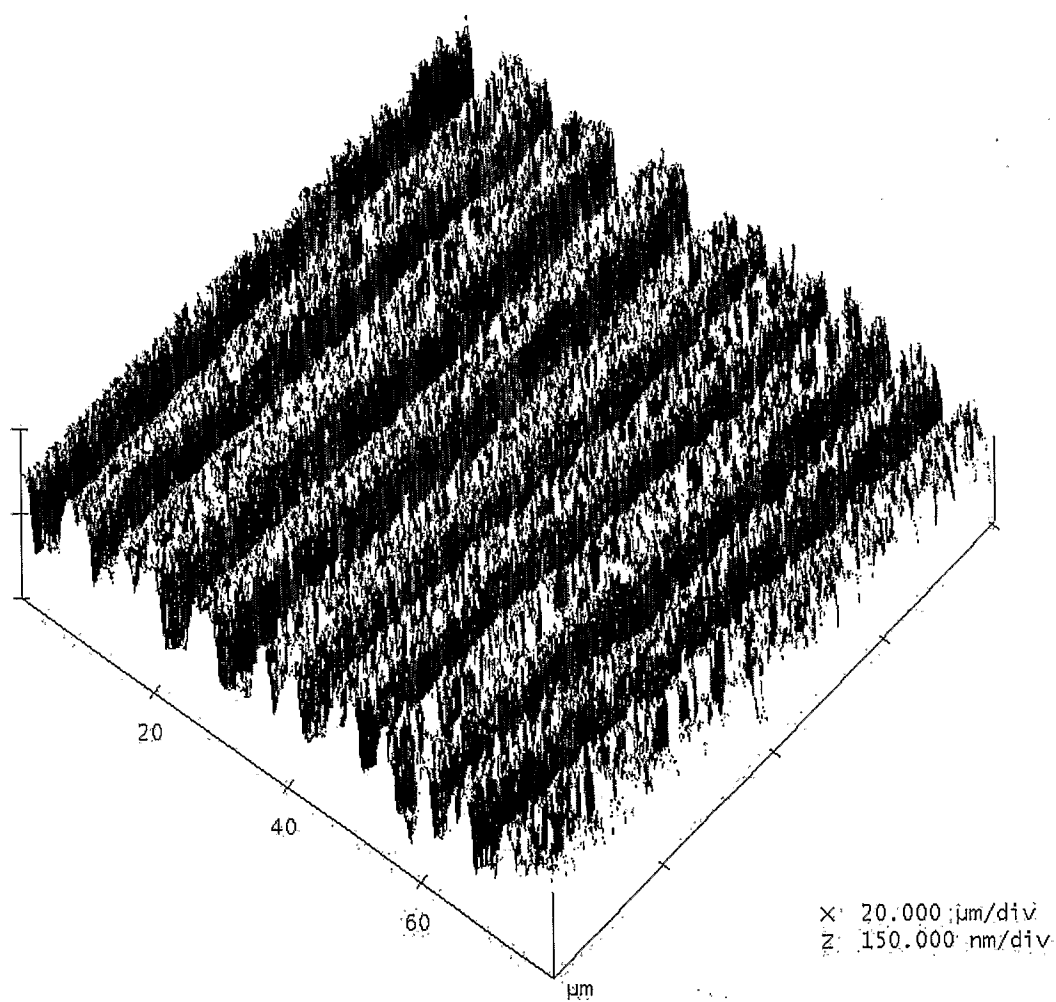
32. The method as claimed in any one of claims 1 to 31 wherein the texture pattern
15 is formed a having rounded features by immersing the textured surface in a solution which isotropically etches the substance.

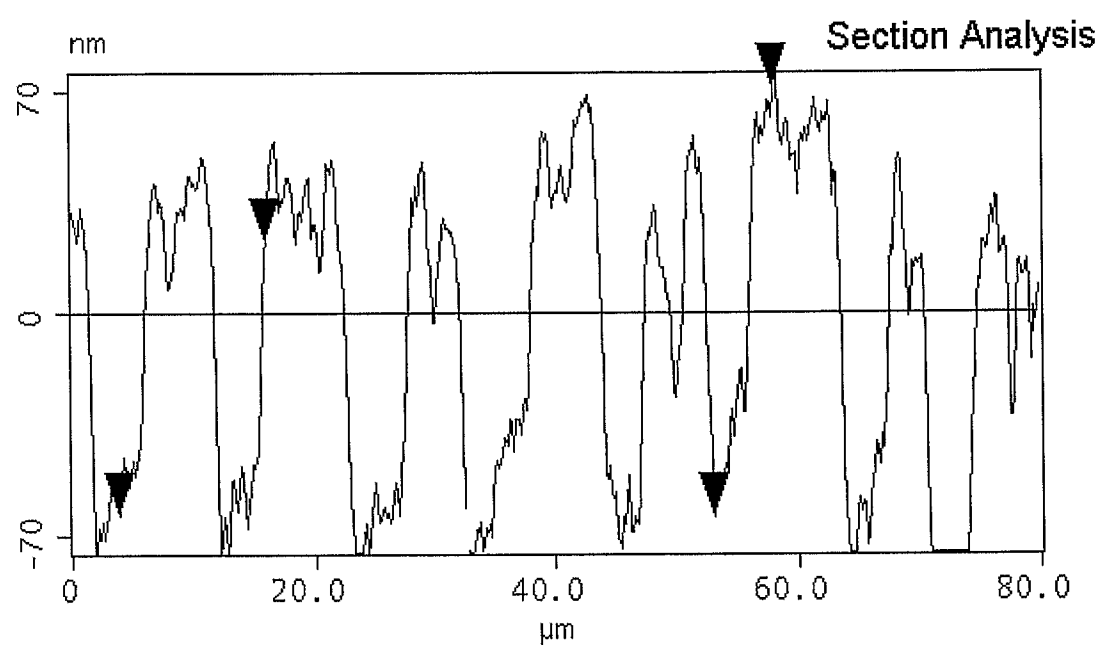
33. The method as claimed in claim 32 wherein the substance is glass and the isotropic etchant is a solution comprising HF or mixtures of HF and NH_4F .

34. The method as claimed in claim 33 wherein a solution comprising 10% 7:1
20 buffered oxide etch is used as the isotropic etchant.

**Fig. 1A****Fig. 1B**

**Fig. 1C****Fig. 1D**

**Fig. 2****Fig. 3**

**Fig. 4**

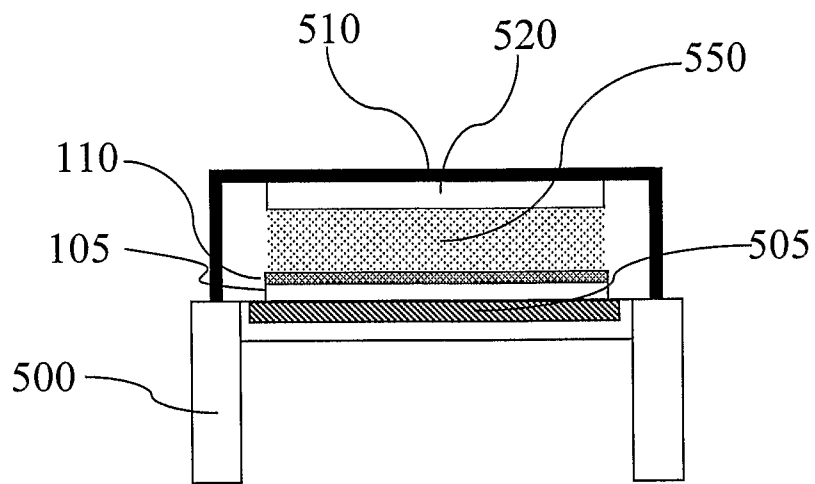


Fig. 5

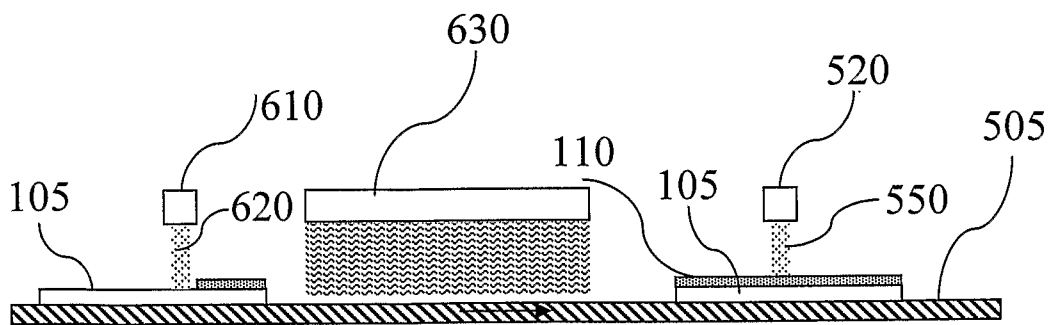


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2010/001208

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

H01L 21/311 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

EPODOC, WPI, & Keywords: texture, print, pattern, design, feature, etch, silicon or semiconductor, layer, film, surface, wafer, substrate? Or glass or dielectric, polymer, resin, fluid, solution, fluoride, liquid, HF, solar, photovoltaic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/094711 A1 (NEWSOUTH INNOVATIONS PTY LIMITED) 6 August 2009 Pages 10-18, Figs. 1A-1E	1-34
X	WO 2002/033740 A1 (SEIKO EPSON CORPORATION) 25 April 2002 Pages 15-18, Figs. 6A-7B	1-34
X	WO 2001/047044 A2 (PLASTIC LOGIC LIMITED) 28 June 2001 Abstract, pages 27-30, Figs. 12a & 12c	1-34



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:

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

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"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

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"Y" document of particular relevance; the claimed invention 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

06 November 2010

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2010/001208

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2009094711	AU	2009208384				
WO	0233740	CN	1404625	EP	1327259	GB	2367788
		JP	2008235284	US	2003029831	US	7431860
WO	0147044	AU	20159/01	AU	20160/01	AU	22066/01
		AU	22069/01	BR	0016643	BR	0016660
		BR	0016661	BR	0016670	CA	2394881
		CA	2394886	CA	2394895	CA	2395004
		CN	1425202	CN	1425201	CN	1425203
		CN	1425204	EP	1243032	EP	1243033
		EP	1243034	EP	1243035	HK	1053011
		HK	1053012	HK	1053013	HK	1054816
		KR	20070072579	US	2003059984	US	6808972
		US	2003059975	US	6905906	US	2003060038
		US	7098061	US	2003059987	US	7176040
		US	2005026317	US	7572651	US	2005274986
		US	7635857	US	2006286726	US	7763501
		WO	0146987	WO	0147043	WO	0147045
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							