

## Medium for etching oxidic, transparent, conductive layers

5 The present invention relates to a novel dispensable, homogeneous etching medium having non-Newtonian flow behaviour for etching oxidic, transparent, conductive layers and to the use thereof, for example for the production of liquid-crystal displays (LCDs) or organic light-emitting displays (OLEDs).

Specifically, it relates to particle-free compositions by means of which fine structures can be etched selectively in oxidic, transparent and conductive layers without damaging or attacking adjacent areas.

10 The object of structuring oxidic, transparent, conductive layers on a support material, such as, for example, on thin glass, arises, inter alia, in the production of liquid-crystal displays. An LC display essentially consists of two glass plates provided with oxidic, transparent, conductive layers, usually indium-tin oxide (ITO), with a liquid-crystal layer in between, which change their light transparency through application of a voltage. Contact with the ITO front and back is prevented through the use of spacers. For the display of characters, symbols or other patterns, it is necessary to structure the ITO layer on the glass sheet. This enables areas within the display to be addressed selectively.

### 1. Prior art and object of the invention

25 The glass sheets used for display production usually have a single-sided ITO layer thickness in the range from 20 to 200 nm, in most cases in the range from 30 to 130 nm.

30 During display manufacture, the transparent, conductive layer on the glass sheets is structured in a series of process steps. To this end, use is made of the process of photolithography, which is known to the person skilled in the art.

35 In the present description, inorganic surfaces are taken to mean oxidic compounds which have increased electrical conductivity due to the addition of a dopant with retention of the optical transparency. The layer

systems known to the person skilled in the art are not suitable for this purpose:

- 5       □ indium-tin oxide  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO)
- fluorine-doped tin oxide  $\text{SnO}_2:\text{F}$  (FTO)
- antimony-doped tin oxide  $\text{SnO}_2:\text{Sb}$  (ATO)
- aluminium-doped zinc oxide  $\text{ZnO}:\text{Al}$  (AZO)

10       It is known to the person skilled in the art to deposit indium-tin oxide by cathodic sputtering (in-line sputtering).

15       ITO layers of adequate conductivity can also be obtained by wet-chemical coating (sol-gel dip process) using a liquid or dissolved solid precursor in a solvent or solvent mixture. These liquid compositions are usually applied to the substrate to be coated by spin coating. These compositions are known to the person skilled in the art as spin-on-glass (SOG) systems.

20       Etching of structures

      Use of etchants, i.e. chemically aggressive compounds, causes dissolution of the material exposed to the attack by the etchant. In most cases, the aim is completely to remove the layer to be etched. The end of the etching is achieved by the encountering of a layer which is substantially resistant to the etchant.

25       Photolithography includes material-intensive and time-consuming and expensive process steps:

30       In known processes, the following steps are necessary for the production of a negative or positive of the etch structure (depending on the photoresist):

- 35       □ coating of the substrate surface (for example by spin coating with a liquid photoresist),
- drying of the photoresist,

- ☐ exposure of the coated substrate surface,
- ☐ development,
- ☐ rinsing
- ☐ if necessary drying
- 5 ☐ etching of the structures, for example by
  - o dip processes (for example wet etching in wet-chemistry benches)  
dipping of the substrates into the etching bath, etching operation
  - 10 o spin-on or spray processes: the etching solution is applied to a rotating substrate, the etching operation can be carried out without/with input of energy (for example IR or UV irradiation)
  - o dry-etching processes, such as, for example, plasma etching in complex vacuum units or etching with reactive gases in flow reactors
- 15 ☐ removal of the photoresist, for example by means of solvent
- ☐ rinsing
- ☐ drying

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In recent years, structuring with the aid of a LASER beam has established itself as an alternative process to photolithography.

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In laser-supported structuring processes, the LASER beam scans the areas to be removed dot by dot or line by line in a vector-oriented system. The transparent, conductive layer spontaneously evaporates at the points scanned with the LASER beam due to the high energy density of the laser beam. The process is quite suitable for the structuring of simple geometries. It is less suitable in the case of more complex structures and especially in the removal of relatively large areas of transparent, conductive layers. The achievable throughput times here are totally inadequate for mass production.

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In some applications, such as, for example, the structuring of transparent, conductive layers for OLED displays, LASER structuring is in principle not very suitable: evaporating, transparent, conductive material

precipitates on the substrate in the immediate vicinity and increases the layer thickness of the transparent conductive coating in these edge regions. This is a considerable problem for the further process steps, in which an extremely flat surface is required.

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An overview of various etching processes is given in

[1] D.J. Monk, D.S. Soane, R.T. Howe, Thin Solid Films 232 (1993), 1;

[2] J. Bühler, F.-P. Steiner, H. Baltes, J. Micromech. Microeng. 7 (1997), R1

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[3] M. Köhler "Ätzverfahren für die Mikrotechnik" [Etching Processes for Microtechnology], Wiley VCH 1983.

The disadvantages of the etching processes described are due to the time-consuming, material-intensive and expensive process steps which are in some cases complex in technological and safety terms and are frequently carried out batchwise.

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### Objective

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The object of the present invention is therefore to provide novel, inexpensive compositions for the selective etching of very uniform, thin lines having a width of less than 500  $\mu\text{m}$ , in particular of less than 100  $\mu\text{m}$ , and of extremely fine structures of doped tin oxide or zinc oxide layers which are used for the production of LC displays. A further object of the present invention is to provide novel etchants and etching media prepared therewith which, after etching, can be removed from the treated surfaces in a simple manner without leaving residues using a suitable, environmentally friendly solvent, optionally with exposure to heat.

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### 2. Description of the invention

Attempts to prepare compositions in the form of pastes which are suitable for achieving the object according to the invention have shown that comparable printing and dispensing properties as with particle-containing pastes can be achieved through the use of selected thickeners. Chemical interactions with the other constituents of the etching medium

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enable a gelatinous network to be formed. These novel gelatinous pastes exhibit particularly excellent properties for paste application by means of the dispenser technique, enabling non-contact paste application.

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The object according to the invention of selectively etching or structuring surfaces of oxidic layers, in particular of tin oxide or zinc oxide layers or corresponding doped layers, such as indium-tin oxide  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO), fluorine-doped tin oxide  $\text{SnO}_2:\text{F}$  (FTO), antimony-doped tin oxide  $\text{SnO}_2:\text{Sb}$  (ATO) or aluminium-doped zinc oxide  $\text{ZnO}:\text{Al}$  (AZO), is, surprisingly, achieved through the use of iron(III) chloride or iron(III) chloride hexahydrate as etching component for corresponding oxidic surfaces. In particular, the object according to the invention is therefore achieved by the provision and use of a novel printable etching medium, preferably having non-Newtonian flow behaviour, in the form of an etching paste for etching doped, oxidic, transparent, conductive layers.

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A corresponding paste comprises thickeners selected from the group polystyrene, polyacrylate, polyamide, polyimide, polymethacrylate, melamine resin, urethane resin, benzoguanine resin, phenolic resin, silicone resin, fluorinated polymers (PTFE, PVDF, inter alia), and micronised wax, in the presence of at least one etching component, and in the presence of at least one solvent. In addition, the composition according to the invention may comprise inorganic and/or organic acid, and optionally additives, such as antifoams, thixotropic agents, flow-control agents, deaerators, adhesion promoters. Compositions according to the invention are effective at elevated temperatures in the range from 30 to 330°C, preferably in the range from 40 to 200°C and very particularly preferably 50 to 120°C or can be activated by input of energy in the form of heat or IR radiation. In particular, the object according to the invention is achieved through the use of iron(III) chloride or iron(III) chloride hexahydrate as selectively etching component in compositions in the form of pastes according to Claims 2 – 7 for etching oxidic surfaces, in particular for etching surfaces which consist of  $\text{SnO}_2$  or zinc oxide, or oxidic, transparent, conductive layers which, besides  $\text{SnO}_2$  or zinc oxide, optionally comprise one or more doping

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components, or for etching uniform, homogeneous, non-porous or porous doped tin oxide surfaces, (ITO and/or FTO) systems and layers of variable thickness of such systems. These surfaces are preferably etched using pastes having the properties claimed in Claim 8. For the  
5 uses claimed, preference is given to the use of compositions according to Claims 12 – 23.

The present application additionally also relates to the use of compositions comprising iron(III) chloride or iron(III) chloride hexahydrate for  
10 etching  $\text{SiO}_2$ - or silicon nitride-containing glasses and above-mentioned oxidic surfaces in special industrial production processes according to Claims 9 - 11.

The pastes according to the invention are preferably used in processes  
15 as claimed by Claims 24 to 29.

#### Detailed description of the invention

A very wide variety of compositions by means of which thin lines can be  
20 etched into inorganic or inorganic oxidic surfaces which are resistant per se are known from patents and the journal literature. However, it was hitherto a problem to etch thin lines selectively into surfaces of tin oxides or zinc oxides since the etching components usually used either  
25 had an excessive etching action or are ineffective with respect to these surfaces.

Experiments have now shown that oxidic surfaces can be etched selectively and in a simple manner using a composition comprising iron(III) chloride or iron(III) chloride hexahydrate as etching component. Such  
30 compositions are particularly suitable for surfaces which comprise or consist of  $\text{SnO}_2$  or zinc oxide. Using these compositions, thin lines and extremely fine structuring can be etched into oxidic, transparent, conductive layers which, besides  $\text{SnO}_2$  or zinc oxide, comprise one or more doping components. However, these compositions can also be used  
35 extremely well for etching uniform, homogeneous, non-porous or porous doped tin oxide surfaces, (ITO and/or FTO) systems and layers

of variable thickness of such systems. Particularly good etching results are achieved if iron(III) chloride or iron(III) chloride hexahydrate is used as described as etching component in a composition for etching oxidic surfaces in the presence of an inorganic mineral acid, where a mineral acid selected from the group hydrochloric acid, phosphoric acid, sulfuric acid and nitric acid is used. Iron(III) chloride or iron(III) chloride hexahydrate can be employed here in the presence of a mineral acid and/or at least one organic acid, which may have a straight-chain or branched alkyl radical having 1-10 C atoms, selected from the group of the alkyl-carboxylic acids, the hydroxycarboxylic acids or the dicarboxylic acids. Particularly suitable for this purpose are organic acids selected from the group formic acid, acetic acid, lactic acid and oxalic acid.

In order to be able to print thin lines having a width of a few microns or thinner, it is advisable to use corresponding compositions in the form of a paste which comprise homogeneously dispersed thickening agents in an amount of 0.5 to 25% by weight, based on the total amount.

Thickening agents which may be present are one or more homogeneously dissolved thickening agents from the group cellulose/cellulose derivatives and/or starch/starch derivatives and/or xanthan and/or polyvinylpyrrolidone, polymers based on acrylates or functionalised vinyl units.

Corresponding pastes which has a viscosity at 20°C in a range from 6 to 35 Pa · s at a shear rate of up to 25 s<sup>-1</sup>, preferably have a viscosity in the range from 10 to 25 Pa · s and very particularly in the range from 15 to 20 Pa · s, have advantageous properties for the use according to the invention. Such etching pastes are highly suitable for etching SiO<sub>2</sub>- or silicon nitride-containing glasses which are in the form of uniform, homogeneous, non-porous and porous solids or for etching corresponding non-porous and porous glass layers of variable thickness which have been formed on other substrates.

The paste-form compositions can also readily be employed for opening layers of doped tin oxide surfaces (ITO and/or FTO) in the process for the production of semiconductor components and integrated circuits thereof or of components for high-performance electronics and give very accurate etching results. Particular possible applications of the compositions comprising iron(III) chloride or iron(III) chloride hexahydrate in the form of pastes are in display technology (TFTs), in photovoltaics, semiconductor technology, high-performance electronics, mineralogy or the glass industry, in the production of OLED lighting, of OLED displays, and in the production of photodiodes and for the structuring of ITO glasses for flat-panel screen applications (plasma displays).

In accordance with the invention, the compositions for etching oxidic layers comprise

- a) iron(III) chloride or iron(III) chloride hexahydrate as etching component
  - b) solvent
  - c) optionally a homogeneously dissolved organic thickening agent
  - d) optionally at least one inorganic and/or organic acid, and optionally
  - e) additives, such as antifoams, thixotropic agents, flow-control agents, deaerators, adhesion promoters, and
- are in the form of pastes which are printable and can be applied to the surfaces to be etched in extremely thin lines or finely structured by suitable printing techniques.

These compositions may comprise the etching component in an amount of 1 to 30% by weight and the thickening agent in an amount of 3 to 20% by weight, based on the total amount. The etching component is preferably present in an amount of 2 to 20% by weight, particularly preferably in an amount of 5 to 15% by weight, based on the total amount.

As already indicated above, it is advantageous for the compositions, in addition to iron(III) chloride or iron(III) chloride hexahydrate, to com-

prise, as etching component, an inorganic mineral acid selected from the group hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid and/or at least one organic acid, which may have a straight-chain or branched alkyl radical having 1-10 C atoms, selected from the group of the alkylcarboxylic acids, the hydroxycarboxylic acids or the dicarboxylic acid solutions, since the etching operation can thus be matched to the requirements of the respective layers to be etched. Particularly suitable organic acids for the preparation of the pastes according to the invention are formic acid, acetic acid, lactic acid and oxalic acid.

In total, the proportion of the organic and/or inorganic acid(s) in compositions according to the invention can be in a concentration range from 0 to 80% by weight, based on the total amount of the medium, where the added acid or mixtures thereof each have a  $pK_a$  value of between 0 to 5.

The compositions according to the invention may comprise, as solvent, water, mono- or polyhydric alcohols selected from the group glycerol, 1,2-propanediol, 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 2-ethyl-1-hexenol, ethylene glycol, diethylene glycol and dipropylene glycol, ethers selected from the group ethylene glycol monobutyl ether, triethylene glycol monomethyl ether, diethylene glycol monobutyl ether and dipropylene glycol monomethyl ether, esters selected from the group [2,2-butoxy(ethoxy)]ethyl acetate, propylene carbonate, ketones, such as acetophenone, methyl-2-hexanone, 2-octanone, 4-hydroxy-4-methyl-2-pentanone and 1-methyl-2-pyrrolidone, as such or in a mixture, in an amount of 10 to 90% by weight, preferably in an amount of 15 to 85% by weight, based on the total amount of the medium. In order to achieve the pasty, thixotropic properties, one or more homogeneously dissolved thickeners from the group cellulose/cellulose derivatives and/or starch/starch derivatives and/or xanthan and/or polyvinylpyrrolidone polymers based on acrylates or functionalised vinyl units may be present in an amount of 0.5 to 25% by weight, based on the total amount of the etching medium. In order to improve the use prop-

erties of the compositions, additives selected from the group antifoams, thixotropic agents, flow-control agents, deaerators and adhesion promoters may additionally be added in an amount of 0 to 5% by weight, based on the total amount.

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Compositions in which the individual components have been combined with one another in an optimal manner and mixed with one another in a suitable manner have, as already described above, a viscosity at a temperature of 20°C in a range from 6 to 35 Pa · s and at the same time a shear rate of up to 25 s<sup>-1</sup>, preferably a viscosity in the range from 10 to 25 Pa · s at a shear rate of 25 s<sup>-1</sup> and very particularly preferably 15 to 20 Pa · s at a shear rate of 25 s<sup>-1</sup>.

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In accordance with the invention, the novel compositions in the form of etching pastes having thixotropic, non-Newtonian properties are used to structure oxidic, transparent, conductive layers in a suitable manner during the process for the production of products for OLED displays, LC displays or for photovoltaics, semiconductor technology, high-performance electronics, of solar cells or photodiodes.

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To this end, the paste is applied or printed in a single process step over the entire surface to be etched or in accordance with the etch structure mask selectively only to the areas on the surface where etching is desired and, when the etching is complete, is removed again after a pre-specified exposure time by rinsing off using a solvent or solvent mixture, or the etching paste is burnt off by heating. After removal by heating, the treated surface can be rinsed again if necessary for cleaning and removal of any residues of the etching paste that may still be adhering.

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In this way, it is possible to etch and structure the surface in the printed areas, while non-printed areas are retained in the original state. In order to carry out the actual etching, the etching paste composition is applied to the surface to be etched and removed again after an exposure time of 10 s - 15 min, preferably after 30 s to 2 min. This procedure is particularly suitable for the treatment of inorganic, glass-like, crystalline

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surfaces, as have to be formed and treated in processes in the semiconductor industry.

5 The surface to be etched here can be a surface or part-surface of oxidic, transparent, conductive material and/or a surface or part-surface of a porous and non-porous layer of oxidic, transparent, conductive material on a support material.

10 In the process according to the invention, the etching of the surfaces to be treated is usually carried out at elevated temperatures in the range from 30 to 330°C, preferably in the range from 40 to 200°C and very particularly preferably 50 to 120°C.

15 In this connection, optimisation experiments have shown that doped tin oxide surfaces (ITO and/or FTO) can be etched with etching rates of 0.5 to 8 nm/s at elevated temperatures in the range from 50 to 120°C. Under particularly suitable conditions, the etching is carried out with etching rates of 1 to 6 nm/s, in particular with etching rates of 3 to 4 nm/s.

20 For the transfer of the etching paste to the substrate surface to be etched, a suitable printing process with a high degree of automation and throughput is used. In particular, suitable printing processes for this purpose which are known to the person skilled in the art are the dispenser technique, screen, stencil, pad, stamp, ink-jet printing processes.  
25 However, manual application is likewise possible.

Depending on the dispenser technique, screen, stencil, klischee, stamp design or cartridge control, it is possible to apply the printable, homogeneous, particle-free etching pastes having non-Newtonian flow behaviour which are described in accordance with the invention over the  
30 entire area or in accordance with the etch structure mask selectively only to the areas where etching is desired. All masking and lithography steps which are otherwise necessary are thus superfluous. The etching operation can take place with or without input of energy, for example in  
35 the form of heat radiation (using IR lamps).

The actual etching process is subsequently completed as already described by washing the surfaces with water and/or a suitable solvent or solvent mixture. When the etching is complete, the residues of the originally printable etching pastes having non-Newtonian flow behaviour  
5 are rinsed off the etched surfaces using a suitable solvent or solvent mixture. The treated surfaces are dried in a known manner.

For environmental reasons, inter alia, the rinsing is preferably carried out using water; only if necessary and advantageous for technical and  
10 qualitative reasons are solvents optionally added to the water or other solvents used alone or as a mixture. For this rinsing operation, solvents as have already been used for the preparation of the compositions can be added to the water. Corresponding solvents have already been mentioned above. In addition, further solvents which are generally  
15 known to the person skilled in the art for this purpose from semiconductor technology can be used. Solvents having suitable physical properties can be employed individually or as a mixture. Preference is given here to the use of solvents which have a good dissolution capacity for the paste residues on the surfaces, have a suitable vapour pressure,  
20 enabling easy drying after the rinsing of the surfaces, and at the same time have environmentally friendly properties.

Use of the etching pastes according to the invention thus enables etching to be carried out inexpensively in mass production on an industrial  
25 scale in a suitable automated process.

In a preferred embodiment, the etching paste according to the invention has a viscosity in the range from 5 to 100 Pa-s, preferably from 10 to 50 Pa-s. The viscosity here is the material-dependent component of the  
30 frictional resistance which counters the movement during sliding of adjacent liquid layers. According to Newton, the shear resistance in a liquid layer between two sliding surfaces arranged parallel and moved relative to one another is proportional to the velocity or shear gradient  $G$ . The proportionality factor is a material constant which is known as  
35 dynamic viscosity and has the dimension m Pa-s. In the case of Newtonian liquids, the proportionality factor is pressure- and temperature-

dependent. The degree of dependence here is determined by the material composition. Liquids or substances of inhomogeneous composition have non-Newtonian properties. The viscosity of these materials is additionally dependent on the shear gradient.

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The more pronounced pseudoplastic or thixotropic properties of the etching paste compositions have a particularly advantageous effect in screen or stencil printing and result in considerably improved results. In particular, this is evident in a shortened etching time or in an increased etching rate with the same etching time and especially in a greater etching depth in the case of thicker layers.

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It has been found that iron(III) chloride, iron(III) chloride hexahydrate, and/or hydrochloric acid solutions are capable of completely etching away doped tin oxide surfaces (ITO) having a layer thickness of 200 nm within a few seconds to minutes at temperatures above 50°C. At 100°C, the etching time is about 60 seconds.

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For the preparation of the particle-free media according to the invention, the solvents, etching components, thickeners and additives are mixed successively with one another and stirred for a sufficient time until a viscous paste having thixotropic properties has formed. The stirring can be carried out with warming to a suitable temperature. The components are usually stirred with one another at room temperature.

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Preferred uses of the printable etching pastes according to the invention arise for the processes described for structuring ITO applied to a support material (glass or silicon layer), for the production of OLED displays, TFT displays or thin-layer solar cells.

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As already mentioned, the pastes can be applied by means of the dispenser technique. Here, the paste is transferred into a plastic cartridge. A dispenser needle is screwed onto the cartridge. The cartridge is connected to the dispenser control via a compressed-air hose. The paste can then be forced through the dispenser needle by means of compressed air. The paste here can be applied as a fine line to a substrate

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for example an ITO-coated glass). Depending on the choice of the internal diameter of the needle, paste lines of various width can be produced.

5 A further possibility for paste application is screen printing.

For application of the pastes to the surfaces to be treated, the etching pastes can be forced through a fine-mesh screen which contains the print stencil (or etched metal screens). In a further step, burning-in of  
10 the pastes can be carried out in the screen printing process by the thick-layer technique (screen printing of conductive metal pastes), enabling the electrical and mechanical properties to be determined. Instead, the burning-in (firing through the dielectric layers) can also be omitted on use of the etching pastes according to the invention, and the  
15 applied etching pastes can be washed off after a certain exposure time using a suitable solvent or solvent mixture. The etching operation is terminated by the washing.

In order to carry out the etching, an etching paste as described, for example, in Example 1 is prepared. Using an etching paste of this type, a  
20 layer of doped tin oxide (ITO) having a thickness of about 120 nm can be removed selectively within 60 seconds at 120°C by the screen printing process. The etching is subsequently completed by dipping the Si wafer into water, followed by rinsing with the aid of a water jet in the  
25 form of a fine spray.

The complete disclosure content of all applications, patents and publications mentioned above and below, and the corresponding application DE 10 2005 031 469.4, filed on 04.07.2005, are incorporated into this application by way of reference.  
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#### 4. Examples

For better understanding and in order to illustrate the invention,  
35 examples are given below which are within the scope of protection of the present invention. These examples also serve to illustrate

possible variants. Owing to the general validity of the inventive principle described, however, the examples are not suitable for reducing the scope of protection of the present application to these alone.

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The temperatures given in the examples are always in °C. It furthermore goes without saying that, both in the description and in the examples, the added amounts of the components always add up to a total of 100% in the compositions.

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#### Example 1

Etching paste consisting of homogeneous thickener

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20 g of iron(III) chloride

is added with stirring to a solvent mixture consisting of

60 g of water

20 g of hydrochloric acid.

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4 g of Finnfix 700 (carboxymethylcellulose sodium salt)

are then added slowly in portions to the solution with vigorous stirring, and the mixture is stirred for a further 30 minutes. The clear paste is then transferred into a dispenser cartridge.

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The paste, which is now ready to use, can then be applied to ITO surfaces by means of the dispenser.

#### Example 2

Etching paste consisting of homogeneous thickener

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20 g of iron(III) chloride

is added with stirring to a solvent mixture consisting of

30 g of water

10 g of ethylene glycol

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20 g of water

20 g of hydrochloric acid.

4 g of Finnfix 2000

are then added slowly in portions to the solution with vigorous stirring, and the mixture is stirred for a further 30 minutes. The clear paste is then transferred into a dispenser cartridge.

5 The paste, which is now ready to use, can then be applied to ITO surfaces by means of the dispenser.

### Example 3

10 Etching paste consisting of homogeneous thickener

20 g of iron(III) chloride

is added with stirring to a solvent mixture consisting of

15 g of water

15 15 g of lactic acid

10 g of ethylene glycol

20 g of water

20 g of hydrochloric acid.

20 4 g of Finnfix 2000

are then added slowly in portions to the solution with vigorous stirring, and the mixture is stirred for a further 30 minutes. The clear paste is then transferred into a dispenser cartridge.

25 The paste, which is now ready to use, can then be applied to ITO surfaces by means of the dispenser.

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Application Example:

For paste application by dispensing and etching, the following parameters are used:

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Application rate XY stage (JR 2204): 100 mm/s

Dispenser (EFD 1500XL) – working pressure: 2-3 bar

Dispensing needle internal diameter: 230–260  $\mu\text{m}$

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Etching parameters: 120°C for 1 min (hotplate)

Rinsing: 30 sec in ultrasound bath

Drying: using compressed air

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Result of an etched ITO layer having a thickness of 125 nm on glass:

Etched line widths from 450 to 550  $\mu\text{m}$ .

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## PATENT CLAIMS

1. A use of iron(III) chloride or iron(III) chloride hexahydrate as an etching component in a composition in the form of a paste which comprises a homogeneously dispersed thickening agent in an amount of 0.5 to 25% by weight, based on a total amount of the composition,  
for etching oxidic surfaces which comprise or consist of  $\text{SnO}_2$  or zinc oxide, one or more doping components, or  
for etching uniform, homogeneous, non-porous or porous doped tin oxide surfaces, (ITO and/or FTO) systems and layers of variable thickness of such systems, in the presence of an inorganic mineral acid, selected from:  
hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid and/or at least one organic acid, wherein the organic acid is selected from formic acid, acetic acid, lactic acid and oxalic acid, or  
for etching  $\text{SiO}_2$ - or silicon nitride-containing glasses which are uniform, homogeneous, non-porous or porous solids, or  
for etching corresponding non-porous or porous glass layers of variable thickness which have been formed on other substrates.
2. The use according to Claim 1 wherein the thickening agents comprise one or more of cellulose/cellulose derivatives, starch/starch derivatives, xanthan, polyvinylpyrrolidone, and polymers based on acrylates or functionalised vinyl units.
3. The use according to one of Claims 1 to 2 wherein the paste has a viscosity at  $20^\circ\text{C}$  in a range from 6 to 35 Pa.s and a shear rate of up to  $25\text{ s}^{-1}$ .
4. The use according to Claim 3 wherein the paste has a viscosity in the range from 10 to 25 Pa.s.
5. The use according to Claim 3 wherein the paste has a viscosity in the range from 15 to 20 Pa.s.
6. The use according to one of Claims 1 to 5 for opening layers of doped tin oxide surfaces (ITO and/or FTO) in the process for production of semiconductor

components and integrated circuits thereof or of components for electronics.

7. The use according to one of Claims 1 to 5 in display technology (TFTs), in photovoltaics, semiconductor technology, high-performance electronics, mineralogy or the glass industry, in the production of OLED lighting, of OLED displays, and for production of photodiodes and for structuring of ITO glasses for flat-panel screen applications.

8. The use according to Claim 1 wherein the thickening agent is 3 to 20% by weight, based on the total amount of the composition, and the etching component is 2 to 20% by weight, based on the total amount of the composition.

9. The use according to Claim 7 wherein the flat panel screen application is a plasma display.

10. The use according to Claim 1, wherein the etching component is 5 to 15% by weight, based on the total amount of the composition.

11. A composition for etching oxidic layers, comprising:

- a) iron(III) chloride or iron(III) chloride hexahydrate as an etching component in an amount of 2 to 20% by weight, based on a total amount of the composition;
- b) a solvent, comprising one or more of
  - water,
  - mono-or polyhydric alcohols selected from the group
    - glycerol, 1,2-propanediol, 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 2-ethyl-1-hexenol, ethylene glycol, diethylene glycol and dipropylene glycol,
  - ethers selected from the group
    - ethylene glycol monobutyl ether, triethylene glycol monomethyl ether, diethylene glycol monobutyl ether and dipropylene glycol monomethyl ether,
  - esters selected from the group
    - [2,2-butoxy(ethoxy)]ethyl acetate and propylene carbonate,

ketones, selected from the group

acetophenone, methyl-2-hexanone, 2-octanone,

4-hydroxy-4-methyl-2-pentanone and 1-methyl-2-pyrrolidone,

in an amount of 10 to 90% by weight based on the total weight of the composition;

- c) a homogeneously dispersed organic thickening agent in an amount of 3 to 20% by weight of the composition, comprising one or more of cellulose/cellulose derivatives, starch/starch derivatives, xanthan, polyvinylpyrrolidone, and polymers based on acrylates or functionalised vinyl units;
- d) at least one inorganic and/or organic acid; and
- e) additives, comprising at least one of antifoams, thixotropic agents, flow-control agents, deaerators, adhesion promoters, and

which is in the form of a paste and is printable and has a viscosity at a temperature of 20°C in a range from 6 to 35 Pa.s at a shear rate of 25 s<sup>-1</sup>,

12. The composition according to Claim 11, wherein the at least one inorganic and/or organic acid is an inorganic mineral acid comprising one or more of:

hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid and at least one organic acid having a straight chain or branched alkyl radical having 1- 10 C atoms, selected from the group of alkylcarboxylic acids, hydroxycarboxylic acids or dicarboxylic acid.

13. The composition according to Claim 11, wherein the at least one inorganic and/or organic acid is an organic acid comprising at least one of formic acid, acetic acid, lactic acid and oxalic acid.

14. The composition according to Claim 11, wherein the at least one inorganic and/or organic acid has a concentration up to 80% by weight based on the total weight of the composition, and has a pK<sub>a</sub> value of 0 to 5.

15. The composition according to one of Claims 11 to 14, wherein the solvent is 15 to 85% by weight, based on the total amount of the composition.

16. The composition according to Claim 11, having a viscosity at a temperature of 20°C in a range from 10 to 25 Pa.s at a shear rate of 25 s<sup>-1</sup>.
17. The composition according to Claim 11, wherein the homogeneously dispersed thickener is 0.5 to 25% by weight, based on the total amount of the composition.
18. The composition according to one of Claims 11 to 17, wherein the additives comprise at least one of antifoams, thixotropic agents, flowcontrol agents, deaerators and adhesion promoters in an amount of up to 5% by weight, based on the total amount of the composition.
19. The composition of Claim 11 having a viscosity at a temperature of 20°C in a range from 15 to 20 Pa.s at a shear rate of 25 s<sup>-1</sup>.
20. A process for etching inorganic, glass-like, crystalline surfaces, comprising:  
applying a composition according to one of Claims 11 -19 over an entire area or in accordance with an etch structure mask selectively only to an area on a surface where etching is desired; and  
after etching is complete, rinsing off the composition using a solvent or solvent mixture or burning off by heating.
21. The process according to Claim 20, wherein the composition is removed after an exposure time of 10 s -15 min.
22. The process according to Claims 20 to 21, wherein the composition is applied by one of dispensers, a screen, a stencil, a pad, a stamp, an ink-jet, or manually.
23. The process according to Claims 20 to 22, wherein the composition is rinsed off using water.
24. The process according to Claims 20 to 21, wherein the step of applying the composition is done at a temperature from 30 °C to 330°C .
25. The process according to Claims 20 to 24, wherein the area etched has a

doped tin oxide surface (ITO and/or FTO) and is etched with an etching rate of 0.5 to 8 nm/s. at a temperature from 50 to 120°C.

26. The process of Claim 21 wherein the composition is rinsed after 30 s to 2 min.

27. The process of Claim 24 wherein the step of applying the composition is done at a temperature from 40 to 200°C.

28. The process of claim 24 wherein the step of applying the composition is done at a temperature from 50 to 120°C.

29. The process of claim 25 wherein the etching rate is 1 to 6 nm/s.

30. The process of claim 25 wherein the etching rate is 3 to 4 nm/s.