

**Dopant Pastes for the Production of p, p+ and n, n+
Regions in Semiconductors**

5 The invention relates to novel boron, phosphorus or boron-aluminium dopant pastes for the production of p, p+ and n, n+ regions in monocrystalline and polycrystalline Si wafers, and of corresponding pastes for use as masking pastes in semiconductor fabrication, power electronics or in photovoltaic applications.

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Boron or phosphorus doping of monocrystalline Si wafers in photovoltaic technology and in the case of power semiconductors (e.g. diodes, thyristors) is carried out via the vapour phase (e.g. POCl_3 , phosphine, BBr_3) or with solids (films or solid slices) or with liquid media such as e.g. phosphoric acid, and other organic B or P systems.

20 Directly patterned application is not possible with these techniques. Defined regions cannot be selectively doped without using elaborate e.g. photolithographic processes to mask the areas that are not to be doped.

25 In photovoltaic technology, an extensive or local back surface field (BSF) can be achieved by p++ doping on the back. Existing production lines currently operate only with an extensive back surface field, which is obtained by either an Al metal layer or a liquid boron source. Local BSFs have currently only been realized
30 on a laboratory scale, for reasons which will be explained in more detail below.

35 An extensive back surface field is especially advantageous, inter alia, in the case of thin Si wafers ($\leq 250 \mu\text{m}$), since otherwise the efficiency of the cell turns out to be significantly lower. Such a BSF is currently obtained in the case of Si wafers of $> 300 \mu\text{m}$

thickness by extensive printing with an aluminium paste [P. Lölgen; F. J. Bisschop; W. C. Sinke; R. A. Steeman; L. A. Verhoef et al. 6th PV Science and Engineering Conference, New Delhi, 1992, pp. 239]. This case is
5 advantageous in that, on the one hand, p+ doping, i.e. a BSF, is built up by the aluminium and, on the other hand, the electricity generated in the cell is also dissipated by the aluminium. In the case of thin
10 wafers, however, curvature of the wafer occurs after the aluminium paste has been burned in. The further handling and processing of such wafers therefore requires special measures since there are pronounced difficulties involved with the incorporation of such bent cells into the usually planar-designed PV modules.

15 In DE 195 08712 C2 and in K. A. Münzer, R. R. King, R. E. Schlosser, H. J. Schmidt, J. Schmalzbauer, S. Sterk, H. L. Mayer, 13th European Photovoltaic Solar Energy Conference, 23-27 10.1995, p. 1398, attempts are made
20 to solve this problem by a spin-on process with boron. In this case, p++ doping is produced by boron and an aluminium framework is implemented in a subsequent print by means of aluminium paste.

25 Disadvantages of this process are

- a) the large material requirement of the spin-on process
- b) the considerable equipment outlay, with which
30 angular wafers are to be coated uniformly using the spin-on process
- c) the high throughput and the expensive handling, which are to be realized in mass production only with great difficulty, and
- 35 d) that selective patterning of the wafers is not possible, as described above.

The object of the present invention was therefore to provide improved, inexpensive dopant pastes usable in

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semiconductor technology, which do not have the disadvantages described above and can be used in a straightforward way. The object of the present invention was also to provide corresponding screen-
5 printable pastes.

The object is achieved by dopant pastes for the selective patterning and for the extensive printing of Si wafers by screen, roller, pad, stencil printing or
10 other printing techniques customary in semiconductor technology for the production of p, p+, p++, n, n+, n++ regions in the Si wafer, containing

- a) one or more components with dopant action,
- b) an SiO_2 matrix,
- 15 c) solvents,
- d) optionally an acid and water,
and optionally
- e) additives such as thickening agents or wetting agents,

20 the total composition having impurities in the form of metal ions in respective concentrations of less than 500 ppb, preferably less than 200 ppb.

Through tests, it was found that the disadvantages
25 mentioned above are eliminated by the screen-printable dopant pastes found here.

The pastes according to the invention may contain a dopant source, selected from the group boron salt,
30 boron oxide, boric acid, organic boron compounds, boron-aluminium compounds and phosphorus salt, phosphorus oxide, phosphorus pentoxide, phosphoric acid, organophosphorus compounds, organic aluminium compounds and aluminium salts.

35 In principle, the compounds known to the person skilled in the art primarily from main groups III and V of the periodic table are suitable.

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The corresponding pastes furthermore contain an SiO_2 matrix consisting of one or more SiO_2 precursors.

5 The dopant pastes which have been found may contain one or more dopant sources selected from the group boron oxide (B_2O_3), phosphoric acid (H_3PO_4), phosphorus pentoxide (P_2O_5) and aluminium salt, it being possible for the doping sources to be used in different concentrations.

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The present invention also relates to dopant pastes which contain one or more dopant sources from the group of organic boron, phosphorus and aluminium compounds, it being possible for the doping sources to be used in
15 different concentrations.

The object is furthermore achieved by dopant pastes, containing one or more dopant sources selected from the group boron oxide (B_2O_3), phosphoric acid (H_3PO_4),
20 phosphorus pentoxide (P_2O_5) and aluminium salt or organic aluminium compounds, and optionally one or more dopant sources from the group of organic boron, phosphorus and aluminium compounds, it being possible for the doping sources to be used in different
25 concentrations.

The SiO_2 matrix, which the dopant paste contains, may according to the invention be formed by an organic silicon compound of the general formula $\text{R}'_n\text{Si}(\text{OR})_{4-n}$,
30 in which

R' denotes methyl, ethyl or phenyl,

R denotes methyl, ethyl, n-propyl or i-propyl,

and

n denotes 0, 1 or 2.

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The present invention furthermore relates to a dopant paste that contains an SiO_2 matrix, which is formed by silanes, selected from the group tetramethoxysilane,

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tetraethoxysilane, tetrabutoxysilane, individually or as a mixture.

5 The present invention also relates to the use of the described new dopant pastes in semiconductor technology, photovoltaic technology or in power electronics.

10 Besides the dopant pastes, the invention also relates to masking pastes, containing

a) an SiO_2 matrix,

b) solvents,

c) optionally an acid and water,
and optionally

15 d) additives, such as thickening agents or wetting agents,

the total composition having impurities in the form of metal ions in respective concentrations of less than 500 ppb, preferably less than 200 ppb.

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The masking pastes, like the dopant pastes mentioned above composed in the same way, except that the masking pastes are free from dopants, are used according to the invention in semiconductor technology, photovoltaic
25 technology and in power electronics.

It is likewise possible to achieve extensive or selective (selective emitter) phosphorus doping inexpensively and with high throughput by means of
30 screen-printable pastes.

Patterning stages, which are currently made possible by photolithographic processes, can be replaced inexpensively by the use of screen-printable dopant
35 paste.

The masking paste, which can be described as pure SiO_2 matrix paste without dopant additives, can be employed for intentionally defined protective layer formation.

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For this purpose, the paste may be applied extensively to the Si wafer, or else in patterned fashion. This makes it possible to protect defined regions from doping during the diffusion process.

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The object is achieved by novel pastes for the selective production of silicate layers doped with phosphorus, boron and boron-aluminium. These pastes are suitable for use in technical printing processes in the electronics industry. These include, especially, screen-printing technology or pad printing.

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Depending on the desired field of application, both the concentrations of the individual components and the viscosities may be varied in the pastes that are used.

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The dopant pastes according to the invention are furthermore distinguished by a defined matrix. This is formed by an SiO_2 -forming component during heating in the diffusion process. Together with the component delivering boron or phosphorus, what is described in the literature [K. Spanowsky, The Diffusion of Boron with the aid of Spin-on Glasses in MOS Technology, diploma dissertation, 1996; R. Fischer, Experiments to Clarify the Diffusion Mechanism of Phosphorus in Silicon, diploma dissertation, 1994] and known to the person skilled in the art as boro- or phosphorus silicate glass $(\text{B}_2\text{O}_3)_x \cdot (\text{SiO}_2)_y$ or $(\text{P}_2\text{O}_5)_x \cdot (\text{SiO}_2)_y$ is formed. This glass forms the actual source of the dopant during the doping.

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The quantity of the SiO_2 -forming component in the dopant paste is in a modifiable range of 0.1-5% by weight. In relation to the dopant components B_2O_3 or P_2O_5 , the ratio of SiO_2 to B_2O_3 or P_2O_5 may be set arbitrarily, although the range of 10-80% dopant in SiO_2 is advantageous. The dopant concentration to be achieved in the silicon can be controlled well through this ratio. The penetration depth of the dopant is, as known in the literature [A.

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Goetzberger; B. Voß; J. Knobloch, Solar Power: Photovoltaic Technology, Teubner Studienbücher Stuttgart 1997, pp. 40; 107], controlled through the parameters of diffusion time and diffusion temperature.

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The doping process is carried out by controlled diffusion in air or oxygen atmosphere. The temperatures for the phosphorus diffusion are e.g. 900-950°C for phosphorus, and for the boron diffusion about 950-1250°C. The diffusion temperature is dictated by the Si wafers used. In the case of monocrystalline wafers, the diffusion temperature can be higher, i.e. up to about 1250°C, since they are thermally more stable than polycrystalline wafers.

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The diffusion may also be carried out with rapid thermal processing (RTP) technology.

The diffusion time may, depending on the application purpose, be from a few minutes to as much as 60 hours or more. Following the diffusion, the wafers are treated with HF (concentration about 2-50% HF), in order to dissolve the phosphorus or borosilicate (PSG, BSG) glass formed. After this treatment, the Si wafer has a free Si surface.

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The dopant component is in the concentration range of 0-10% in relation to the dopant paste. In the case of a dopant-free (0% by weight) composition, a masking paste is produced. This is done under the same process conditions as in the case of the dopant pastes.

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The solvent forms the main constituent of the paste. The proportion may be in the range of 50-80% by weight of the total quantity.

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The proportion of the thickening agents, which are needed for controlled adjustment of the viscosity range and fundamentally for the printability of the dopant,

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i.e. to form a printable paste, is in the range of about 1-20% by weight in relation to the total quantity of the paste.

- 5 Other additives with properties advantageous for the desired purpose are antifoaming agents, adhesion moderators, thickening agents, wetting agents, levelling agents or thixotropic agents. These can positively affect the printability of the paste.

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Alkoxysilanes are generally suitable for forming the silicon matrix, in particular silanes of the general formula $R'_nSi(OR)_{4-n}$,
in which

- 15 R' denotes methyl, ethyl or phenyl,
 R denotes methyl, ethyl, n-propyl or i-propyl,
and
 n denotes 0, 1 or 2.

- 20 Examples of suitable silanes are tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetrapropoxysilane, as well as higher and mixed examples, i.e. silanes with longer alkyl chains or silanes with various alkyl residues.

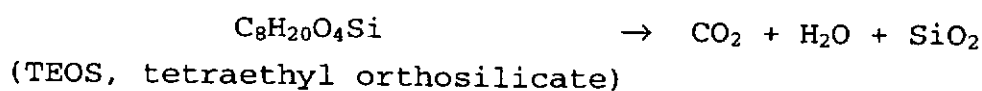
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Mixtures of various alkyl- or alkoxysilanes may also be used advantageously.

It may be necessary to prehydrolyse these compounds.

- 30 The use of such siloxanes as need no pretreatment, such as e.g. polysiloxanes, is advantageous for the production of the pastes according to the invention.

- When the substrate is heated in the diffusion furnace,
35 the organic silicon compounds form silicon dioxide, e.g. according to the following equation:



In order to produce the dopant matrix, compounds of boron and phosphorus, as well as aluminium compounds, may be used as the inorganic components. Examples
5 include boron oxide B_2O_3 , boric acid $B(OH)_3$, phosphoric acid H_3PO_4 , P_2O_5 and Al salts or organic aluminium compounds.

Organic compounds of boron and phosphorus as well as
10 organic aluminium compounds can be used as the organic components.

Additives may furthermore be mixed with the pastes according to the invention. These may be both organic
15 and inorganic acids, such as e.g. nitric acid, hydrochloric acid, lactic acid, oxalic acid, formic acid or the like. In particular, these acids are added when hydrolysis of the organic Si compound needs to be carried out. Generally, such organic acids whose alkyl
20 residues have a chain length of $n = 1 - 10$ are usable. It is possible to use organic acids that have a residue $R = OH$ or $= alkyl$ with $n = 1 - 10$. The alkyl residues of the salts that can be used may be both straight-chained and branched.

25 Corresponding additives in the pastes according to the invention are necessary when the organic silicon compound needs to be prehydrolysed. However, in the case of siloxane for example, this additive may be
30 omitted.

Suitable thickening agents include Thixoton® (ricinus oil), Borchigen TS® (rheological additive for silicic acids), bentonites with various qualities and
35 properties, generally inorganic rheology additives for various polar solvent mixtures, nitrocellulose, ethylcellulose and other cellulose compounds, polyvinylpyrrolidones with variable quality, starch ($+NH_4OH$), gelatine, alginic acid, highly disperse

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- amorphous silicic acid (Aerosil®), polyvinylbutyral (Mowital®) (highly soluble e.g. in butyl glycol), sodium carboxymethylcellulose (vivistar), thermoplastic polyamide resin (Eurelon®) (needs to be boiled down at about 180°C), organic ricinus oil derivative (Thixin R®), diamide wax (Thixatrol plus®), swelling polyacrylates (Rheolate®), polyetherurea-polyurethane (Rheolate®), polyether-polyols (Rheolate®).
- 10 Polysiloxanes, siloxanes and trisiloxanes may be used as levelling agents.

Particularly highly suitable additives are those that bind well with the other components, advantageously can be predried tack-free at temperatures below 200°C and burn without leaving residues at 200-500°C.

The viscosity of the highly pure dopant paste is adjusted by the thickening agent, as well as by the solvent used.

A basic requirement for a good dopant paste in photovoltaic technology is the lowest possible contamination with metallic compounds. In particular, the cations of the metals iron, chromium, copper, nickel, gold, calcium etc., often referred to in the literature as carrier lifetime "killers", in particular, are undesirable. Their concentrations should be as far as possible below 500 ppb in the paste. In particular cases, the concentrations should as far as possible not exceed 200 ppb. In order to make it possible to comply with these conditions, in particular cases only purified starting materials can be used.

Besides the components mentioned so far, the addition of solvents is necessary for the production of the pastes.

Suitable organic solvents include hydrophilic polyalcohols, such as ethylene glycol, methylcellosolve, methylcellosolve acetate, ethylcellosolve, diethylcellosolve, cellosolve acetate, 5 ethylene glycol monobutyl ether, ethylene glycol monophenyl ether, methoxymethoxyethanol, ethylene glycol monoacetate, ethylene glycol diacetate, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether acetate, diethylene 10 glycol monobutyl ether, diethylene glycol monobutyl ether acetate, diethylene glycol dimethyl ether, diethylene glycol methylethyl ether, diethylene glycol diethyl ether, diethylene glycol acetate, triethylglycol, triethylene glycol monomethyl ether, 15 triethylene glycol monoethyl ether, tetraethylene glycol, liq. polyethylene glycols, propylene glycol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, 1-butoxyethoxypropanol, dipropylglycol, dipropylene 20 glycol monomethyl ether, dipropylene glycol monoethyl ether, tripropylene glycol monomethyl ether, polypropylene glycols, trimethylene glycol, butanediol, 1,5-pentanediol, hexylene glycol, glycerine, glyceryl acetate, glyceryl diacetate, glyceryl triacetate, 25 trimethylolpropyne, 1,2,6-hexanetriol or hydrophilic derivatives thereof, as well as aliphatic and aromatic polyvalent alcohols such as e.g. 1,2-propanediol, 1,5-pentanediol, octanediol and also esters and ethers thereof or mixtures of these solvents.

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A suitable constituent may, for example, contain 1,2-butanediol as its main constituent. Such solvent mixtures as contain 30-95% by weight 1,5-pentanediol have proved suitable. Such a mixture may contain 35 ethylene glycol monobutyl ether (EGB), diethylene glycol monobutyl ether (DGB), dipropylene glycol monomethyl ether (DPM), 1,4-butanediol (1,4BD) and 1,3-butanediol (1,3BD) as other solvents.

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- Hydrophilic ethers, such as dioxane, trioxane, tetrahydrofuran, tetrahydropyran, may furthermore be used as solvents. Methylal, diethylacetal, methyl ethyl ketone, methyl isobutyl ketone, diethyl ketone, acetonylacetone, diacetone alcohol or hydrophilic esters such as methyl formate, ethyl formate, propyl formate, methyl acetate and ethyl acetate are also suitable.
- 10 Tests have shown that application of a 50-100 mg quantity of paste to a customarily used wafer, e.g. a 4-inch wafer, is sufficient to achieve a dopant effect. The application of the paste according to the invention to the wafer to be treated can be carried out with the
- 15 methods known to the person skilled in the art. In particular, application by the screen-printing process is suitable for this purpose. The conversion of the applied paste into the desired dopant layers takes place, in the known fashion, by heating to temperatures
- 20 of 200 to 600°C, preferably to about 500°C. The required heating time depends on the thickness of the layer of paste applied.

The paste according to the invention is suitable for

25 the production of p-n junctions, such as e.g. in semiconductor technology, in particular, but also for use in the production of solar cells used in solar technology.

30 For example, it has been found that through using boron pastes according to the invention for the production of doped glass layers, the efficiency of solar cells, which is usually 14% in production, is increased by about 1.5 to 2%.

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For better understanding and for clarification, examples will be given below which fall within the scope of protection of the present invention but do not restrict the invention to these examples.

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Example 1:

TEOS (1.43 g) was placed in a beaker. The solvent N-methylpyrrolidone NMP (83 g) was then added and the
5 basic mixture was prepared with the aid of a stirrer. Polyvinylpyrrolidone (11 g), diboron trioxide (4.6 g) and finally lactic acid (3 g) were then added in succession. During the addition, it was furthermore
10 necessary to stir vigorously. After the addition had been completed, the mixture was stirred for about 30 min more. Transfer to containers took place after a short waiting time. This waiting time was necessary for the bubbles formed in the mixture to be able to break-up.

15 This mixture gave a paste by means of which a boron glass was formed on the wafer, i.e. doping of the monocrystalline and polycrystalline Si wafer was obtained in a controlled way with the desired boron
20 concentration.

The paste obtained is stable in storage, easy to handle and printable. It can be removed from the screen-printing cloth with standard solvents.

25 2. Examples of pastes with a solvent or with solvent mixtures:

30 I. P paste:

30 g	1,4-butanediol	
5 g	P ₂ O ₃	
53 g	1,2-propanediol	
1.5 g	Trasil®	(silicon source; alkylsilicone resin with alkoxy groups)
0.2 g	Foamex N®	(Polydimethylsiloxane; deaerator)

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0.2 g	Aerex®	(high-molecular-weight organic polymer with silicone spikes; antifoaming agent)
3 g	Byk 410®	(modified urea; thixotropic agent)
0.05g	TEGO Glide 400®	(Polyether-modified polysiloxanes; levelling agent)
4 g	PVP	(polyvinylpyrrolidone; thickener)

II. Boron paste:

83 g	1,2-propanediol	
4.6 g	B ₂ O ₃	
1.43 g	TEOS	
3 g	Lactic acid	
2.5 g	Byk 410®	thixotropic agent
0.05 g	TEGO Glide 400®	levelling agent
0.2 g	Aerex®	antifoaming agent
0.2 g	Foamex N®	deaerator
4 g	PVP	thickener

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II. Si paste:

48 g	1,2-propanediol	
3 g	TEOS	
3 g	Lactic acid	
35 g	ethylene glycol monobutyl ether	
3 g	Trasil®	
5 g	Byk 410®	thixotropic agent
0.4 g	TEGO Glide 400®	levelling agent
4 g	PVP	thickener

PATENT CLAIMS

1. Dopant pastes for the selective and extensive printing of Si wafers by screen, roller, pad, stencil printing or other printing techniques customary in semiconductor technology for the production of p, p+, p++, n, n+, n++ regions in the Si wafer, containing

- a) one or more components with dopant action,
- b) an SiO₂ matrix which is formed by silanes of the general formula R'_nSi(OR)_{4-n}, in which

R' denotes methyl, ethyl or phenyl,

R denotes methyl, ethyl, n-propyl or i-propyl,
and n denotes 0, 1, 2,

- c) solvents,
 - d) optionally an acid and water, and
 - e) additives such as thickening agents or wetting agents,
- the total composition having impurities in the form of metal ions in respective concentrations of less than 500 ppb, preferably less than 200 ppb.

2. Dopant paste according to Claim 1, containing a dopant source selected from the group boron salt, boron oxide, boric acid, organic boron compounds, boron-aluminium compounds and phosphorous salt, phosphorus oxide, phosphorus pentoxide, phosphoric acid, organophosphorus compounds, organic aluminium compounds and aluminium salts.

3. Dopant paste according to Claims 1 and 2, containing an SiO₂ matrix containing one or more SiO₂ precursors.

4. Dopant paste according to Claims 1 to 3, containing one or more dopant sources selected from the group boron

oxide (B_2O_3), boric acid $B(OH)_3$, phosphoric acid (H_3PO_4), phosphorus pentoxide (P_2O_5) and aluminium salt and organic Al compounds, it being possible for the doping sources to be used in different concentrations.

5. Dopant paste according to Claims 1-3, containing one or more dopant sources from the group of organic boron, phosphorus and aluminium compounds, it being possible for the doping sources to be used in different concentrations.

6. Dopant paste according to Claims 1-3, containing one or more dopant sources selected from the group boron oxide (B_2O_3), boric acid $B(OH)_3$, phosphoric acid (H_3PO_4), phosphorus pentoxide (P_2O_5) and aluminium salt and optionally one or more dopant sources from the group of organic boron, phosphorus and aluminium compounds, it being possible for the doping sources to be used in different concentrations.

7. Dopant paste according to Claims 1 to 3, containing an SiO_2 matrix which is formed by silanes selected from the group tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetrapropoxysilane, tetramethoxysilane individually or as a mixture.

8. Dopant paste according to Claims 1 to 7, containing one or more solvents selected from the group of hydrophilic polyalcohols, their ethers or esters, of hydrophilic ethers, aldehydes, ketones or esters or mixtures.

9. Dopant paste according to Claim 8, containing 30-95% by weight 1,2-propanediol as a mixture with one or more

solvents selected from the group ethylene glycol monobutyl ether (EBG), diethylene glycol monobutyl ether (DGB), dipropylene glycol monomethyl ether (DPM), 1,4-butanediol (1,4BD) and 1,3-butanediol (1,3BD) and/or one or more solvents selected from the group dioxane, trioxane, tetrahydrofuran, and tetrahydropyran methylal, diethylacetal, methyl ethyl ketone, methyl isobutyl ketone, diethyl ketone, acetonylacetone, diacetone alcohol methyl formate, ethyl formate, propyl formate, methyl acetate and ethyl acetate.

10. Dopant paste according to Claims 1 to 9, containing tetraethyl orthosilicate as SiO_2 matrix, 1,2-propanediol, N-methylpyrrolidone, ethylene glycol monobutyl ether, 1,4-butanediol or mixtures thereof as solvents, lactic acid as acid, P_2O_5 or B_2O_3 as dopant and, as additives, levelling agents, thixotropic agents, thickeners and optionally antifoaming agents and deaerators, the quantity of SiO_2 -forming component in the dopant paste being in a range of 0.1-5% by weight and, in relation to the dopant components B_2O_3 or P_2O_5 , in the range of 10-80% dopant in SiO_2 .

11. Use of a dopant paste according to Claims 1 to 10 in semiconductor technology, photovoltaic technology or in power electronics.

12. Printable masking paste, containing

a) an SiO_2 matrix which is formed by silanes of the general formula $\text{R}'_n\text{Si}(\text{OR})_{4-n}$, in which

R' denotes methyl, ethyl or phenyl,

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R denotes methyl, ethyl, n-propyl or i-propyl,
and n denotes 0, 1, 2,

- b) solvents,
 - c) optionally an acid and water, and
 - d) additives, thickening agents or wetting agents,
- the total composition having impurities in the form of metal ions in respective concentrations of less than 500 ppb, preferably less than 200 ppb.

13. Use of a printable masking paste according to Claim 12 in semiconductor technology, photovoltaic technology and in power electronics.