CLAIMS

1. Method of preparing an electrically insulating film at the surface of an electrical conductor or semiconductor substrate, such as a silicon substrate, characterized in that it comprises:

a) bringing said surface into contact with a liquid solution comprising:

- a protic solvent;
- at least one diazonium salt;
- at least one monomer that is chain-polymerizable and soluble in said protic solvent;
- at least one acid in a sufficient quantity to stabilize said diazonium salt by adjusting the pH of said solution to a value less than 7, preferably less than 2.5;

b) the polarization of said surface according to a potentio- or galvano-pulsed mode for a duration sufficient to form a film having a thickness of at least 60 nanometres, and preferably between 80 and 500 nanometres.

2. Method according to Claim 1, characterized in that the protic solvent is chosen from the group consisting of water~~, preferably deionized or distilled water~~; hydroxylated solvents, in particular alcohols having 1 to 4 carbon atoms; carboxylic acids having 2 to 4 carbon atoms, in particular formic acid and acetic acid, and mixtures thereof.

3. Method according to Claim 2, characterized in that the water is deionized water.

4. Method according to Claim 2, characterized in that the water is distilled water.

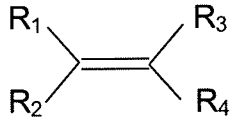
5~~3~~. Method according to ~~Claim 1 or 2~~any one of the preceding claims, characterized in that the diazonium salt is an aryldiazonium salt chosen from the compounds of the following formula (I):

$$R\text{-}N_2^+,A^- \qquad (I)$$

in which:

- A represents a monovalent anion,
- R represents an aryl group.

6~~4~~. Method according to any one of Claims 1 to 5~~3~~, characterized in that the chain-polymerizable monomer is soluble in the protic solvent and is chosen from the group of vinyl monomers chosen from the monomers of the following formula (II):



II

in which the, identical or different, groups R_1 to R_4 represent a monovalent non-metal atom such as a halogen atom or a hydrogen atom, or a saturated or unsaturated chemical group such as a C_1-C_6 alkyl or aryl, a -$COOR_5$ group in which R_5 represents a hydrogen atom or a C_1-C_6 alkyl, nitrile, carbonyl, amine or amide group.

7~~5~~. Method according to any one of Claims 1 to 6~~4~~, characterized in that the aforementioned liquid solution comprises:

- at least 0.3M of polymerizable monomer(s),
- at least 5×10^{-3}M of diazonium salt(s),

the molar ratio of the polymerizable monomer(s) to the diazonium salt(s) being between 10 and 300.

8~~6~~. Method according to any one of Claims 1 to 7~~5~~, characterized in that the polarization of said surface is produced in a pulsed mode, each cycle of which is characterized by:

- a total period P of between 10 ms and 2 s~~, preferably of around 0.6 s~~;
- a polarization time T_{on} of between 0.01 and 1 s, ~~preferably around 0.36 s,~~ during which a potential difference or a current is applied to the surface of the substrate; and
- an idle period with zero potential or current of a duration of between 0.01 and 1 s~~, preferably of around 0.24 s~~.

9. Method according claim 8, characterized in that the total period P is around 0.6s.

10. Method according claim 8, characterized in that the polarization time T_{on} is around 0.36s.

11. Method according claim 8, characterized in that the idle period with zero potential or current of a duration of around 0.24s.

12~~7~~. Method of preparing a coating of an electrical conductor or semiconductor substrate, such as a silicon substrate, said coating consisting of an internal layer forming an electrically insulating film and an external layer forming a copper diffusion barrier, characterized in that:

A. said internal layer is produced by employing the method according to any one of the preceding claims;

B. said external layer is produced by:

a) the formation by wet process, at the surface of the internal layer thus obtained, of an organic film containing particles, especially nanoparticles, of metals or metal alloys, in particular of nickel or cobalt;

b) bringing the film thus formed into contact with a liquid solution containing at least one metal salt, ~~preferably of the same nature as the metal incorporated into the organic film,~~ a stabilizing agent, and at least one reducing agent under conditions enabling the formation of a metal film having a thickness of at least 100 nm.

13. Method according to Claim 12, characterized in that the at least one metal salt is of the same nature as the metal incorporated into the organic film.

14~~8~~. Method according to Claim 12~~7~~, characterized in that the aforementioned step B.a) is carried out in non-electrochemical conditions by bringing the free surface of the aforementioned internal layer into contact with a liquid solution containing:

- at least one solvent~~, preferably a protic solvent~~;
- at least one diazonium salt;
- at least one monomer that is chain-polymerizable by free radical methods and soluble in said solvent; and
- at least one chemical initiator enabling the formation of radical entities from said diazonium salt.

15. Method according to Claim 14, characterized in that the at least one solvent is a protic solvent.

16~~9~~. Method according to either of Claims 12~~7~~ or 14~~8~~, characterized in that the chain-polymerizable monomer used in step A.a) is a vinylpyridine, ~~preferably 4-vinylpyridine,~~ or a methacrylate, ~~preferably 2-hydroxyethyl methacrylate~~, and in that the monomer which is chain-polymerizable by free radical methods used in step B.a) is 2-hydroxyethyl methacrylate.

17. Method according to Claim 16, characterized in that the vinylpyridine is 4-vinylpyridine.

18. Method according to Claim 16, characterized in that the methacrylate is 2-hydroxyethyl methacrylate.

19~~0~~. Method according to one of Claims 14~~8~~ to~~or~~ 18~~9~~, characterized in that the aforementioned chemical initiator is chosen from a metal reducing agent in finely divided form or an organic or inorganic base in sufficient proportions for the pH of the liquid solution to be greater than or equal to 4.

20~~11~~. Method according to Claim 12~~7~~, characterized in that the chain-

polymerizable monomer used in step A.a) is a vinylpyridine, ~~preferably 4-vinylpyridine~~ and in that step B.a) is carried out by bringing the free surface of the internal layer of polyvinylpyridine into contact with a liquid solution comprising:

- at least one solvent~~, preferably a protic solvent~~;

- at least one polymer that is soluble in said solvent and comprising functional groups capable of bonding with the functional groups of the polyvinylpyridine by hydrogen bonds or Van der Waals bonds, said polymer being chosen from the polymers containing one or more functional groups chosen from the following functional groups: hydroxyl, primary or secondary amine, ammonium, carboxylic acid, carboxylic acid salts, cyclic or linear carboxylic anhydride, amide: C(=O)NHR where R represents a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, an amino acid, phosphonic acid, phosphonic acid salts, phosphoric acid, phosphoric acid salts, sulphonic acid, sulphonic acid salts, sulphuric acid, sulphuric acid salts, succinamic acid, succinamic acid salts, phthalimide, phthalimide salts, $Si(OH)_n$ where n is an integer between 1 and 3;

for a sufficient duration to enable the formation of said hydrogen or Van der Waals bonds.

21. Method according to Claim 20, characterized in that the vinylpyridine is 4-vinylpyridine.

22. Method according to Claim 20, characterized in that the at least one solvent is a protic solvent.

23~~12~~. Method according to Claim 20~~11~~, characterized in that the chain-polymerizable monomer used in step A.a) is 4-vinylpyridine and in that the soluble polymer used in step B.a) is an acrylic polyacid.

24~~13~~. Method according to any one of Claims 12~~7~~ to 23~~12~~, characterized in that the aforementioned metal salt is chosen from the group consisting of the acetate, acetylacetonate, hexafluorophosphate, nitrate, perchlorate, sulphate or tetrafluoroborate of the aforementioned metal.

25~~14~~. Method according to any one of Claims 12~~7~~ to 24~~13~~, characterized in that the aforementioned reducing agent is chosen from the group consisting of hypophosphorous acid and its salts, borane derivatives, glucose, formaldehyde and hydrazine.

26~~15~~. Method of preparing a coating of an electrical conductor or semiconductor substrate, such as a silicon substrate, said coating consisting of an internal layer forming an electrically insulating film, an intermediate layer

forming a copper diffusion barrier, and an external layer forming a copper seed layer, characterized in that:

A. said internal layer is produced by implementing the method according to any one of Claims 1 to 8~~6~~;

B. said intermediate layer is produced by:

a) the formation by wet process, at the surface of the internal layer thus obtained, of an organic film containing particles, especially nanoparticles, of metals or metal alloys, in particular of nickel or cobalt;

b) bringing the film thus formed into contact with a liquid solution containing at least one metal salt, preferably of the same nature as the metal incorporated into the organic film, a stabilizing agent, and at least one reducing agent under conditions enabling the formation of a metal film having a thickness of at least 100 nm,

C. said external layer is produced by:

a) bringing the free surface of the intermediate layer into contact with a liquid solution comprising:

- at least one solvent;
- copper ions in a concentration of between 14 and 120mM;
- ethylenediamine;
- the molar ratio of ethylenediamine to copper being between 1.80 and 2.03;
- the pH of said composition being between 6.6 and 7.5;

b) polarization of said free surface of the second layer for a sufficient duration to form said external layer.

27~~16~~. Method according to Claim 26~~15~~, characterized in that the liquid solution used in the aforementioned step C.a) comprises cupric ions coming from copper sulphate in an amount between 16 and 64 mM and in that the molar ratio of ethylenediamine to the copper ions is between 1.96 and 2.0.

28~~17~~. Wafer of a conductor or semiconductor material, especially made of silicon, comprising one or more vias, characterized in that the walls of each via are covered with an internal layer made of poly-4-vinylpyridine with a thickness of between 200 and 400 nanometres forming an electrical insulator, which is itself coated with a layer of nickel, optionally alloyed with boron, with a thickness of between 100 and 300 nanometres forming a copper diffusion barrier, which is itself covered with a copper layer with a thickness of between 200 and 500 nanometres forming a seed layer.

2918. Wafer of a conductor or semiconductor material, especially made of silicon, comprising one or more vias, characterized in that the walls of each via are covered with an internal layer made of poly-2-hydroxyethyl methacrylate with a thickness of between 200 and 400 nanometres forming an electrical insulator, which is itself coated with a layer of nickel, optionally alloyed with boron, with a thickness of between 100 and 300 nanometres forming a copper diffusion barrier, which is itself covered with a copper layer with a thickness of between 200 and 500 nanometres forming a seed layer.