Metal Pattern Formation

G00002

Specification:

The invention relates to a method of forming a metal pattern on a dielectric substrate coated with a layer of metal, preferably with a copper film, and to an electrophoretic varnish.

In the past, many different methods of producing circuit patterns on electric circuit carriers have been proposed. In the panel plating process, a copper layer that completely covers the drilled printed circuit board material is first produced in the thickness required for the circuit structures. Then, those regions of the outer sides of the printed circuit boards are covered with a resist layer that correspond to the circuit structures to be formed so that these regions are protected during the subsequent etching process, thus being preserved. In the pattern plating process but a thin copper film is at first formed on the printed circuit board material. A layer of photoresist is for example applied there onto and the copper film is exposed again by photostructuring at the places that correspond to the circuit structures to be formed. Thereafter first a further copper layer is deposited to the exposed copper regions in order to form the circuit pattern and then a galvanoresist layer is formed. Subsequently, the layer of photoresist is removed and the bare copper film is removed by etching, the layer of galvanoresist protecting the metal layer located underneath against the etching agent. In the subcase of the metal resist process, a layer of metal resist, a tin/lead layer for example, is applied as a galvanoresist layer.

These methods and other known methods present considerable disadvantages. More specifically, it is not possible to manufacture under manufacturing conditions circuit structures of widths of less than 100 µm in a reproducible way. Numerous attempts have been made to achieve this goal. With the help of

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some complicated methods and starting materials, such circuits could finally be produced. Such methods however are not suited for mass production since they are too expensive and complex and/or require very expensive starting materials. These methods are not suited to produce circuits with lines having a structure width of less than 50 µm though.

DE-A-18 11 377 discloses a method of manufacturing printed circuit boards with circuit lines applied on both sides thereof, in which an etch resist layer, more specifically a layer of tin, is exclusively applied to the copper film in the bores of the printed circuit boards that have been contacted through and in which the desired circuit line pattern is made by etching. For this purpose, the outer sides of the boards are provided with a layer of varnish extending as far as the edges of the bores prior to applying the etch resist layer.

DE 37 32 249 A1 indicates a method of manufacturing three-dimensional printed circuit boards in subtractive/semi-additive technique with pattern transmission on an insulating substrate in which the substrate coated with a copper film is at first coated all over with a tin metal resist that may be electroless plated and/or electrolytically deposited. The metal resist is then selectively exposed to laser radiation without using a mask so that the circuit pattern created is a negative. The copper regions that have been exposed may then be removed by etching.

EP 0 062 300 A2 also describes a method of producing printed circuit boards in which a copper film is applied on at least one side of a plastic substrate, the circuit pattern being then formed in the copper film by depositing a metallic etch resist layer onto the copper film, the etch resist layer being selectively evaporated according to the desired circuit pattern by means of a laser beam and the remaining copper film being removed by etching as far as the surface of the plastic substrate at the places removed by way of the laser treatment.

In Derwent Abstracts to JP-A-59227186 a method is outlined in which a

photoresist is applied to the outer sides only of a printed circuit board that has been contacted through, then a metallic layer of etch resist, among others of solder metal or tin, is deposited on the walls of the bores, whereupon the photoresist with the circuit pattern is exposed to light and developed prior to finally removing by etching the exposed copper.

EP 0 757 885 B1 indicates a method of forming metallic circuit patterns on electrically isolating substrates in which at first a metal layer is applied to the substrate prior to applying thereupon an organic protective layer with an electrophoretic dip coat. Then, the protective layer is removed in the regions of the circuit patterns to be formed by means of laser radiation. An etch resistant metal layer is deposited onto the exposed metal surface. Then, the organic protective layer is cleared off in the regions adjacent the future circuit pattern by means of laser radiation and the exposed metal layer is also removed in these regions by means of an etching process. Laser radiation is generated by an Nd-YAG-laser.

DE 41 31 065 A1 discloses still another method of manufacturing printed circuit boards, in which at first a metal layer and then a metallic or an organic layer of etch resist is applied onto a substrate. It suggests using as a metallic layer of etch resist a layer of tin or of an alloy of tin and lead and as an organic layer of etch resist a layer that may be produced by electrophoretic or electrostatic coating. In the regions directly adjacent the future circuit pattern, the layer of etch resist is then removed by etching by means of electromagnetic radiation, by means of laser radiation for example, in such a way that the circuit pattern and islands of the metal layer that are electrically isolated from the pattern by etching trenches remain on the substrate. Laser radiation is generated by a Nd-YAG-laser. The document indicates that etching trenches of 150 µm width are produced with this method, the undercut of the metal layers on each flank of the etching trenches amounting to 35 µm.

DE 44 17 245 A1 discloses a method of manufacturing metal structures on the

surface of printed circuit boards, wherein the method comprises coating the substrate with a primer and thereafter applying onto the primer layer a second layer, both layers not being electrically conducting, then ablating part of the second layer by means of an excimer laser and finally electroless plating a metal on the exposed primer layer surface.

EP 0 469 635 A1 also describes a method of producing printed circuit boards in which a metal layer and then an organic layer of etch resist are applied onto a substrate. The organic etch resist layer used is an electrophoretic dip coating. Subsequently, the etch resist layer in the regions directly adjacent the future circuit pattern is cleared off by means of a Nd-YAG-laser and the thus exposed metal layer is removed by etching.

EP 0 489 560 A1 describes a resin composition for forming a positive photoresist which is used as an anaphoretic varnish for manufacturing printed circuit boards. The resin composition is obtained by copolymerization of the following compounds: a) acrylic acid and methacrylic acid, b) compounds that are unstable to acids, for example *tert*-butyl acrylate and *tert*-butyl methacrylate and further c) a polymerizable monomer with which a homopolymer can be obtained that has a glass transition temperature T_g of 0°C or less, e.g. ethyl acrylate, *iso*-propyl acrylate, *n*-propyl acrylate, *iso*-butyl acrylate, 2-ethyl hexyl acrylate, *n*-hexyl methacrylate, *n*-octyl methacrylate and *n*-decyl methacrylate. The resist also contains a photoacid generator, e.g. a phosphonium, sulphonium, diazonium and iodonium salt. For structuring, the resist is exposed to light and developed, the regions being altered by the exposure in such a way that they are soluble in the processing solution.

The known methods either are extremely sophisticated and thus expensive or it is not possible to manufacture very fine structures having a width of 50 µm and less in a reproducible way. Further the known processes also suffer in being laborious in those cases in which no photoresist is used but a resist which is not sensitive to light. This is because it takes a long time to remove the resist in

these cases entirely from the surface of the substrate. One possibility to produce such fine structures consists in starting from a material being provided with a copper film of no more than 5 µm thick. But it is extraordinarily complicated and thus expensive to manufacture such materials with this process. In using the customary materials with a thick copper film (usually 17 µm), it has been found that, on account of considerable undercut, the circuit structures often have no rectangular section, so that the area with which they rest on the substrate is very small, the desired adhesion of the circuit lines being not achieved as a result thereof.

In using the method described in DE 37 32 249 A1, it has been found that, even after laser ablation, considerable amounts of tin are still to be found on those regions of the copper surfaces that have previously been freed from tin so that the result obtained of subsequent etching is not satisfactory. More specifically when manufacturing circuit carriers with circuit lines having structure widths of less than 50 µm, no reproducible results may be obtained. The shape and width of the circuit lines varies over wide limits. In parts, either the spaces between the circuit lines are interconnected or the circuit lines are disrupted. Sometimes, pitting-like etchings of the circuit pattern were observed after the copper film had been removed by etching.

Additionally, the circuit patterns produced with this method often create problems in subsequent processes, for example when a solder resist mask is being formed and in processes in which the end layers deposited are layer combinations of nickel/gold. In the first case, the adhesion of the mask to the circuit structures is not sufficient and in the second case, the copper structures that have been freed from the layer of tin cannot perfectly be etched to form the layer of nickel/gold.

The methods in which an etch resist layer is made with an electro dip coat and in which said layer is structured with an Nd-YAG-laser by selectively allowing the varnish layer to evaporate, also present difficulties, since in this case too,

unreproducible residues are formed that may deposit again onto the already exposed metal surfaces. If, for structuring metallic layers, a conventional method is utilized in which photosensitive layers are deposited onto the metallic surface, an additional step in development is necessary. Moreover, these resists and the substrates coated with said resists are difficult to manipulate because it is not evident to use them in daylight. It has been found that the known electrophoretic photoresist systems do not readily permit error-free resolution of finest structures.

The basic problem of the present invention is therefore avoiding the disadvantages of the known methods and finding more specifically a method that makes it possible to readily and, most of all, very quickly, carry out structuring which may also be performed in mass production and that permits to reproducibly manufacture finest structures with structure widths of 50 µm and less. Furthermore, the problems experienced with the known methods with regard to the capability of further processing the finished circuit patterns are not to occur. The shape of the circuit lines too is to be reproducible and is to come the nearest possible to a rectangular section.

The problem is solved by the method according to claim 1 and by an electrophoretic varnish according to claim 16. Preferred embodiments of the invention are indicated in the subordinate claims.

The method according to the invention serves to form a metallic pattern on dielectric substrates. The electrophoretic varnish according to the invention is particularly useful in performing the method.

The method is more specifically used to produce highly integrated circuit carriers for the microelectronics industry, e.g. chip carriers, multichip modules (MCM) and other hybrid circuit carriers. Of course, the method may also be used for manufacturing other products, e.g. for manufacturing printed circuit boards (PCB) with structure widths in excess of 50 µm, of micro reactors,

storage media, solar collectors, and for forming metal patterns on plastics for decorative effect.

In that the varnish contains at least one ablation ampifier matching the ultraviolet radiation extremely fast removal of the applied varnish layer by ultraviolet radiation is made possible. This is achieved by extremely increasing the ablation rate. As a result thereof, with ultraviolet radiation, exposure times are achieved for removing the varnish layer without leaving any residue that are considerably shorter than processing times of known methods.

The ablation amplifier more specifically is an aromatic carbonyl compound, comprising e.g. acetophenone and the derivatives thereof, e.g. *trans*-benzylidene acetophenone, benzophenone and the derivatives thereof, e.g. hydroxy benzophenones, dihydroxy benzophenones and polyhydroxy benzophenones, as well as cinnamic acid, tropolone and the derivatives thereof. Furthermore on principle, polycyclic hydrocarbons in the form of anthracene, 9-anthracene methanol, *1.4*-dimethoxy anthracene, *9.10*-diethyl anthracene, 9-phenoxy methyl anthracene, *9.10-bis*-(trimethylsilyl ethinyl) anthracene, pyrene and perylene, further diphenyl butadiene and the derivatives thereof, chrysene as well as diphenyl fulvene, are suitable. Furtheron heterocycles, especially polycyclic heterocycles, may be used e.g. carbazole and the derivatives thereof, more specifically with hydrophilic groups, e.g. phenolic hydroxy and carboxyl groups, further dipyridyl amines, phenoxazine, 2-phenyl benzimidazole and isoquinoline oxide, may be applied. Also aromatic nitro compounds, e.g. nitrophenoles, nitroanilines, ω-nitrostyrene as well as *1.5*-dinitro naphthaline, are suited.

In that the varnish contains an ablation amplifier that matches the ultraviolet radiation, a profitable ablation time is achieved. Comparative tests carried out with and without ablation amplifier yielded an enormous increase in the ablation rate of the varnish layers: the radiation time required to achieve complete removal could be reduced by a factor of at least 15, more specifically of 30 to 50

when these compounds were included. *Trans*-benzylidene acetophenone, dihydroxy benzophenone, nitrophenol and dipyridyl amine are particularly well suited. The reason therefore possibly is that these compounds are readily soluble in the copolymer particles so that the molecules of the ablation amplifier do not aggregate into larger sized bodies, these compounds being rather uniformly distributed in the matrix of the copolymer.

The ablation amplifier may be added to the varnish as an additional component in the usual way. In an alternative embodiment, a covalent bond can also be formed between the ablation amplifier and the skeleton of the copolymer. In this case, the required proximity in space of the sensitizer to the copolymer in the varnish layer is already achieved by this bond.

For carrying out the method according to the invention, a substrate provided with a base metal surface, preferably with a copper film, is used and the base metal surface is etched upon structuring according to the invention so that the desired metal pattern is created. If a base metal layer is used, said layer may be completely removed upon structuring in the exposed regions. The following process steps are performed to structure the base metal surface:

a) providing a substrate comprising a base metal surface;
b) applying a varnish layer to the substrate by means of an electrophoretic process, the varnish layer containing at least one ablation amplifier adjusted to ultraviolet radiation,
c) ablating the varnish layer with ultraviolet radiation ($\leq$ 450 nm) in at least parts of the regions that do not correspond to the metal pattern to be formed, the base metal surface being laid bare (the lower wavelength limit of the ultraviolet radiation being among others determined by whether exposure to light is carried out in air ($\geq$ 190 nm) or under vacuum, whereas in the latter case radiation with a wavelength of below 190 nm may be used);
d) etching of the exposed base metal surface.

The varnish layer may for example be completely removed in the regions that do not correspond to the metal pattern to be formed. In another embodiment, the varnish layer is only removed in parts of these regions, e.g. only in those regions that are directly adjacent the metal pattern to be formed, so that e.g. large areas of metal remain between the discrete areas of the metal pattern to be formed (cf. in this regard DE 41 31 056 A1, EP 0 469 635 A1 and EP 0 361 192 A2 for example). The advantage of this way of proceeding is that in cases in which the metal pattern only incompletely or unevenly covers the surface of the substrate, so that large regions are left unaffected by the pattern, the varnish layer can be removed much faster from the substrate surface than in cases in which the varnish layer is to be completely cleared off in the whole region in which metal patterns are not to be formed.

The energy radiation preferably used is laser radiation because this radiation is provided with a sufficiently high energy density and can moreover be sharply focused in order to be capable of manufacturing the finest structures and more specifically because in the focused laser beam an energy density is achieved that is sufficiently high to ablate the varnish layer. The surface regions in which the varnish layer is to be removed and which are to be exposed to light are scanned in this latter case so that the surface regions are one after the other captured by the beam.

It is of course also possible not to focus the laser beam so that the entire surface of the substrate for example is simultaneously exposed to light. In this case, a mask is used (either in contact with the substrate or without contact by way of an optical system) to shield the surface regions in which the metal pattern is to be formed so that, in these regions, the varnish layer is protected from the laser beam.

To selectively remove the varnish layer in the regions of the base metal surface that are to be exposed, an excimer laser is preferably used, e.g. an ArF-, KrCl-, KrF-, XeCl-, XeF- or an F_2 laser with a constant output of 300 watts for example.

This radiative source is particularly well suited to ablate varnish layers consisting of organic material without leaving any residue since the chemical bonds in the organic molecules of the varnish layer can be broken by means of ultraviolet radiation.

When using an excimer laser, the energy density at the location of treatment preferably amounts to at least 50 mJ/cm^2. On principle, lower energy densities may be adjusted though, when the speed at which the laser is scanned across the board is reduced or when exposure time is accordingly prolonged when at the same time the entire substrate surface is exposed to a non-focused laser beam.

The method according to the invention permits to form circuit patterns in which the circuit lines have structure widths of 50 µm and less. Circuit lines may for example be formed which have an almost rectangular section with a base width of 15 µm. The section of the circuit lines is substantially shaped like a trapezoid and it has been found that the base area of the circuit lines abutting the dielectric is wider than the surface. As a result, a large area of contact between the circuit lines and the dielectric is obtained and optimal adhesion to the substrate is accordingly achieved. With circuit lines of about 20 µm wide and about 20 µm high, the steepness of the flanks of the circuit lines, called undercut, amounts to approximately 2.5 µm. This signifies that the base area on each flank of the circuit lines protrudes by the indicated distance from under the surface of the circuit lines.

The width of the circuit lines can be set to be reproducible. Circuit lines with a substantially constant structure width of about 20 µm may for example be obtained. Variation in width lies within the range of at most ± 1 µm. Electric integrity of the entire electric circuit is thus secured.

More specifically, the problems that have been observed with the method described in DE 37 32 249 A1 do not occur. Failures in subsequent etching of

the exposed copper layer have not been observed. All of the surface regions of the circuit to be processed, in which the varnish layer is removed after the surface regions corresponding to the circuit lines have been treated by laser and after a protective coating for etching made from metal has subsequently been deposited in these regions, may be etched without problem and without leaving residues.

Pitting-like etchings in the metal pattern have not been observed even after the copper layer has been etched.

Moreover, there exists no problem of further processing the etched circuit carriers: In contrast to known methods, application of a solder resist mask and subsequent deposition of an end layer of nickel/gold do not present any difficulties. In the first case, adhesion of the solder resist mask to the circuit lines is good enough, in the second case, the surfaces of the circuit lines can be satisfactorily etched prior to applying the end layer.

The method of ablating by means of an energy radiation source according to the invention is of greater ease as compared to conventional structuring techniques using photoresists and screen printing resists. The varnish layer in particular requires no further chemical development. Additionally, a maximum flexibility of the structuring process is achieved since it may be carried out without masks.

As contrasted with radiative sources emitting in the visible, more specifically in the red or infra-red region of the spectrum, (such methods are described in EP 0 062 300 A2, DE 41 31 065 A1, EP 0 757 885 B1 and EP 0 469 635 A1), the ultraviolet radiative sources used according to the present invention are particularly well suited to form finest metal patterns, more specifically with structure widths of 50 µm and less. This is made possible by the fact

that the varnish layer may be removed from the underlying base metal

surface

a. readily

b. without any residue

c. leaving sharp contours

d. that the base metal layer may be removed in the exposed regions without substantial undercut after the varnish layer has been readily cleared off without any residue and leaving sharp contours.

It has been found that on using radiative sources in the (visible and infrared) region of longer wavelength, ablation of the varnish layer is not secure and can more particularly not be carried out leaving sharp contours. On the contrary, the structured varnish layer often shows flanks with unsharp contours. Moreover, in these cases, residues remain in the channels formed on the base metal area. The reason therefore may be that removal of the varnish layer using the electromagnetic radiation in the visible and infrared region is thermal (pyrolytic) and not substantially photolytic as it is the case when ultraviolet radiation is used. In the thermal process, reaction products from the varnish layer are formed in an undefined way, these reaction products may in parts be of high molecular weight so that removal of the varnish layer is incomplete on account of its low vapor pressure.

Excimer lasers are particularly well suited to generate radiation in the ultraviolet range of the spectrum, because they permit to attain a high radiation density in this wavelength range. Processing time needed for selectively removing the varnish layer is considerably reduced as a result thereof so that the throughput of a processing plant provided with such facilities is high enough and hence the cost for carrying out this method is sufficiently low.

The method according to the invention has further advantages over the known methods:

a) in the process of etching used to structure the base metal surface,

protection of the bores in the substrates is effective so that a dependable resistance to etching is guaranteed and metal layers in these areas are not affected; the same is true for the varnish layer remaining over the metal patterns on the surfaces of the substrates;

b) the substrates coated with the varnish layer are mechanically insensitive since after having been submitted to drying and if need be to a heat treatment, the varnish layer is scratch resistant and more specifically resistant to fingerprints;

c) the varnish is not photosensitive and accordingly is easier to handle than conventional photoresists;

d) moreover, the varnish layer may readily be removed.

An anaphoretic varnish is preferably used to form the varnish layer. Such varnishes are readily removable by means of alkaline solutions.

The copolymer should have the following properties:

a) Good adhesion to the base metal surfaces, more specifically to the copper surfaces;

b) Good resistance to acid copper etchants, to a hydrochloric acid $FeCl_3$ solution for example;

c) It should easily be removable from the base metal surfaces and should not leave any residue behind when irradiated with ultraviolet radiation;

d) It should be easily removable from the base metal surfaces with an aqueous, alkaline solution upon etching the base metal layers (2 % by weight NaOH solution);

e) Good emulsifying power in aqueous solvents for use as an anaphoretic varnish;

f) Low glass transition temperature T_g below 100°C in order to guarantee thermosetting even for sensitive substrates.

For an optimum varnish formed with the copolymers, a compromise has to be

found between the need for sufficient thickness required for making sure of sufficient resistance to etching and minimum thickness for guaranteeing fast ablation rates with ultraviolet radiation.

For this purpose, the varnish is preferably made of at least one copolymer formed by the copolymerization of monomers selected from the group comprising methacrylic acid, C_1 - C_2 alkyl methacrylate and other esters thereof, C_3 to C_{10} alkyl (meth)acrylate and other esters thereof as well as hydroxy alkyl methacrylate and other esters thereof, the alkyl groups of which have 2 - 4 carbon atoms. The term alkyl (meth)acrylate designates both alkyl acrylates and alkyl methacrylates. It is to be understood that the copolymer may also comprise monomers other than the above mentioned monomers, e.g. styrene, maleic acid and the esters thereof. In a preferred embodiment methacrylic acid and the esters thereof may be substituted by maleic acid and the esters thereof. Furthermore it is to be understood that the varnish may also comprise other polymers than the copolymer formed by copolymerizing the above acrylic monomers.

To form the copolymer, methyl methacrylate is more specifically used as the C_1 - C_2 alkyl methacrylate, butyl acrylate as the C_3 - C_{10} alkyl acrylate, and 1-hydroxy ethyl methacrylate, 2-hydroxy ethyl methacrylate or the respective hydroxy propyl acrylates are used as the hydroxy alkyl methacrylate.

To produce the copolymer, the monomers are preferably used in the following amounts:

a) methacrylic acid: 1 - 25 % by weight,
b) C_1 - C_2 alkyl methacrylate: 20 - 80 % by weight,
c) C_3 - C_{10} alkyl acrylate: 1 - 50 % by weight,
d) hydroxy alkyl methacrylate: 0 - 20 % by weight,

the sum of the amounts of the above mentioned monomers amounting to a total

of 100 % by weight.

If a C_3 - C_{10} alkyl methacrylate is used instead of a C_3 - C_{10} alkyl acrylate, this former monomer is to be used in a considerably higher concentration, e.g. in a concentration of 25 - 75 % by weight. Such an increase reduces by the same amount the content of C_1 - C_2 alkyl methacrylate, e.g. to a proportion of 5 - 40 % by weight.

The copolymer contains methacrylic acid to optimize adhesion of the varnish layer to the base metal surface and to guarantee sufficient emulsifying power of the copolymer in aqueous alkaline solvents. If proportion of this compounds in the copolymer is too low, adhesion is too low. On the other side, too high a proportion is also to be avoided to make certain that the varnish layer may be completely (without leaving any residue) cleared off when ablated by laser radiation and more specifically when the layer with the base metal surface is subsequently removed with an alkaline aqueous solution.

The copolymer contains methyl and/or ethyl methacrylate to adjust mechanical properties, more specifically to adapt stiffness of the copolymer to the practical requirements. If its proportion is too high, the copolymer embrittles and can fracture when heat treated. Moreover, manipulation of such layers is problematic. If its proportion is too low, the layer obtained is too soft and does not have the desired resistance to etching when the base metal surface is being structured.

The C_3 - C_{10} alkyl acrylates, more specifically butyl acrylate, are also used to optimize rigidity of the copolymer, wherein these components proved to be antagonists to methyl and ethyl methacrylate. This component furthermore affects glass transition temperature T_g of the copolymer. This temperature should be the lowest possible in order to keep the temperature for heat treatment after laser ablation as low as possible. This is necessary to minimize thermal stress of the dielectric substrate and of possibly other electronic

components that have already been placed on the circuit carriers to be processed. An increase in the proportion of C_3 - C_{10} alkyl acrylates causes the T_g value to drop. On the other hand, too high a proportion of butyl acrylate yields too soft a layer. Moreover in this case, protection of the base metal surface against an aqueous chemical etchant is additionally improved.

By using the hydroxy alkyl methacrylates, adhesion of the varnish layer to the base metal surface is optimized. By increasing the concentration thereof in the copolymer, adhesion is enhanced. The upper limit to the proportion is reached when the copolymer can no longer be completely removed from the base metal surface using an alkaline aqueous solution.

If the reaction occurring during the synthesis of the copolymers is adequately run, the properties thereof can be optimized further. The previously mentioned properties are achieved in producing copolymers having a mean value by weight of the molecular weight M_W of 15,000 to 100,000 g/mol, more specifically of 50,000 to 60,000 g/mol. If M_W is too low, the copolymer obtained is again too soft and does not have the required resistance to etching. A varnish with a copolymer having too high a value for this parameter can no longer be readily and completely removed from the base metal surface.

The index of polydispersiveness P_I of the copolymer, which is defined by the ratio M_W/M_N, M_N being the mean value by numbers of the molecular weight of the copolymer, can also be optimized by the way the reaction occurring during the synthesis of the copolymers is run. In choosing a value of 1.5 to 3.5 for P_I, more specifically of 2.0 to 2.5, varnish layers can be produced that make good resistance to etching possible.

This parameter is also an indicator for the action of the varnish containing the copolymer: the lower the value of P_I, the more the mixture of copolymers with various molecular weights obtained by synthesis is homogeneous, so that, if the value for M_W is high enough, less parts of copolymers having a low value for M_W

are contained. Through the use of such copolymers, improved resistance to etching is made possible.

The mean value by weight of the molecular weight M_W is for example determined by means of size exclusion chromatography (SEC), more specifically by means of gel permeation chromatography (GPC). The mean value by numbers of the molecular weight M_N may for example be determined by osmometry. The two methods are actually known.

By utilizing the special copolymer composition and more specifically in using the specific ablation amplifiers, extremely fast removal of the applied varnish layer by ultraviolet radiation is made possible. This is achieved on one hand by having the varnish composition formulated in such a way that, although thickness of the layer is small and amounts to no more than 5 µm, preferably to no more than 3 µm and more specifically to from 1 to 2 µm, resistance to etching of the metal pattern areas coated with the varnish layer in an acid etchant suitable for copper patterns is sufficient. In that the varnish layer is capable of protecting so well the underlying layers of base metal against etchants, thickness of the varnish layer can be chosen to be small so that ablation rate can be considerably increased compared to known methods. On the other hand by additionally inserting the compounds of the ablation amplifier, ablation rate is additionally increased to the extent mentioned. As a result thereof, with ultraviolet radiation, exposure times are achieved for removing the varnish layer without leaving any residue that are considerably shorter than processing times of known methods.

The electrophoretic varnish may contain further customary components such as dyes and pigments for improving processing properties of the varnish and an optical inspection after structuring, then plasticizers and inorganic fillers that influence flow properties (rheology) of the varnish for example, moreover bonding agents, e.g. benzotriazole or other similar compounds that may enhance adhesion of the applied varnish layer to the copper film lying

underneath. In addition, the varnish may also contain surface lubricants for optimizing processing properties of the substrates coated with the varnish layer as well as emulsifying agents, e.g. surface-active agents.

The substances mentioned are preferably dissolved or emulsified in an aqueous solvent. In addition to water, the solvent may also contain organic solvents, more specifically hydrophilic solvents such as methyl ethyl ketone, dioxane, methoxyethanol, diethylene glycol as well as esters of ethylene glycol and diethylene glycol, ethers of ethylene glycol and diethylene glycol, esters of propylene glycol and ethers of propylene glycol.

To produce the varnish, the above mentioned components may first be homogeneously dissolved in the organic solvent in a concentration preferably of from 10 to 30 % by weight. Then, the solution/emulsion thus obtained is received in water. Subsequently, at least one base is added to neutralize the acid groups of the copolymer, the base preferably being selected from the group comprising triethyl amine, monoethanolamine, morpholine, ammonia and sodium hydroxide. Other mono-, di- or trialkyl amines may also be used, e.g. tributylamine. pH of the emulsion is adjusted to a value ranging of from neutral to slightly alkaline. The optimum pH depends on the type of copolymer. In adding the base, the solubility/emulsifying power of the composition in water is improved so that an initially turbid emulsion in water turns into an almost clear solution. The solids content of the emulsion obtained preferably amounts to from 5 to 20 % by weight. The production process indicated herein above may also be changed.

The varnish layer can be applied to the substrate by means of a customary electrophoretic method. For this purpose, the substrate provided with the base metal surface is brought, together with a counter electrode, into contact with the varnish emulsion and a voltage is applied between the substrate and the counter electrode.

Layer thickness of the varnish preferably amounts to no more than 5 µm, more specifically to no more than 3 µm and most specifically to from 1 to 2 µm. This makes certain of an extremely fast and dependable removal on ablating with ultraviolet radiation.

Once the varnish layer has been formed, the substrate is generally dried and posteriorly hardened by heat treatment to solidify the layer, thus providing it with the required resistance to etching. For this purpose, the substrate is for example dried in a convection drier or with infrared heating by radiation. A combination of a continuous-flow drier and infrared heating by radiation or hot air path may also be made use of.

Then, the substrate is exposed to the radiative source in the way indicated. The thereby generated gaseous products are drawn by way of appropriate pumps from the immediate surroundings of the substrate in order to prevent a new layer from forming.

In using a very sharply focused laser beam from which leakage radiation surrounding the main beam is blanked out and which is scanned across the surface of the resist layer, extremely fine structures may be formed in the resist layer. The structure widths that may be obtained are considerably lower than 20 µm. Alternatively, scattered laser radiation, with a section of the beam of 5 cm by 5 cm for example, may also be used. In this case, radiation is either directed onto the surface via a mask that is in direct contact with the substrate surface, or radiation is projected onto the surface by way of an optical system. Extremely fine structures with straight and steep flanks may be formed in these cases too.

After the layer of varnish has been structured by means of ultraviolet radiation, the base metal surfaces that have been laid bare are removed by etching. If the base metal surface of concern is a copper layer, a customary acid etch solution for copper can be used for the purpose. A hydrochloric acid $CuCl_2$ etch solution

or a hydrochloric acid $FeCl_3$ solution are particularly well suited. Alternatively an ammoniacal etch solution may be used as well, since the resist offers sufficient resistance (> 5 min) to alkali at pH < 10.

After removal of the base metal layer that has been laid bare, the varnish layer is preferably removed so that the metal patterns are exposed. Further metal layers may thus be deposited onto the metal patterns. Aqueous alkaline solutions are particularly well suited for the purpose, for example an aqueous solution of sodium carbonate or a solution of sodium hydroxide.

The thus obtained copper pattern is provided with sharply contoured, very fine copper structures that have steep and straight flanks.

After the metal patterns have been laid bare, at least one more metal layer can be applied onto the metal patterns by means of a method of electroless plating. Appropriate metal layers or combinations of metal layers are deposited in particular in order to protect the surfaces from corrosion and to form solderable and bondable surfaces or to preserve those during a long storage time. A layer of tin or of an alloy of tin can be deposited in order to form solderable surfaces. To obtain bondable surfaces, first a layer of nickel in particular and thereupon a layer of gold may be applied onto the copper surfaces.

In order to be capable of depositing the additional metal layers, the copper surfaces of the metal patterns are first prepared in using for example solutions containing surface-active agents. Another additional possibility for preparing the surfaces consists in slightly etching the copper surfaces in order to create a microscopic roughness for example so that the further metallic layers adhere tightly to the copper surface. For this purpose, customary etch solutions for copper are employed, that is acid, aqueous solutions of oxidizing agents, e.g. solutions of alkali peroxo disulphate, hydrogen peroxide or caroate. Between these and further process stages, the surfaces are rinsed in order to completely remove rests of liquid still sticking on them from the previous treatment.

Then, in the exposed copper regions a layer of tin or of a tin alloy for example serving as a solder layer or a layer of nickel and thereupon a layer of gold serving as a bondable surface are formed by metal deposition. These layers also serve to protect the metal patterns against oxidation.

The plating baths used to form the metal layers by means of electroless plating are actually known.

After the coating steps mentioned have been carried out, the substrate is rinsed and dried.

The method mentioned hereinabove can be carried out using various techniques. The substrates provided with the copper films may for example be immersed into the processing solutions contained in tanks. A preferred method for bringing the substrates into contact with the processing solutions consists in using a process of continuous horizontal operation for forming the varnish layer and for removing the exposed copper films. This process consists in conveying the substrates through such a plant in horizontal direction of transportation. The substrates are thereby held either vertically or horizontally. In the first case, the substrates can again be conveyed in a horizontal direction of transportation. The solutions can be delivered to the substrate surfaces by means of appropriate nozzles in that they are brought into contact by means of flow nozzles, jet nozzles or spray nozzles or, in processing baths, with the processing fluids.

To produce highly integrated circuit carriers, the base material used for the substrates can consist of a dielectric that is provided on one or on both sides with base copper films. The production process of these materials is actually known. Depending upon the wiring density needed, the dielectric layers can be applied on one or on both sides of the carrier substrate. Multiple coatings are also conceivable, a circuit pattern being formed in each new layer by means of the method according to the invention. This permits to almost indefinitely

increase signal wiring density. It is evident that the respective conductive pattern must be finished before an additional dielectric layer can be constituted.

Fig. 1 is a schematic illustration of the method according to the invention:

By electrophoresis a varnish layer **3** is applied onto a substrate being provided with a copper film **1** and substantially comprising layers of epoxy resin **2.**

According to **Fig. 1A,** the varnish layer is partially covered with a mask **4**, e.g. with a contact metal mask. Ultraviolet laser radiation **5**, emitted by a KrF-excimer laser for example, is radiated through the mask **4** onto the varnish layer. In the exposed regions, the varnish layer **3** is thereby removed from the the copper film surfaces **1**. This can be surveyed from **Fig. 1B** at the places **6** where the varnish layer **3** has been partially removed.

Then, the exposed substrate is brought into contact with a chemical etch solution, a hydrochloric acid $CuCl_2$ solution for example. The exposed copper surfaces are attacked in the process so that the copper film **1** is removed from the epoxy resin **2** in these regions. This may be surveyed from **Fig. 1C** at the places **6'**. In the process of etching, the desired circuit pattern is created on the surfaces of epoxy resin **2.**

Then, the remaining varnish layer is removed using a stripping solution, e.g. a NaOH solution. The metal pattern produced is left on the substrate (**Fig. 1D**).

Results of the assays for optimizing the method are indicated hereinafter:

Synthesis of the copolymers:

1. At first, the copolymers were produced in batches:

To produce the copolymers, methyl ethyl ketone (MEK) and

azobisisobutyronitrile (AZDN) were given into a double-necked flask. Then, the monomers were added. The reaction mixture was kept hermetically sealed during the entire duration of the reaction. The proportion of ingredients utilized for producing the copolymers is indicated in **Table 1**.

To initiate the polymerization reaction, the mixture was heated. The mixture was kept at reflux for 24 hours (h). The conversion in [%] determined upon completion of the reaction is also indicated in **Table 1**.

Upon completion of the reaction, the polymer was precipitated from the reaction mixture with water at a weight ratio of 7 parts of water to 1 part of the reaction mixture. After separation, a colorless powder was obtained that was dried under vacuum for 48 h at 60 to 70°C.

Molecular weights of the copolymers were determined by means of gel permeation chromatography (M_W) or by osmometry (M_N), a PMMA standard being used each time for calibration.

2. In further experiments, synthesis of copolymers was carried out by semi-continuous processing. For this purpose, only part of the individual reactants were added at the beginning of the reaction, the rest of them was added at a later stage.

BA or BMA, resp., were added in a batch to the reaction mixture, i.e. the whole amount at the beginning of the reaction. The initiator AZDN was also added in a batch for the copolymer No. 6. One part of MAA, MMA and HEMA, resp., was added at the beginning of the reaction and another part (approximately from 33 to 39 %, referred to the whole amount of this monomer) was added within 9 h of reaction time.

The mixing ratio of the monomers and the properties of the copolymers made from these monomers are indicated in **Table 2.** The values of the added

proportions of monomers indicated in brackets are the amounts added within 9 h of reaction time whereas the respective other values are the amounts added at the beginning of the reaction. For AZDN, the different additions are indicated separately, the instant of time of addition is given in brackets (for example T3h: addition after 3 h).

Characterization of the varnishes and of the varnish layers:

Some of the copolymers that were produced in batches or according to the semi-continuous method were applied onto a copper plate by spin-coating, varying rotational speeds having been set according to desired layer thickness. The layers were dried in an oven at 70°C or 100°C, resp., depending on T_g of the copolymer. The oven was equipped with a fan. It is to be noted that drying may be performed also below T_g of the polymer. Due to the presence of additional substances in the varnish T_g of the varnish is lower than that of pure copolymer.

Thickness, resistance to etching and capacity of removal in aqueous alkaline solution were determined. The conditions under which this was determined were as follows:

a) Layer thickness: To determine layer thickness, a device was used by means of which induced currents or eddy currents were measured (Bykotester 7500). Repeatability of the values measured amounted to ± 1 µm. The values obtained were verified by optical microscopy.

b) Resistance to etching: Etch solution: 30 % by weight $FeCl_3$ solution + 10 % by weight HCl + 60 % by weight water
Temperature: 40°C, immersion time: 1 min

c) Capacity of removal in alkaline solution: 2 % by weight NaOH solution
Temperature: 50°C, immersion time: 1 min

The results are reproduced in **Table 3.**

3. Further copolymers were produced to test reproducibility of the production process. The mixing ratio of the monomers and the physical properties of the copolymers obtained from the monomers are indicated in **Table 4.**

Copolymer No. 13 was produced under the same conditions as copolymer No. 6. But here, conversion achieved was higher so that glass transition temperature T_g was lower.

Copolymers No. 14 and 15 were polymerized within 6 h instead of within 9 h. Therefore, the percentage of conversion was not the same.

In order to increase reproducibility, copolymers No. 16 and 20 were polymerized, semi-continuously adding the monomers and the initiator. Conversions achieved was the same.

Copolymer No. 17 was produced under the same conditions but with a higher proportion of BA. It was observed that glass transition temperature T_g was lower (approximately 74°C).

Further results with regard to resistance to etching are indicated in **Table 5.** It may be deduced therefrom that, with copolymers No. 16 and 17, etch resistant layers of 3 µm thick were obtained. These layers may also be completely removed from the copper areas in alkaline aqueous solution within the indicated immersion time.

Furthermore, it was investigated how the copolymers produced are suited to formulate an anaphoretic varnish. For this purpose, varnishes were produced that had the following composition:

Polymer	10 % by weight

Solvent (MEK)	18.6 % by weight
Base (triethyl amine)	0.4 to 1.2 % by weight
Water	the rest

By varying the amount of the added base different pH of the varnishes were adjusted. Different conditions of the emulsion formed were obtained thereby: when pH of the varnish was below a certain transition point, the fluid obtained was turbid. Above this value, the emulsion was clear. At the transition point itself, the turbid fluid turned into a clear emulsion.

Varnishes were produced with copolymers No. 6, 16 and 20 and examined. **Fig. 2** shows the dependence of pH on the amount of triethyl amine [% by weight] added to the varnish. It can furthermore be seen from **Fig. 2** at which pH the fluid was turbid and at which pH a clear emulsion was obtained.

To form an anaphoretic varnish, a pH at which the emulsion was clear was respectively adjusted slightly above the transition point hinted at with vertical lines in **Fig. 2**.

To deposit the varnish by anaphoresis an experimental array was chosen in which a copper plate serving as an anode having an overall area of 6 cm^2 was arranged between two plates of special steel (stainless steel) serving as cathodes. The spacing anode/cathode was set to 2 cm. This array was arranged in a tank containing the emulsion. The volume of the fluid amounted to 100 cm^3. By means of a power supply, a voltage was applied between the anode and the cathodes, the current flowing being kept constant.

Table 3 shows, for different cathodic current densities, typical voltage/time dependencies for a varnish produced with copolymer No. 6. It has been found that the varnish produced with copolymer No. 16 exhibits a similar behavior.

By adjusting the cathodic current density, varnish layers produced with

copolymer No. 6 could be produced in a wide range of different thicknesses. By selecting the duration of deposition at a set cathodic current density layers of a certain thickness could be obtained.

After the varnish layers made from copolymer No. 6 had been deposited onto the copper anode, said copper anode was rinsed and dried in order to remove excess amount of the solvent (MEK) and of the base (triethyl amine) from the layer and to condense the layer.

Fig. 4 shows the results of the measurement of layer thickness for varnishes that were obtained with copolymer No. 6, the layers having been produced in this case with two different cathodic current densities.

After production, the layers were treated by heating at 95°C for 30 min. Temperature was 10°C above glass transition temperature T_g of this copolymer.

It may be seen from **Fig. 4** that layers of a thickness of merely from 1 to 2 µm could be obtained.

Resistance to etching of these layers was determined in further tests. Resistance to etching was tested with a solution the composition of which was as follows:

$FeCl_3$	30 % by weight
HCl	10 % by weight
Water	the rest

Temperature of the etching bath amounted to 40°C and etching time amounted to 1 min.

Table 6 indicates results obtained for varnishes with copolymer No. 6, the varnish layer having in this case been deposited with a cathodic current density

of j = 0.50 mA/cm².

Table 6 indicates, in addition to the copolymers required for the formulation of the varnish, the cut-off voltage (voltage at which deposition was terminated), the duration of deposition, the layer thickness determined and the resistance to etching.

Table 7 contains further results for the resistance to etching of various varnishes obtained with copolymer No. 6 that were deposited at a cathodic current density of j = 0.33 mA/cm².

Tables 6 and **7** show that the minimum thickness of the varnish layer with copolymer No. 6 amounted to from 2 to 3 µm, the anodic current density did not matter. This minimum thickness of the layer corresponded to the minimum thickness of the layers applied by spin-coating. Tests made with a varnish that had been produced with copolymer No. 16 yielded the same result.

Moreover, the layers that had been deposited by anaphoresis were examined by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surfaces of the layers were found to be rougher than the corresponding surfaces of the layers produced by spin-coating. The mean roughness of a layer of 2.9 µm thick determined by means of the AFM-technique amounted to 320 nm, whereas the mean roughness of a layer of 3.4 µm thick applied by the spin-coating technique amounted to 70 nm. The layers produced by anaphoresis were substantially of a column-shaped structure.

Then, tests were carried out to include an ablation amplifier in the varnish composition of copolymer No. 16. The ablation amplifier used was *trans*-benzylidene acetophenone at a concentration of 10 % by weight referred to the amount of copolymer. Inclusion of the ablation amplifier did not substantially influence emulsifying behavior of the copolymer. pH was only increased by

approximately 0.15 units. The characteristic remained substantially unchanged.

The following anaphoresis experiments were carried out using a varnish having the following composition:

Copolymer No. 16	10 % by weight
trans-benzylidene acetophenone	1 % by weight
MEK	18.6 % by weight
Triethyl amine	0.5 % by weight
Water	69.9 % by weight

pH of the emulsion was 7.84.

Layers of a thickness of 3.8 µm and 11.5 µm, resp., were deposited under the conditions mentioned hereinabove.

Ablation was then examined with an ultraviolet laser source on a plate of epoxy resin that was provided with a copper film of 10 µm thick and with a varnish layer of 3 µm thick applied thereon. For this purpose, a KrF laser with an output of 50 watt was employed. The focused laser beam was scanned across the coated surface. Energy density in the laser beam amounted to from 150 mJ/cm^2 to 200 mJ/cm^2. As a result the varnish layer was removed from the copper surface.

The copper laid bare in the process of laser structuring was removed at 45°C using an acid copper chloride etch solution having the following composition:

Copper chloride	80 to 160 g Cu^{2+} per liter
Hydrochloric acid	280 to 300 ml (HCl at 32 % by weight) per liter

A pattern consisting of copper circuit lines was formed. Subsequently, using a

2 % by weight solution of NaOH the varnish layer was completely removed from the base copper surface.

Images were taken with a scanning electron microscope in order to verify the etch result: the circuit lines had a very regular section: the circuit lines were trapezoid in shape and had a width of approximately 20 µm. The area of the circuit lines resting on the FR4 material was larger than the surface of the circuit lines. The flanks of the circuit lines were regular, straight and so steep that the undercut amounted to less than 2.5 µm. No notches, funnel-shaped etchings and other irregularities were observed. No etching tracks could be seen on the surface regions that were protected by the varnish layer during the etching process.

To determine the effect of the ablation amplifier, a varnish layer was applied over the whole surface of printed circuit board material by means of spin-coating, said layer having a thickness of 2.5 µm and containing the ablation amplifier in a concentration of 10 % by weight. Various regions of a layer thus produced were exposed to a varying number of laser pulses with a laser wavelength of 308 nm, a laser energy of 600 mJ and an energy density of 400 mJ/cm². Then, the exposed copper was etched. This allowed to determine how many laser pulses were needed to completely remove the polymer. **Table 8** reproduces the results of these tests.

In a further experiment additional emulsion varnishes were prepared from copolymer No. 16. The emulsions had the following compositions, different ablation amplifiers being used in each individual varnish:

Copolymer No. 16	10 % by weight
Ablation amplifier	1 % by weight
MEK	11.8 % by weight
Triethyl amine	0.5 % by weight
Water	76.7 % by weight

The varnish emulsions were applied to printed circuit board material at a cathodic current density of j = 0.50 A/cm^2. The cut-off voltage amounted to 80 V. As for the rest the deposition conditions corresponded to the respective conditions given hereinabove.

Thereafter the resist layers formed were ablated under the conditions described hereinabove. The number of laser pulses required for complete removal of the layers is given in **Table 9** for different ablation amplifiers.

Table 1:

Monomer	Copolymer No. 1 content [% by weight]	Copolymer No. 2 content [% by weight]	Copolymer No. 3 content [% by weight]	Copolymer No. 4 content [% by weight]	Copolymer No. 5 content [% by weight]
MAA	12.5	12.5	12.5	12.5	12.5
MMA	51.8	51.8	60.9	12.5	34.1
BA	28.5	28.5	19.4		
BMA				67.8	46.2
HEMA	7.2	7.2	7.2	7.2	7.2
AZDN	0.48	0.48	0.48	0.48	0.48
Conversion [%]	94.80	94.80	92.40	93.60	92.80
T_g [°C] estimated	50	50	70	50	70
T_g [°C] measured *)	81.2	81.5	99.9	83.1	89.3
T_g [°C] measured **)	68.7		63		
M_N [g/mol]		23,450	24,430	25,450	25,200
M_W [g/mol]		56,320	55,960	57,700	53,460
P_I		2.4	2.3	2.2	2.1

MAA: methacrylic acid
BMA: *n*-butyl methacrylate
BA: *n*-butyl acrylate
HEMA: 2-hydroxy ethyl methacrylate
MMA: methyl methacrylate
*) precipitated copolymer
**) dried copolymer from the solution

Table 2:

Monomer	Copolymer No. 6 content [% by weight]	Copolymer No. 7 content [% by weight]	Copolymer No. 9 content [% by weight]	Copolymer No. 10 content [% by weight]	Copolymer No. 11 content [% by weight]
MAA	12.5 (39.7)	12.5 (39.7)	12.5 (40.1)	12.5 (39.8)	12.5 (59.9)
MMA	60.9 (39.2)	51.8 (39.2)	45.3 (69.7)	12.5 (40.1)	45.3 (59.9)
BA	19.4	28.5	35		35
BMA				67.8	
HEMA	7.2 (33.1)	7.2 (33.1)	7.2 (39.8)	7.2 (40.1)	7.2 (81.5)
AZDN	0.48	0.48 (T0) + 0.24 (T4h)	0.3 (T0) + 0.2 (T3h) + 0.2 (T6h)	0.3 (T0) + 0.2 (T3h) + 0.2 (T6h)	0.3 (T0) + 0.2 (T3h) + 0.2 (T6h)
Conversion [%]	82.80	94.90	99.70	97.20	
T_g [°C] estimated	70	50	<50	50	<50
T_g [°C] measured *)	86	67.9	73	62	73.7
T_g [°C] measured **)	55		62.4	56	55.3
M_N [g/mol]	25,410	11,680	13,640	16,640	11,630
M_W [g/mol]	56,680	43,300	43,980	45,800	37,180
P_I	2.23	3.71	3.22	2.75	3.2

MAA: methacrylic acid
BMA: *n*-butyl methacrylate
BA: *n*-butyl acrylate
HEMA: 2-hydroxy ethyl methacrylate
MMA: methyl methacrylate
*) precipitated copolymer
**) dried copolymer from the solution

Table 3:

Copolymer No.	Thickness [µm]	Resistance to etching *)	Capacity of removal *)
3	9.3	+	+
3	6.1	+	+
6	6.4	+	+
6	5.4	+	+
9	10	Oxidation	+
9	10	Oxidation	+
10	5	Oxidation	Not possible
10	4.4	Oxidation	Not possible
11	7.4	Slight oxidation	-
11	4.6	Slight oxidation	-

*) „+": all right (for resistance to etching: no oxidation to be seen)

Table 5:

Copolymer No.	Thickness [µm]	Resistance to etching *)	Capacity of removal *)
16	5.28	+	+
16	4.04	+	+
16	3	+	+
17	5.36	+	+
17	4.04	+	+
17	3	+	+

*) „+": all right (for resistance to etching: no oxidation to be seen)

Table 4:

Monomer	Copolymer No. 13 content [% by weight]	Copolymer No. 14 content [% by weight]	Copolymer No. 15 content [% by weight]	Copolymer No. 16 content [% by weight]	Copolymer No. 17 content [% by weight]	Copolymer No. 20 content [% by weight]
MAA	12.5 (39.7)	12.5 (39.7)	12.5 (39.7)	12.5 (39.7)	12.5 (39.7)	12.5 (39.7)
MMA	60.9 (39.2)	60.9 (39.2)	60.9 (39.2)	60.9 (39.2)	51.8 (39.2)	60.9 (39.2)
BA	19.4	19.4	19.4	19.4	19.4	19.4
HEMA	7.2 (33.1)	7.2 (33.1)	7.2 (33.1)	7.2 (33.1)	7.2 (33.1)	7.2 (33.1)
AZDN	0.48	0.48	0.48	0.48 (semi-cont. 6h)	0.48 (semi-cont. 6h)	0.48 (semi-cont. 6h)
Semi-cont. for monomers	9h	6h	6h	6h	6h	6h
Conversion [%]	92.3	89.1	94.4	92.1	88.6	92.5
T_g [°C] measured *)	81	93	92	92.5	74	
T_g [°C] measured **)	67	50.7	85.5	68	68	
M_N [g/mol]	15,130	24,400	25,570	24,520	22,120	
M_W [g/mol]	38,470	54,200	69,410	55,240	52,400	
P_I	2.5	2.2	2.71	2.25	2.37	

MAA: methacrylic acid
HEMA: 2-hydroxy ethyl methacrylate
*) precipitated copolymer
**) dried copolymer from the solution

BMA: *n*-butyl methacrylate
MMA: methyl methacrylate

BA: *n*-butyl acrylate

Table 6:

Sample No.	Cut-off voltage [V]	Deposition time [sec]	Film thickness [µm]	Resistance to etching
13	2.6	12	0	poor
4	9.5	14.4	0	poor
14	9.0	16.8	0	poor
5	19.0	24	0.7	poor
6	28.6	24	1.55	satisfactory
7	38.1	26.4	1.9	satisfactory
8	47.6	40.8	2.65	good
9	57.1	50.4	4	good
10	66.6	74.4	5	good
11	71.4	100.8	8.6	good
12	71.9	144	11.5	good

Table 7:

Sample No.	Cut-off voltage [V]	Deposition time [sec]	Film thickness [µm]	Resistance to etching
16	19.0	50.4	0	poor
12	39.1	55.2	0.5	poor
9	52.4	57.6	0.8	poor
10	47.6	60	0.8	poor
6	66.6	64.8	1.7	poor
4	76.2	74.4	2	satisfactory
5	71.4	74.4	1.6	satisfactory
2	80.9	86.4	2.9	good
21	117.6	105.6	2.5	good
22	114.2	110.4	6.4	good
24	106.0	115.2	6.4	good
23	110.0	124.8	6.6	good
27	118.0	134	7.9	good

Table 8:

Copolymer No.	Ablation amplifier	Result
9	benzylidene acetophenone	7 pulses
9	2.4-dihydroxy benzophenone	7 pulses
10	*trans*-stilbene	> 90 pulses, no ablation
10	benzylidene acetophenone	6 pulses
10	2.4-dihydroxy benzophenone	6 pulses
9	without	> pulses, no ablation

Table 9:

Ablation amplifier	Thickness [µm]	Result
2.4-dihydroxy benzophenone	1.9	6 pulses
4-nitrophenol	2.1	4 pulses
pyrene	2.5	30 pulses
2.2'-dipyridyl amine	2.8	5 pulses
ω-nitrostyrene	1.8	15 pulses
without	2.5	> 100 pulses

Claims:

1. Method of forming a metal pattern on a dielectric substrate comprising the following method steps:

a) providing a substrate comprising a base metal surface;

b) applying a varnish layer to the substrate by means of an electrophoretic process,

c) ablating the varnish layer in at least parts of regions that do not correspond to the metal pattern to be formed, the base metal surface being laid bare by means of ultraviolet radiation;

d) etching of the base metal surface that has been laid bare,

wherein the varnish contains at least one ablation amplifier adjusted to ultraviolet radiation.

2. Method according to claim 1, **wherein** the at least one ablation amplifier is selected from the group comprising aromatic carbonyl compounds, polycyclic hydrocarbon compounds, heterocyclic compounds and aromatic nitro compounds.

3. Method according to one of the previous claims, **wherein** the ablation amplifier is selected from the group comprising derivatives of acetophenone, benzophenone, cinnamic acid, tropolone, further diphenylbutadienes and the derivatives thereof, chrysenes, diphenylfulvenes, dipyridyl amines, phenoxazines, 2-phenyl benzimidazoles, isoquinoline oxides, nitrophenoles, nitroanilines, ω-nitrostyrenes and *1.5*-dinitronaphthalines

4. Method according to one of the previous claims, **wherein** the ultraviolet radiation is generated by a laser.

5. Method according to one of the previous claims, **wherein** the ultraviolet radiation is generated by an excimer laser.

6. Method according to one of the previous claims, **wherein** the varnish layer is formed with an anaphoretic varnish.

7. Method according to one of the previous claims, **wherein** the varnish is formed with at least one copolymer produced by copolymerization of monomers, selected from the group comprising methacrylic acid, C_1 - C_2 alkyl methacrylate, C_3 - C_{10} alkyl (meth)acrylate and hydroxy alkyl methacrylate; the alkyl groups of which have 2 - 4 carbon atoms.

8. Method according to claim 7, **wherein** C_1 - C_2 alkyl methacrylate is methyl methacrylate; C_3 - C_{10} alkyl (meth)acrylate is butyl acrylate; and/or hydroxy alkyl methacrylate is 1-hydroxy ethyl methacrylate and/or 2-hydroxy ethyl methacrylate .

9. Method according to one of claims 7 and 8, **wherein** the copolymer is formed from monomers with the following amounts:

a) methacrylic acid: 1 - 25 % by weight
b) C_1 - C_2 alkyl methacrylate: 20 - 80 % by weight
c) C_3 - C_{10} alkyl acrylate: 1 - 50 % by weight
d) hydroxy alkyl methacrylate: 0 - 20 % by weight,

the sum of the aforementioned monomers amounting to a total of 100 % by weight.

10. Method according to one of claims 7 to 9, **wherein** the mean value by weight of the molecular weight M_W of the copolymer is set in the range of from 15,000 to 100,000 g/mol.

11. Method according to claim 10, **wherein** M_W is set in the range of from 50,000 to 60,000 g/mol.

12. Method according to one of claims 7 to 11, **wherein** the index of polydispersiveness P_I of the copolymer is set to a value in the range of from 1.5 to 3.5.

13. Method according to claim 12, **wherein** the value of P_I is set in the range of from 2.0 to 2.5.

14. Method according to one of the previous claims, **wherein** the varnish is anaphoretic and contains at least one base selected from the group comprising mono, di, trialkyl amines, monoethanol amine, morpholine, ammonia and sodium hydroxide.

15. Method according to one of the previous claims, **wherein** the varnish layer is removed from the based metal surface after method step d).

16. Electrophoretic varnish containing at least one ablation amplifier adjusted to ultraviolet radiation.

17. Electrophoretic varnish according to claim 16, **wherein** the at least one ablation amplifier is selected from the group comprising aromatic carbonyl compounds, polycyclic hydrocarbon compounds, heterocyclic compounds and aromatic nitro compounds.

18. Electrophoretic varnish according to one of claims 16 and 17, **wherein** the ablation amplifier is selected from the group comprising derivatives of acetophenone, benzophenone, cinnamic acid, tropolone, further diphenylbutadienes and the derivatives thereof, chrysenes, diphenylfulvenes, dipyridyl amines, phenoxazines, 2-phenyl benzimidazoles, isoquinoline oxides, nitrophenoles, nitroanilines, ω-nitrostyrenes and 1.5-dinitronaphthalines

19. Electrophoretic varnish according to one of claims 16 to 18, **wherein** the varnish is an anaphoretic varnish.

20. Electrophoretic varnish according to one of claims 16 to 19, **wherein** the varnish is formed with at least one copolymer produced by copolymerization of monomers, selected from the group comprising methacrylic acid, C_1 - C_2 alkyl methacrylate, C_3 - C_{10} alkyl (meth)acrylate and hydroxy alkyl methacrylate; the alkyl groups of which have 2 - 4 carbon atoms.

21. Electrophoretic varnish according to claim 20, **wherein** C_1 - C_2 alkyl methacrylate is methyl methacrylate; C_3 - C_{10} alkyl (meth)acrylate is butyl acrylate; and/or hydroxy alkyl methacrylate is 1-hydroxy ethyl methacrylate and/or 2-hydroxy ethyl methacrylate .

22. Electrophoretic varnish according to one of claims 20 and 21, **wherein** the copolymer is formed from monomers with the following amounts:

a) methacrylic acid: 1 - 25 % by weight
b) C_1 - C_2 alkyl methacrylate: 20 - 80 % by weight
c) C_3 - C_{10} alkyl acrylate: 1 - 50 % by weight
d) hydroxy alkyl methacrylate: 0 - 20 % by weight,

the sum of the aforementioned monomers amounting to a total of 100 % by weight.

23. Electrophoretic varnish according to one of claims 20 to 22, **wherein** the mean value by weight of the molecular weight M_W of the copolymer is set in the range of from 15,000 to 100,000 g/mol.

24. Electrophoretic varnish according to one of claims 20 to 23, **wherein** the index of polydispersiveness P_I of the copolymer is set to a value in the range of from 1.5 to 3.5.

25. Substrate coated with the electrophoretic varnish according to one of claims 16 to 24.