FORM 4

COMMONWEALTH OF AUSTRALIA

45964/85

PATENTS ACT 1952-69

594644

Convention Application for a Patent

PATENT OFFICE 100 ONE HUNDRED DOLLARS

PATENT OFFICE 100 ONE HUNDRED DOLLARS

LODGED AT SUB-OFFICE 9 AUG 1985 Sydney

~~I,~~ We SIEMENS AKTIENGESELLSCHAFT

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 9-1-90

of Wittelsbacherplatz 2,
D-8000 München 2,
Federal Republic of Germany

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 9-1-90

hereby apply for the grant of a Patent for an invention entitled

"A THERMOSTABLE POLYMER SYSTEM FOR MICROELECTRONIC APPLICATIONS WHICH CAN BE CROSS-LINKED BY IRRADIATION"

LODGED AT SUB-OFFICE
9 AUG 1985
Sydney

PATENT OFFICE 60 SIXTY DOLLARS

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which is described in the accompanying complete specification.
This application is a Convention Application and is based on the application numbered P 34 29 606.9

for a patent or similar protection made in

Federal Republic of Germany

on 10 August 1984

FEE STAMP TO VALUE OF
$ 265 ATTACHED
MAIL OFFICER

~~My~~ Our address for service is:

Care: SPRUSON & FERGUSON
PATENT ATTORNEYS
St. Martins Tower
31 Market Street ~~ESSO HOUSE, 127 KENT STREET~~
SYDNEY, NEW SOUTH WALES.
AUSTRALIA.

The Common Seal of Siemens Aktiengesellschaft was hereto affixed in the presence of

Siemens Aktiengesellschaft

Dated this 2nd day of August 1985

Drost
Prokurist

Dr. Fuchs
Prokurist

To:
The Commissioner of Patents

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

THE PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

AUSTRALIA CONVENTION STANDARD & PETTY PATENT DECLARATION

In support of the Convention Application made for a patent for an invention entitled:

Title of Invention

"A THERMOSTABLE POLYMER SYSTEM FOR MICROELECTRONIC APPLICATIONS WHICH CAN BE CROSS-LINKED BY IRRADIATION"

Full name(s) and address(es) of Declarant(s)

I/~~We~~ Peter Drost
Procurist

of Franziskanerstraße 14, D-8000 München 80
Federal Republic of Germany

do solemnly and sincerely declare as follows:–

Full name(s) of Applicant(s)

1. ~~I am/We are the applicant(s) for the patent~~

(or, in the case of an application by a body corporate)

1. I am/~~We are~~ authorised by Siemens Aktiengesellschaft Berlin und München

the applicant(~~s~~) for the patent to make this declaration on its/~~their~~ behalf.

2. The basic application(~~s~~) as defined by Section 141 of the Act was/~~were~~ made

Basic Country(ies) in Federal Republic of Germany

Priority Date(s) on 10 August 1984

Basic Applicant(s) by SIEMENS AKTIENGESELLSCHAFT

Full name(s) and address(es) of inventor(s)

3. ~~I am/We are the actual inventor(s) of the invention referred to in the basic application(s)~~

(or where a person other than the inventor is the applicant)

3. KLAUS BUDDE, FRIEDRICH KOCH and FERDINAND QUELLA

of Ottobrunner Str. 5, D-8025 Unterhaching; Schaidlerstrasse 10, D-8000, München 70 and Cramer-Klett-Str. 2, D-8014 Neubiberg all in Federal Republic of Germany (respectively)

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant(~~s~~) is/~~are~~ entitled to make the application are as follows:

Set out how Applicant(s) derive title from actual inventor(s) e.g. The Applicant(s) is/are the assignee(s) of the invention from the inventor(s)

The said applicant is the assignee of the actual inventors.

4. The basic application(~~s~~) referred to in paragraph 2 of this Declaration was/~~were~~ the first application(~~s~~) made in a Convention country in respect of the invention (~~s~~) the subject of the application.

Declared at Munchen Federal Republic of Germany this 25th day of June 19 85

Peter Drost
Signature of Declarant(s)

To: The Commissioner of Patents

SFP4 1/81

(12) PATENT ABRIDGMENT (11) Document No. AU-B-45964/85
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 594644

(54) Title
THERMOSTABLE POLYMER SYSTEM FOR MICROELECTRONIC APPLICATIONS

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(57) Claim

1. A process for the production of a multi-layered wiring laminate using a polymer system comprising an irradiation cross-linkable thermostable polymer for use in the manufacture of multi-layer wiring systems having a reaction product of a fluorinated linear oligomer having at least two reactive end groups per polymer molecule with radiation-sensitive substances, the process comprising the steps of

a) coating a metal foil, preferably of copper, with a layer of said polymer system;

b) producing a desired wiring structure by expOsing said layer to light through a suitable mask and dissolving away the unexposed parts of the polymer layer;

c) reinforcing exposed metal by electroplating; and

d) in the same way producng further wiring layers by coating, structuring and electroplating.

594644

FORM 10 SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

45964/85.

Class Int. Class

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant: SIEMENS AKTIENGESELLSCHAFT

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Complete Specification for the invention entitled:

"A THERMOSTABLE POLYMER SYSTEM FOR MICROELECTRONIC APPLICATIONS WHICH CAN BE CROSS-LINKED BY IRRADIATION"

The following statement is a full description of this invention, including the best method of performing it known to us.

SBR/JAP 0079F

ABSTRACT OF THE INVENTION

"A THERMOSTABLE POLYMER SYSTEM FOR MICROELECTRONIC APPLICATIONS WHICH CAN BE CROSS-LINKED BY IRRADIATION"

In order to achieve a low dielectric constant and to improve the continuous temperature resistance of radiation-sensitive synthetic resin lacquers, a polymer system is provided which contains as starting material for reaction with a radiation-sensitive material, a linear fluoropolymer having at least two reactive end groups per polymer molecule. Preferably, perfluorinated polyether compounds and perfluorinated alkanes are used. The product is used as a coating (2, 13, 4) for the production of multi-layer printed circuits and economises on through-bores and additional intermediate copper layers. A further field of application is integrated semiconductor circuits in the VLSI-technique for use as negative photo-resists.

(Fig. 2)

The present invention relates to thermostable polymer systems for microelectronic applications which can be cross-linked by irradiation.

It is known to produce printed multi-layer wiring by pressing thin-layer laminates which contain the appropriate wiring image, on to one another using adhesive films. The thin-layer laminates and adhesive films form insulating layers between the individual conductor path levels. After the formation of the multi-layer circuit boards, the wiring connections and contact points between the individual layers are produced by means of bores and subsequent through-contacting via these bores.

In order to avoid crack formations in the contact layer and in the intermediate layers, and possible de-lamination effects during soldering, or in the event of temperature changes, this process as described above has been improved by providing that both sides of the thin-layer laminates are covered with copper and then coated with a photo-resist. This resist, which may be either a negative or a positive resist, is covered with an appropriate mask, exposed to light and developed. The residual developed resin layers serve as a resist during the subsequent etching of the copper. When the unrequired copper has been removed by etching, the desired conductor image is formed to which the photoetch-resist adheres when a negative resist is used. These resists residues are removed, either using organic solvents, or mechanically, and the next layer is then applied.

In the case of structure formation by means of irradiation, it is necessary to differentiate between a low energy region (wavelength exceeding 100 nm) and a high energy region, for example X-rays, or electron rays. Naturally, the resolution of the step of exposure to light increases when radiation of a shorter wavelength is used. As disclosed in an article by A Ledwith "IEE Proceedings", Vol. 130, Part 1, No. 5, October 1983 on pages 245 to 251, the limits are about 1 μm for UV-radiation and about 80 Å for electron radiation.

Intervals between conductor paths of less than 20 μm are required in the construction of microelectronic components. Consequently, the material which is used must have a low dielectric constant. As disclosed in an article by A J Blodgett in "Spektrum der Wissenschaft", September 1983, pages 94 to 106, the dielectric constant should have a value of less than 3. It is stated in the same article that, in the case of highly integrated components, during operation a continuous high thermal stress, in the region of about 100°C, occurs.

~~It is an object of the present invention to provide~~ a polymer system which can ~~be cross-~~linked by exposure ~~to light and which is to have the following properties :~~

It is an object of the present invention to provide an improved process for the production of a multi-layered wiring laminate using a polymer system.

According to one aspect of the present invention there is disclosed a process for the production of a multi-layered wiring laminate using a polymer system comprising an irradiation cross-linkable thermostable polymer for use in the manufacture of multi-layer wiring systems having a reaction product of a fluorinated linear oligomer having at least two reactive end groups per polymer molecule with radiation-sensitive substances, the process comprising the steps of

a) coating a metal foil, preferably of copper, with a layer of said polymer system;

b) producing a desired wiring structure by expOsing said layer to light through a suitable mask and dissolving away the unexposed parts of the polymer layer;

c) reinforcing exposed metal by electroplating; and

d) in the same way producng further wiring layers by coating, structuring and electroplating.

It is preferable to have a polymer system which can be cross-linked by exposure to light and which is to have the following properties:

1. the dielectric constant to be less than 3;
2. the continuous temperature resistance to be greater than 100°C;
3. a short exposure time is desirable; if possible, times of less than 5 minutes at an intensity of 100 mw/cm^2 (for UV-curing);
4. it is to be suitable for multi-layer construction without intermediate copper layers.

A polymer material which has both the required high resolution, good structural stability, and the required thermal load stability, and can also be easily processed using conventional photolithographic processes, has not hitherto been described.

An article by C D Eisenbach in the journal "Angewandte Makromolekulare Chemie" 109/110 (1982), on pages 101 to 102, has described polyimide systems which do in fact exhibit good thermal properties after hardening but during hardening suffer a loss of about 40% in mass and therefore a strong shrinkage.

Moreover, the same article describes oligoquinoline systems which have very good electrical properties, but are insensitive during light exposure and also have intrinsic colourings.

A radiation-sensitive synthetic resin layer having a cinnamic acid epichlorhydrin-bisphenol A basis, capable of partly fulfilling the object of the present invention, has been proposed in German Patent Application P 34 24 119.1.

Good structural resolution and suitable electrical properties are achieved by the use of this polymer system; however, the thermal load stability is not as good as it should be.

A polymer system which fulfils the above-described requirements is provided by a thermo-stable polymer system. ~~the present invention, in accordance with which there is provided a thermostable polymer system~~ for microelectronic applications which can be cross-linked by irradiation, produced by reacting a linear fluoro-oligomers having at least two reactive end groups per molecule as starting material with a radiation-sensitive material.

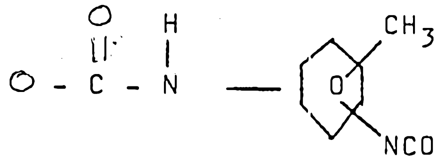
The starting materials may be perfluorinated ether compounds of the chemical formula

$$X - CF_2O - (C_2F_4O)_m - (CF_2O)_n - CF_2 - Y$$

and/or

$$Z - CF_2 - (C_2F_4O)_m - (CF_2O)_n - CF_2 - Z$$

where X and Y are $- CH_2OH$, $- COOH$, $- COCl$, $- NCO$, Z is an isocyanate of the formula



and m and n are greater than 2, preferably between 5 and 20. (The starting compounds are commercially available from the Montedison Company).

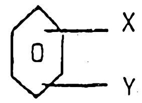
However, it is equally possible to use as the starting materials perfluorinated alkanes of the chemical formula X - $(CF_2)_m$ - X, where X is a hydroxyl group (OH), or iodine (I) and n is preferably a number between 3 and 25. (These starting compounds are commercially available from the Hoechst Company).

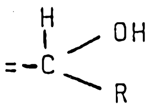
In order to form products which can be cross-linked by radiation, the perfluorinated starting material can be directly reacted. The direct reaction of the fluorinated starting material with cinnamic acid, acrylic acid, or methacrylic acid and the chlorides or derivatives thereof, such as furfurylacrylic acid chloride, produces products which can be cured by UV-radiation, whilst reaction with bifunctional carboxylic acids containing double bonds, such as maleic acid, or the corresponding anhydrides, such as maleic acid anhydride, leads to products which can be cured by X-rays.

In order to increase the size of the molecules and to promote the cross-linking which increases the stability, the fluorinated starting materials having at least two reactive end groups (for example COCl-groups) may first be linked to polyfunctional, non-radiation-reactive materials, and in a subsequent step be reacted with the radiation-sensitive substances.

Examples of polyfunctional materials with which the starting materials can be reacted are :-

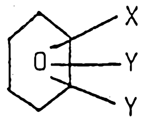
multifunctional alcohols, such as glycerol or pentaerythritol; poly-substituted phenols such as

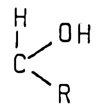


where X = -OH, Y = 

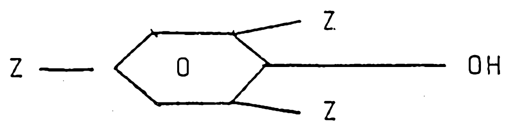
and/or Y = - COOH

and R = -H or an alkyl group; or



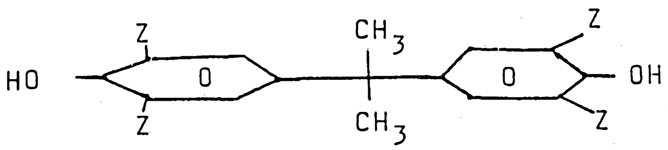
where X = - OH, Y = 

and R = - H or alkyl group; or



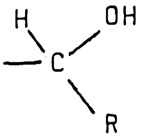
where Z = - CH_2OH; or

bisphenol - A - derivatives, such as

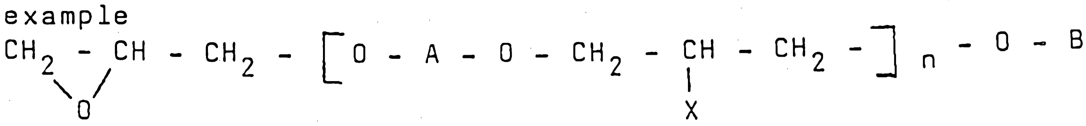


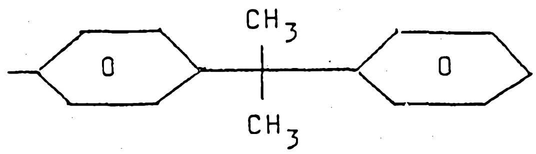
where Z = - CH_2OH; or

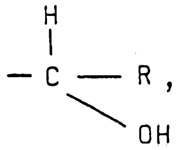
polymers which contain one or more epoxy groups per molecule and one or more groups of the formulae -OH

or 

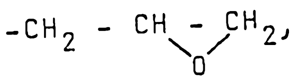
where R = - H or alkyl group, per polymer unit; for example



where A preferably = 

X = - OH or , R = - H or an alkyl group,

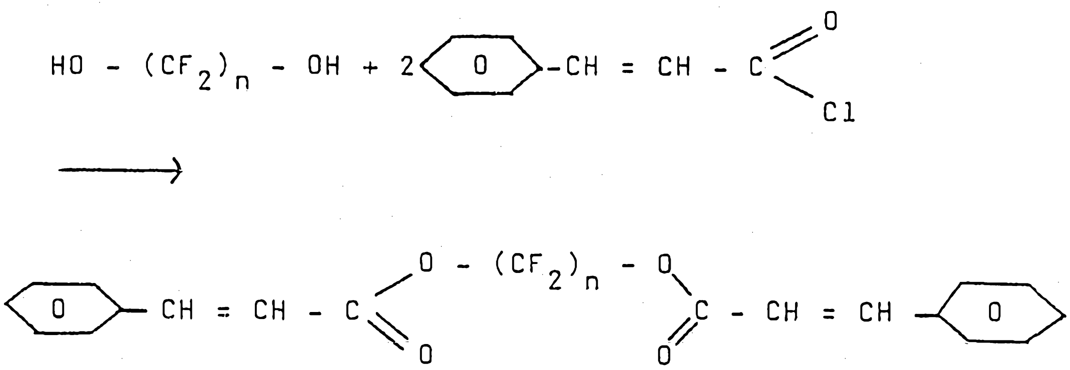
B = - H, an alkyl group, or a phenyl group, and in particular is

, and $n \geq 2$, preferably $10 \leq n \leq 30$.

Another possibility for obtaining the desired photo-cross-linkable polymer consists in first linking the fluorinated starting material with a material having photo-reactive groups and reacting the product A so formed, in a further step, with the polyfunctional photo-reactive materials. An exemplary embodiment is as follows :-

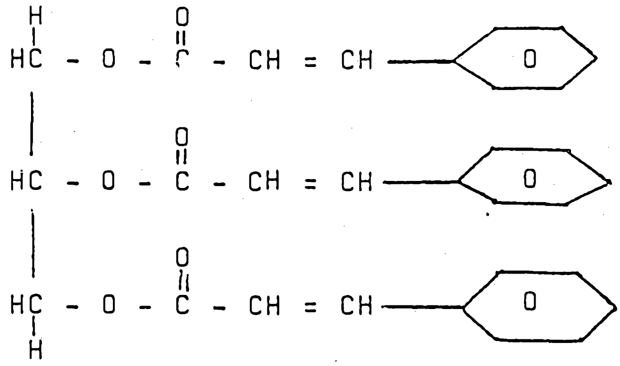
First Step:

Reaction of the fluorinated starting material with, for example, cinnamic acid chloride produces product A.

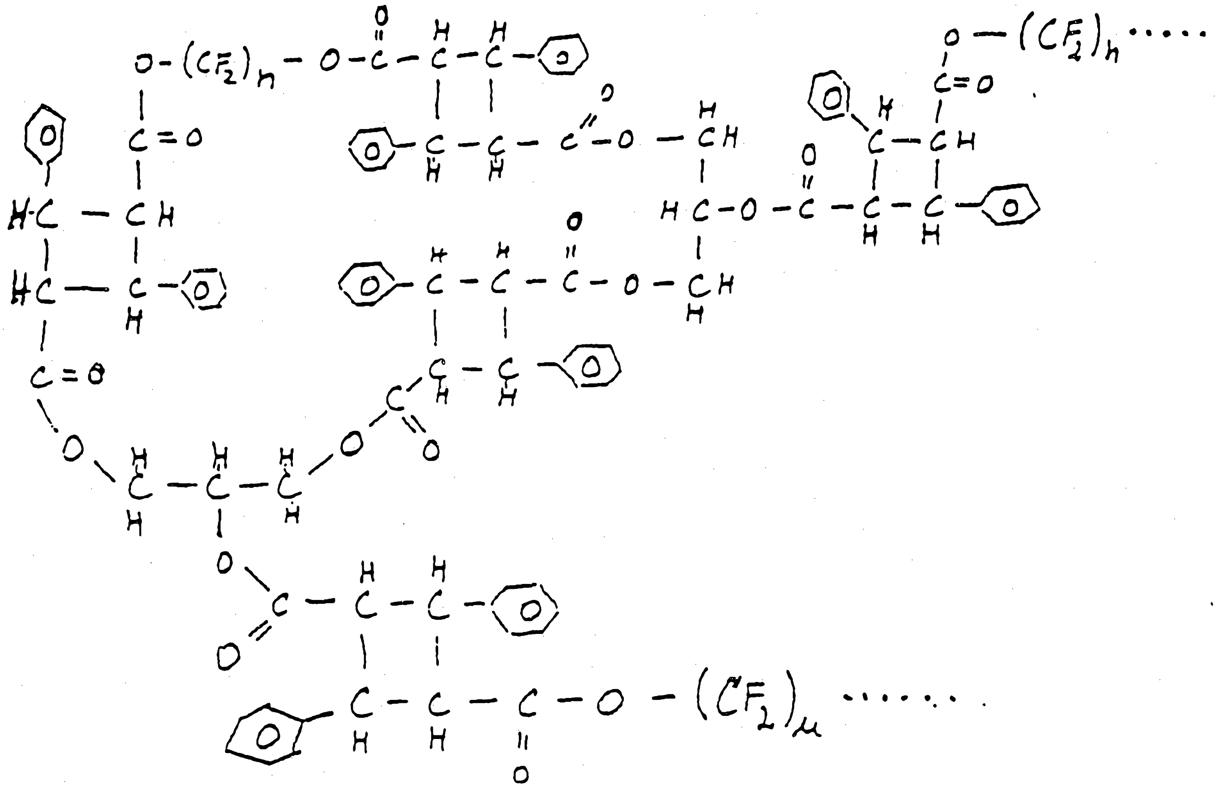

(A)

Second Step:

Reaction of A with product B consisting of 1 mol glycerol and 3 mol cinnamic acid


(B)

in the approximate ratio A:B = 10:1 produces an end product having approximately the following chemical formula:



The formula given above is only one of an infinite number of possibilities for the arrangement of A and B in the cross-linked product. Such variation occurs because

1) all the possible combinations

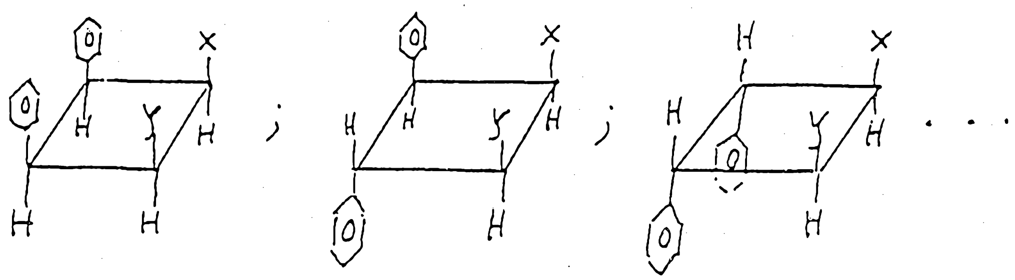
a) A - A
b) A - B } with A or B } with A or B ....
c) B - B

can occur. The product is 3-dimensionally, "infinitely" cross-linked.

2) an infinite number of stereoisomers can occur.

For A ≙ ⟨O⟩—CH = CH – X and B ≙ ⟨O⟩— CH = CH – Y,

a plurality of stereoisomers exist for each cyclobutane formation (cross-linking):



As a result of the various combinations under 1), an infinite number of different conformations for the product are produced.

In carrying out the reactions, known processes for epoxide conversion or condensation reactions, are used, such as those described, for example, by D. Braun "Praktikum der Makromolekularen Chemie", published by Hüthig and Wepf.

The product in accordance with the invention can be processed as a film by compression/lamination, preferably in the temperature range of from 40 to 200°C, with or without metallic intermediate layers, particularly of copper or copper alloys, or as a solute in a suitable solvent for coating substrates, in particular metal foils or sheets, by lacquering, spraying or dipping, and/or with further additives which serve as photo-initiators or stabilisers (with as photo-initiator for cinnamates, in particular, Michlers ketone, and for acrylates, for example, benzoin derivatives in concentrations of about 1 to 5%; and with stabilisers, for example, hydroquinone, in concentrations of about 0.1 to 0.5%).

The use of the polymer system in accordance with the invention to produce a multi-layer wiring will now be described with reference to an exemplary embodiment, and to the drawing, in which Figures 1 and 2 are similar schematic side sectional views to illustrate two stages in the production of a printed circuit. As a result of the properties of the polymer material, a new structure is obtained for the insulating carrier provided with electrical conductor paths and electrical through-contacts.

Referring to Figure 1, a copper foil 1 is used as carrier, on to which a layer 2 of the photo-cross-linkable insulating material according to the invention is applied, after the addition of, for example, Michlers ketone as photo-initiator, by dipping or spray-lacquering, in a layer thickness of, for example, 5 to 20 μm. The layer 2 is preferably exposed to UV-radiation and developed in such a way as to form the through-contacts which are to be produced within it, i.e. the terminal points of the chips, as openings 3 in the insulating layer 2. The irradiation is effected by a contact or projection process using a mask (not shown) which covers the region of the openings 3 in the layer 2 (when using a negative lacquer). The covered parts 3 are then dissolved away using an appropriate solvent, such as, for example, a chlorofluorohydrocarbon, for example, Freon (Registered Trade Mark) marketed by the Dupont Company, or Fluorinert (Registered Trade Mark) by the 3M Company), whereas in the case of the exposed parts 13 of the layer 2, a chemical cross-linking has taken place under the action of the radiation which prevents dissolution, so that these parts 13 remain as an insulating layer. After the production of the openings 3 for the through-contacts assigned to this first insulating layer 2 (13), the openings 3 are filled in association with the copper foil 1 which serves as carrier by metal plating using an electrically highly conductive material, for example copper (23 in Figure 2).

Referring now to Figure 2, a further layer 4 of the photo-cross-linkable insulating material in accordance with the invention is then applied to the insulating layer 13 which contains the through-contacts 23, in the same way as described with reference to Figure 1, into which layer conductor paths 5 and further through-contacts are introduced. The exposure and development of the layer 4 likewise takes place as described with reference to Figure 1. In addition to the openings 6 for the through-contacts 3 of the first insulating layer 2 (13), trench-shaped recesses 5 for the desired conductor paths are also produced in the second insulating layer 4, which recesses 5 are so arranged that at least one through-contact 23 of the first insulating layer 2 (13) projects into a recess 5. For the formation of the conductor paths, recesses 5 are provided with a metallisation by electroplating. Further through-contacts and conductor paths can then be applied by corresponding repetition of the above-described production steps. Between the formation of the individual layers, the arrangements are subjected to a drying and/or thermal curing process in the range from 40 to 150°C.

The novel wiring structures produced using the polymer system of the invention require no copper intermediate layers. The required high thermal loading stability is achieved by the polymer system itself; processing using known resist techniques is problem-free. This simplifies not only the production of such structures but also reliability in respect of electrical data.

For this reason, and also because of the very low dielectric constant and the good resolution, the polymer system in accordance with the invention is particularly suitable for use as a high-temperature-resistant negative resist for the production of integrated semiconductor circuits in VLSI-technology in which the production of dimensionally accurate microstructures and patterns is of great significance. The exposure time is comparable with that of other lacquer systems which can be used in this field. Further details can be obtained from the article by C. D. Eisenbach in the Journal "Die Angewandte Makromolekulare Chemie" 109/110 (1982) on pages 101 to 112.

The claims defining the invention are as follows:

1. A process for the production of a multi-layered wiring laminate using a polymer system comprising an irradiation cross-linkable thermostable polymer for use in the manufacture of multi-layer wiring systems having a reaction product of a fluorinated linear oligomer having at least two reactive end groups per polymer molecule with radiation-sensitive substances, the process comprising the steps of

a) coating a metal foil, preferably of copper, with a layer of said polymer system;

b) producing a desired wiring structure by expOsing said layer to light through a suitable mask and dissolving away the unexposed parts of the polymer layer;

c) reinforcing exposed metal by electroplating; and

d) in the same way producng further wiring layers by coating, structuring and electroplating.

2. A process as claimed in claim 1, wherein in step b. irradiation with UV-light is effected using a mask in a contact or projection process.

3. A process as claimed in claim 1, or claim 2, wherein a halogenated hydrocarbon, preferably a chlorofluorohydrocarbon, is used as solvent for said polymer layer.

4. A process as claimed in one of claims 1 to 3, wherein, prior to the formation of a following layer, an intermediate drying and/or annealing step is carried out in the temperature range of from 40 to 150°C.

~~5. A process of producing an integrated semiconductor circuit in the VLSI-technique, wherein a polymer system is used as a negative photo-resist~~.

~~6.~~ 5. A process of producing a multi-layer printed circuit using a polymer system said process substantially as hereinbefore described with reference to the drawings.

DATED this TWENTY FOURTH day of NOVEMBER 1989

Siemens Aktiengesellschaft

Patent Attorneys for the Applicants

SPRUSON & FERGUSON

nas/0115y

FIG 1

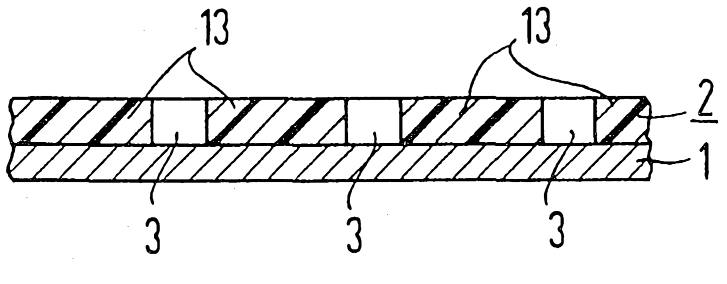


FIG 2