

Description

This invention relates to printed circuit boards. In another aspect this invention relates to the plating of poly(arylene sulfide) boards with a conductive metal to produce printed circuit boards. In yet another aspect this invention relates to the adhesion between a poly(arylene sulfide) substrate and a conductive metal plated thereon.

Printed circuit boards represent today a very substantial and rapidly growing market. They can be used, for example, in communications, instruments, controls, military, aerospace and business applications. Printed circuit boards other than copper clad laminates are typically manufactured by plating an epoxy or phenolic compound or some other heat-stable dielectric resin with a conductive metal such as, for example, copper. It is also known to plate flexible films of polyester and polyimide for this purpose. The successful production of printed circuit boards is a complex and sophisticated art that, though rapidly advancing, has yet to pass beyond the adolescence of its evolution.

Processing techniques known in the art include methods commonly identified as the subtractive method, the semiadditive method, the additive method and modifications and variations of the above. Electroless plating of the board (i.e. epoxy resin, phenolic resin, etc.) with a conductive metal is a crucial part of the overall process. After electroless deposition of a layer of the conductive metal onto the board the board is typically further plated with more of the conductive metal in accordance with conventional electroplating techniques to increase the thickness of the layer.

Absolutely essential to the success of the finished product is good adhesion of the conductive metal (which after processing represents the circuitry) to the board (i.e. epoxy resin, phenolic resin, etc.). In the absence of satisfactory adhesion the circuitry loses its structural integrity and the printed circuit board fails to perform its intended function. Those of skill in the art seek to discover new materials which can be used in the manufacture of printed circuit boards. The challenge is to find materials which will give good adhesion and yet possess other attributes (such as, for example, high temperature resistance) that are needed in printed circuit boards.

Poly(phenylene sulfide) is a material which possesses many of these desired attributes (such as, for example, high temperature resistance). The European patent application 23 313 describes a process for producing poly(arylene sulfide). The publication also mentions a wide variety of uses of this polymer including electrical parts, such as switches and electronic boards. To the limited extent poly(phenylene sulfide) has been considered at all it has been rejected by those of skill in the art as a material suitable for printed circuit board application, the belief being that satisfactory adhesion of the conductive metal to the poly(phenylene sulfide) cannot be obtained.

In accordance with this invention a printed circuit board and process for its production are provided as they are defined in the claims. The board is produced by electroless plating of a conductive metal onto a poly(arylene sulfide) board. The electroless plating step can be followed with an electroplating operation to deposit more conductive metal onto the board. By allowing the plated board to age, improved adhesion can be obtained.

In the preferred embodiment of this invention the poly(arylene sulfide) board is made of poly(phenylene sulfide) and the conductive metal is copper.

In accordance with this invention a printed circuit board is produced by electroless plating of a conductive metal such as, for example, copper onto a poly(arylene sulfide) board. The electroless plating step can be followed by an electroplating step to deposit more conductive metal onto the board.

Various techniques can be used to create the circuitry on the board. Subtractive methods can be used to remove undesired conductive metal from the plated board thus leaving the remaining conductive metal in the form and shape needed to define the desired circuitry. Additive methods can be used such that the conductive metal is plated only onto pre-selected portions of the board thus creating the desired circuitry upon deposition. These circuitry-creating techniques and modifications and variations thereof are known in the art and can be readily adapted to produce the printed circuit boards of this invention. This invention can also be practiced in combination with other circuitry-creating techniques yet to be developed or commonly practiced.

The key to this invention resides not in any particular circuitry-creating technique but rather more fundamentally in the recognition that poly(arylene sulfide) such as, for example, poly(phenylene sulfide), can be successfully used in the manufacture of printed circuit boards with satisfactory adhesion. One of the purposes of this disclosure is to teach how to obtain and recognize this success.

Electroless plating, also known as autocatalytic plating, is commonly defined as the deposition of a metallic coating or film onto a substrate by the interaction in solution of a metal salt and a chemical reducing agent, whereby this chemical reduction is catalyzed by the metal or alloy being deposited. In the practice of this invention the electroless metal can be any conductive metal capable of being used in an electroless plating operation. Copper and nickel are two such metals, each being especially well suited for this purpose. The term conductive metal is intended to include conductive alloys.

The substrate, for the purposes of this invention, is a poly(arylene sulfide) board. Poly(arylene sulfide) is used here to designate arylene sulfide polymers.

Without being limited thereto, uncured or partially cured poly(arylene sulfide) whether homopolymer, copolymer, terpolymer, and the like, or a blend of such polymers, can be used in the practice of my

invention. The uncured or partially cured polymer is a polymer the molecular weight of which can be increased by either lengthening of a molecular chain or by crosslinking or by combination of both by supplying thereto sufficient energy, such as heat. Suitable poly(arylene sulfide) polymers include, but are not limited to, those described in U.S. 3,354,129, incorporated by reference herein. Examples of poly(arylene sulfide) polymers suitable for purposes of my invention include poly(2,4-tolylene sulfide), poly(4,4'-biphenylene sulfide) and poly(phenylene sulfide). Because of its availability and desirable properties (such as high chemical resistance, nonflammability, and high strength and hardness) poly(phenylene sulfide) is the presently preferred poly(arylene sulfide).

For the purpose of understanding this disclosure and of interpreting the appended claims, it should be noted that the poly(arylene sulfide) board is comprised of poly(arylene sulfide) and can include, as desired, other materials such as, for example, fillers and processing aids. The presence of glass fibers is preferred because of their reinforcement utility. Calcium carbonate and calcium sulfate can also be present.

The board is a substrate which supports a conductive metal circuitry deposited thereon. Preferably the board is an injection molded board having molded-in holes.

Good adhesion requires careful preparation of the poly(arylene sulfide) board prior to the electroless plating operation. This preparation entails treating the normally smooth poly(arylene sulfide) board surface to create a coarser, rougher, more uneven or more irregular surface. This can be accomplished by chemically and/or physically altering the surface. Chemical etchants, grit blasting or mechanical abrading can be used for this purpose.

Poly(arylene sulfide) polymers such as poly(phenylene sulfide) polymers are well known for their strong chemical resistance. This strong chemical resistance makes selection of an effective chemical etchant very important. A strong oxidizing agent such as nitric acid alone or, even more advantageously, in combination with hydrofluoric acid can be used as the chemical etchant. The nitric acid not only causes chemical degradation of the polymer but also dissolves calcium carbonate, calcium sulfate and certain other fillers which can be found in the polymer. The hydrofluoric acid contributes by partially dissolving glass fillers in the polymer.

It is believed that chemical etchants improve adhesion in two ways. First, by altering the physical structure of the polymer surface (i.e. by making it coarser, rougher, etc.) a better mechanical "lock" of metal to the polymer surface is effected. Secondly, by chemically modifying the polymer surface to give a more hydrophilic surface, stronger chemical bonding of the metal to the polymer results.

Grit blasting can be used to physically remove a polymer-rich surface and thereby expose a more filled surface area to the chemical etchant. Grit blasting can be followed by ultrasonic cleaning to remove particles from the surface.

A catalyst is usually needed to initiate the electroless deposition process. The poly(arylene sulfide) board can be treated with the catalyst, for example a palladium-tin catalyst, prior to the electroless plating operation. Note that the need for the catalyst is short-lived since once initiated the electroless process is autocatalytic, i.e. catalyzed by the conductive metal (e.g. copper, nickel, etc.) deposited on the polymer surface.

The electroless plating operation itself can be conducted in a bath-containing tank. Preferably the tank is made of plastic or lined with plastic or made of passivated stainless steel to prevent plating of the tank itself. The electroless plating bath contains (typically in solution) the conductive metal (e.g. copper, nickel, etc.) to be deposited on the poly(arylene sulfide) board. The electroless plating operation can be carried out in accordance with conventional electroless plating methods and techniques.

Persons of skill in the relevant art possess sufficient knowledge of electroless plating that, when coupled with this disclosure, will enable them to practice this invention. More detailed and complete information concerning electroless plating is readily available to those who seek it. One such source of information, incorporated by reference herein, is the Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 8, pages 738 to 750 and 859-860.

Electroless plating is a relatively slow process in that it requires a relatively long time to build up a sufficiently thick deposit of conductive metal on the poly(arylene sulfide) board. For this reason it is preferred to terminate the electroless plating operation after the deposited conductive metal has obtained a thickness of at least about 20 microns and to use electroplating to supply the desired additional conductive metal. The thin deposit of conductive metal deposited during the electroless plating operation is referred to as an electroless film. The electroless film serves two purposes. First, it provides the poly(arylene sulfide) board with an electrically conductive surface needed to allow further deposition of conductive metal by electroplating. Secondly, the electroless film creates a bond between the poly(arylene sulfide) board and the electroplated conductive metal.

Electroplating is essentially the electrodeposition of an adherent metallic coating onto an electrode. This invention can be successfully practiced by employing conventional electroplating methods and apparatus. Typically, the poly(arylene sulfide) board having the electroless film can be positioned in a tank containing a plating solution (usually aqueous). The plating solution provides ions of the conductive metal to be deposited.

The conductive metal can be any conductive metal capable of being electroplated onto the electroless film coated poly(arylene sulfide) board. Examples of such metals include, but are not limited to, copper and

nickel. The term conductive metal is intended to include conductive alloys. The conductive metal need not be the same metal of which the electroless film is comprised.

Persons of skill in the relevant art possess sufficient knowledge of electroplating such that this knowledge coupled with this disclosure will enable them to practice this invention. More detailed and complete information concerning electroplating is readily available to those who seek it. One such source of information, incorporated by reference herein, is the Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 8, pages 826 to 869.

The electroplating operation continues until the desired amount of conductive metal has been deposited. The thickness of the total amount of conductive metal deposited (by both the electroless plating and electroplating operations) onto the poly(arylene sulfide) board will depend upon the intended application of the product (i.e. the printed circuit board). Typically, this thickness will be within the range of about 25 to about 100 microns (about 1 mil to about 4 mils).

The strength of the adhesion between the conductive metal and the poly(arylene sulfide) board is of crucial importance to the successful manufacture of the printed circuit board. If the adhesion strength is too low the detailed circuitry (which is comprised of the conductive metal) cannot maintain its structural integrity and the printed circuit board is useless for practical application. For this reason it is absolutely essential that the adhesion between the conductive metal and the poly(arylene sulfide) board be sufficiently strong to withstand the rigors to which printed circuit boards are typically subjected. This adhesion strength is commonly referred to, and measured in terms of, peel strength. To be useful at all for practical applications the printed circuit board must have sufficient metal to board adhesion strength such that the peel strength is at least about 4 pounds per inch. A good product, however, will be characterized by a peel strength of at least about 890 g/cm (5 pounds per inch) and preferably at least about 1070 g/cm (6 pounds per inch). In some instances, experiments conducted in accordance with this invention have yielded plated poly(arylene sulfide) boards having outstanding peel strengths of above 1250 (7) and even above 1430 g/cm (8 pounds per inch). The above peel strengths reflect values as measured in accordance with ASTM Test Method Part 9 B533-79 Procedure A which is the ASTM test for peel strength of metal-electroplated plastics. For the purposes of this disclosure and the appended claims this ASTM test method is modified to the extent that the test procedure is carried out irrespective of the thickness of the metallic coating.

It has been discovered that the adhesion between the conductive metal and the poly(arylene sulfide) board improves significantly with aging. Immediately after the electroplating operation (or electroless plating operation if electroplating is not employed) adhesion strength is at a minimum. If allowed to age the adhesion strength can reach a maximum level within a matter of a few days. After about 5 days a peel strength test will indicate this maximum level. Thus, properly plated poly(arylene sulfide) boards when initially tested for peel strength can give peel strength results far below the minimum acceptable level. But rather than discarding the boards and giving up, success can still be achieved by patiently allowing the boards to age until they exhibit peel strengths of at least about 714 g/cm (4 pounds per inch) or, for good results, of at least about 890 g/cm (5 pounds per inch).

The aging period can be accelerated by heating above ambient temperature, curing or drying the poly(arylene sulfide) board.

The following example is given to facilitate a full and complete disclosure of this invention. The example was chosen because of the good results obtained and because those results clearly demonstrate the utility of the above-described post-plating improvement of adhesion.

Example

Two poly(phenylene sulfide) boards, designated samples A and B, were used in this Example. Each board was about 10 cm×10 cm (4"×4") and had a thickness of about 4.8 mm (3/16"). The compositions corresponding to Samples A and B are set forth below:

	A	B
Poly(phenylene sulfide)	58.9%	35.0%
Glass fibers 3.2 mm (0.125") long×0.016 mm (0.00062") dia.	40.0%	35.0%
Calcium carbonate	—	28.75%
Lithium carbonate	1.0%	1.0%
Polyethylene	—	0.25%
Zinc stearate	0.1%	—

The percentages given above are weight percentages and are based upon total weight of the

composition. The poly(phenylene sulfide) in Sample A was characterized by a flow rate of 100—140 g/10 min. The poly(phenylene sulfide) in Sample B was characterized by a flow rate of 750—950 g/10 min. The above flow rates correspond to ASTM Test Method D 1238, Procedure B modified to use a temperature of 316°C (600°F) and a 5 kg weight.

5 The glass fibers reinforce the composition and impart strength to it. Calcium carbonate is used primarily to reduce material cost since it is less expensive than poly(phenylene sulfide) or glass fibers. Lithium carbonate is a mold corrosion inhibitor. Polyethylene and zinc stearate are conventional processing aids.

10 The experiment proceeded as outlined below except as otherwise indicated. To facilitate teaching the best mode of this invention as presently contemplated certain steps not actually performed in this particular experiment are also set forth below. These non-performed steps are designated as such.

Step 1—Grit blast:

Both boards were lightly grit blasted with 80 mesh aluminum oxide at 620 kPa (90 psi). The grit blasting removes gloss and roughens the board's surface.

Step 2—Ultrasonic cleaning:

20 The boards were immersed for 5 minutes in an ultrasonic bath containing a water solution of a nonsilicated soap, Microcleaner™ (sold by International Products Corp. of Trenton, New Jersey). The solution consisted of 74 ccm (2-1/2 oz) of Microcleaner per 3.8 l (gallon) of water.

Step 3—Rinse:

The boards were rinsed in tap water for 30 seconds at room temperature.

25 Step 4—Drying:

The boards were dried overnight in an oven at about 66°C (150°F).

Step 5—Acid etch:

30 The boards were immersed in a concentrated solution of hydrofluoric acid (reagent grade HF) for 5 minutes at room temperature.

Step 6—Rinse:

The boards were rinsed in de-ionized water for 30 seconds at room temperature.

35 Step 7—Acid etch:

The boards were immersed in concentrated nitric acid (reagent grade 67% HNO₃) for 15 seconds at 150°C.

Step 8—Rinse:

40 The boards were rinsed in de-ionized water for 30 seconds at room temperature.

Step 9—Ultrasonic cleaning

Same as step 2 above.

45 Step 10—Mechanical scrub:

The boards were scrubbed with scouring pads to remove powdery poly(phenylene sulfide) from the surface of each board.

Step 11—Rinse:

50 The boards were rinsed in de-ionized water for 30 seconds at room temperature.

Step 12—Preprep:

Though not actually employed in this experiment it is believed that this step is advisable since it reduces the risk of contamination of the catalyst bath. In accordance with this step the boards would be immersed in an aqueous 3 normal solution of hydrochloric acid.

Step 13—Catalyst and activation:

60 The boards were immersed in a solution for 3 minutes at room temperature. This solution consisted of (a) 1.9 l (1/2 gallon) de-ionized water, (b) 170 grams catalyst, and (c) 340 ml of 37% hydrochloric acid. The catalyst was a palladium-tin catalyst marketed by the McGean Chemical Co. under the trademark Besbon Catalyst DC-3.

Step 14—Rinse:

65 The boards were thoroughly rinsed 3 times in de-ionized water at room temperature. Stannous hydroxide forms during this step.

Step 15—Acceleration:

The boards were immersed at room temperature for 4 minutes in a solution consisting of (a) 0.95 l (1/4 gallon) de-ionized water, (b) 19 ml of 37% hydrochloric acid, and (c) 113 grams of D-25. D-25 is the trademark for a mild acid salt with fluorides marketed by the McGean Chemical Co. This step removes excess stannous hydroxide and thus exposes palladium nuclei for subsequent electroless deposition.

Step 16—Rinse:

The boards were rinsed in de-ionized water for 30 seconds at room temperature.

Step 17—Preprep:

Though not actually employed in this experiment it is advisable to immerse the boards at room temperature for 1-1/2 minutes in a preprep solution consisting of de-ionized water and 10% by volume FL-1. FL-1 is a proprietary product of the McGean Chemical Co. sold under the trademark Besbon FL-1.

Step 18—Electroless plating:

The boards were immersed in a solution consisting of (a) de-ionized water, (b) FL-1 (10% by volume), and (c) FL-2 (1.5% by volume). FL-1 and FL-2 are proprietary products sold by the McGean Chemical Co. of Cleveland, Ohio under the trademarks Besbon FL-1 and Besbon FL-2 for 12 minutes to produce a copper plating having a thickness of about 20 microns.

Step 19—Rinse:

The boards were rinsed in de-ionized water for 30 seconds at room temperature.

Step 20—Oven dry:

The boards were dried in an oven at 66°C (150°F) for 12 hours.

Step 21—Pretreatment:

Though not actually employed in this experiment this step is believed advisable. The boards can be given a quick dip into a 5% hydrosulfuric acid in water solution at room temperature.

Step 22—Electroplating:

The boards were immersed in an acid copper solution contained in a conventional electroplating tank having conventional electroplating apparatus. The acid copper solution consisted of (a) water, (b) 12 oz of copper sulfide per gallon of water, (c) 828 cc (28 oz) of sulfuric acid per gallon of water, (d) 25 ppm reagent grade HCl, and (e) 5 cc of 339 Brightener™ per liter of water. The 339 Brightener is a proprietary product of the McGean Chemical Company. A cathode clip was connected to the board. The rectifier (part of the conventional electroplating apparatus) was initially set at 1/2 amp. After 3 minutes of current the rectifier setting was raised to 2 amps and maintained there for about 2 hours to produce a copper plating having a total thickness of about 100 microns (4 mils).

Step 23—Rinse:

The boards were rinsed in tap water for 30 seconds at room temperature.

Step 24—Oven cure:

The boards were cured in an oven at 66°C (150°F) for 12 hours.

Step 25—Aging:

The boards were stored at room temperature for 20 days.

Each board was tested once for peel strength after step 23. The first board (A) was tested twice for peel strength after step 25. The second board (B) was tested 3 times for peel strength after step 25. The results of these tests are presented below in Table I.

TABLE I

Board	Initial peel strength (after step 23)	Peel strength after aging (after step 25)
First (A)	464 g/cm (2.6 lb/inch)	1457 g/cm (8.16 lb/inch) 1261 g/cm (7.06 lb/inch)
Second (B)	513 g/cm (2.87 lb/inch)	906 g/cm (5.07 lb/inch) 984 g/cm (5.51 lb/inch) 1088 g/cm (6.09 lb/inch)

The peel strength tests were made using a Chatillon pull tester Model DPP 5000 made by John

Chatillon and Sons, New York, New York. For each test, a strip 6 mm x 10 cm (1/4" by 4") was cut on the board. A 6 mm (1/4") long portion of the strip was peeled up from the board. Strapping tape was attached to both sides of the peeled up portion. The pull tester was hooked up to the strapping tape. Using this arrangement the strip was peeled from the board. The pull tester indicated peel strength in terms of g/cm (pounds per inch). This simple test was used to approximate the test results that would have been obtained with the ASTM test method.

The data in Table I show that for each sample the initial peel strength (and thus the initial adhesion of copper to the poly(phenylene sulfide) board) was unacceptable for printed circuit boards. However, after aging, the peel strength improved significantly to the levels needed to give a high quality printed circuit board.

Claims

1. A printed circuit board comprising a board of a polymeric material and a circuitry of a conductive metal deposited onto said board by electroless plating and, optionally, additional conductive metal electroplated onto said conductive metal deposited by electroless plating, characterized in that said polymeric material is poly(arylene sulfide) and in that the peel strength as measured by ASTM Test Method Part 9 B 533-79 Procedure A is at least about 0.7 kg/cm, more particularly at least about 0.9 kg/cm.

2. The printed circuit board of claim 1 characterized in that said poly(arylene sulfide) is poly(phenylene sulfide).

3. The printed circuit board of claim 1 or 2 characterized in that said conductive metal is copper or nickel.

4. The printed circuit board of any of claims 1 to 3 characterized in that said board is comprised of poly(phenylene sulfide) and glass fibers and, optionally, calcium carbonate.

5. A process for the production of a printed circuit board comprising (i) depositing a conductive metal onto said board by electroless plating and, optionally, (ii) electroplating additional conductive metal onto the conductive metal deposited in accordance with step (i), characterized by using a board of poly(arylene sulfide) and by aging the board after the electroless plating step (i) or the electroplating step (ii) and thereby improving the adhesion between the conductive metal and the poly(arylene sulfide).

6. The process of claim 5 characterized by allowing the plated board to age for at least 5 days and in particular until the adhesion between said conductive metal and said poly(arylene sulfide) board is so strong that the peel strength associated therewith is at least about 0.7 kg/cm, preferably at least about 0.9 kg/cm as measured in accordance with ASTM Test Method Part 9 B 533-79 Procedure A.

7. The process of claim 5 or 6 characterized in that, to accelerate said aging step, one of the following steps is performed with the plated board:

- a) said poly(arylene sulfide) board is at least partially dried,
- b) said poly(arylene sulfide) board is at least partially cured,
- c) said poly(arylene sulfide) board is heated above ambient temperature.

8. The process of any of claims 5 to 7 characterized in that prior to step (i) said board is subjected to a treatment with a chemical etchant, in particular with a strong oxidizing agent, more particularly with nitric acid, in particular wherein said poly(arylene sulfide) board is also etched with hydrofluoric acid.

9. The process of claim 8 characterized in that said poly(arylene sulfide) board is grit blasted prior to said treatment with a chemical etchant to remove loose material from the surface of said board.

10. The process of claim 9 characterized in that said board, after the grit-blasting step, is subjected to ultrasonic cleaning to remove loose material from the surface of said board.

11. Printed circuit board comprising a substrate of poly(arylene sulfide) and producible in accordance with a process of one of the claims 5 to 8.

Patentansprüche

1. Gedrucktes Schaltbrett mit einem Brett aus polymerem Material und einem Schaltkreis aus leitfähigem Metall, abgeschieden auf diesem Brett durch stromlose Plattierung und gewünschtenfalls weiteres leitfähiges Metall, elektroplattiert auf das leitfähige Metall, das durch stromlose Plattierung abgeschieden wurde, dadurch gekennzeichnet, daß das polymere Material Polyarylensulfid ist und dadurch, daß die Abziehfestigkeit gemessen nach ASTM-Testverfahren Teil 9 B 533-79, Verfahrensvariante A, zumindest etwa 0,7 kg/cm, und insbesondere zumindest 0,9 kg/cm beträgt.

2. Gedrucktes Schaltbrett nach Anspruch 1, dadurch gekennzeichnet, daß das Polyarylensulfid Polyphenylensulfid ist.

3. Gedrucktes Schaltbrett nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das leitfähige Metall Kupfer oder Nickel ist.

4. Gedrucktes Schaltbrett nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Brett Polyphenylensulfid und Glasfasern und gewünschtenfalls Calciumcarbonat enthält.

5. Verfahren zur Herstellung eines gedruckten Schaltbrettes bei dem (i) ein leitfähiges Metall auf das Brett durch stromloses Plattieren abgeschieden wird und gewünschtenfalls (ii) weiteres leitfähiges Material elektroplattiert wird auf das leitfähige Material, das nach Stufe (i) abgeschieden wurde, gekennzeichnet

Chatillon and Sons, New York, New York. For each test, a strip 6 mm×10 cm (1/4" by 4") was cut on the board. A 6 mm (1/4") long portion of the strip was peeled up from the board. Strapping tape was attached to both sides of the peeled up portion. The pull tester was hooked up to the strapping tape. Using this arrangement the strip was peeled from the board. The pull tester indicated peel strength in terms of g/cm (pounds per inch). This simple test was used to approximate the test results that would have been obtained with the ASTM test method.

The data in Table I show that for each sample the initial peel strength (and thus the initial adhesion of copper to the poly(phenylene sulfide) board) was unacceptable for printed circuit boards. However, after aging, the peel strength improved significantly to the levels needed to give a high quality printed circuit board.

Claims

1. A printed circuit board comprising a board of a polymeric material and a circuitry of a conductive metal deposited onto said board by electroless plating and, optionally, additional conductive metal electroplated onto said conductive metal deposited by electroless plating, characterized in that said polymeric material is poly(arylene sulfide) and in that the peel strength as measured by ASTM Test Method Part 9 B 533-79 Procedure A is at least about 0.7 kg/cm, more particularly at least about 0.9 kg/cm.

2. The printed circuit board of claim 1 characterized in that said poly(arylene sulfide) is poly(phenylene sulfide).

3. The printed circuit board of claim 1 or 2 characterized in that said conductive metal is copper or nickel.

4. The printed circuit board of any of claims 1 to 3 characterized in that said board is comprised of poly(phenylene sulfide) and glass fibers and, optionally, calcium carbonate.

5. A process for the production of a printed circuit board comprising (i) depositing a conductive metal onto said board by electroless plating and, optionally, (ii) electroplating additional conductive metal onto the conductive metal deposited in accordance with step (i), characterized by using a board of poly(arylene sulfide) and by aging the board after the electroless plating step (i) or the electroplating step (ii) and thereby improving the adhesion between the conductive metal and the poly(arylene sulfide).

6. The process of claim 5 characterized by allowing the plated board to age for at least 5 days and in particular until the adhesion between said conductive metal and said poly(arylene sulfide) board is so strong that the peel strength associated therewith is at least about 0.7 kg/cm, preferably at least about 0.9 kg/cm as measured in accordance with ASTM Test Method Part 9 B 533-79 Procedure A.

7. The process of claim 5 or 6 characterized in that, to accelerate said aging step, one of the following steps is performed with the plated board:

- a) said poly(arylene sulfide) board is at least partially dried,
- b) said poly(arylene sulfide) board is at least partially cured,
- c) said poly(arylene sulfide) board is heated above ambient temperature.

8. The process of any of claims 5 to 7 characterized in that prior to step (i) said board is subjected to a treatment with a chemical etchant, in particular with a strong oxidizing agent, more particularly with nitric acid, in particular wherein said poly(arylene sulfide) board is also etched with hydrofluoric acid.

9. The process of claim 8 characterized in that said poly(arylene sulfide) board is grit blasted prior to said treatment with a chemical etchant to remove loose material from the surface of said board.

10. The process of claim 9 characterized in that said board, after the grit-blasting step, is subjected to ultrasonic cleaning to remove loose material from the surface of said board.

11. Printed circuit board comprising a substrate of poly(arylene sulfide) and producible in accordance with a process of one of the claims 5 to 8.

Patentansprüche

1. Gedrucktes Schaltbrett mit einem Brett aus polymerem Material und einem Schaltkreis aus leitfähigem Metall, abgeschieden auf diesem Brett durch stromlose Plattierung und gewünschtenfalls weiteres leitfähiges Metall, elektroplattiert auf das leitfähige Metall, das durch stromlose Plattierung abgeschieden wurde, dadurch gekennzeichnet, daß das polymere Material Polyarylensulfid ist und dadurch, daß die Abziehfestigkeit gemessen nach ASTM-Testverfahren Teil 9 B 533-79, Verfahrensvariante A, zumindest etwa 0,7 kg/cm, und insbesondere zumindest 0,9 kg/cm beträgt.

2. Gedrucktes Schaltbrett nach Anspruch 1, dadurch gekennzeichnet, daß das Polyarylensulfid Polyphenylensulfid ist.

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4. Gedrucktes Schaltbrett nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Brett Polyphenylensulfid und Glasfasern und gewünschtenfalls Calciumcarbonat enthält.

5. Verfahren zur Herstellung eines gedruckten Schaltbrettes bei dem (i) ein leitfähiges Metall auf das Brett durch stromloses Plattieren abgeschieden wird und gewünschtenfalls (ii) weiteres leitfähiges Material elektroplattiert wird auf das leitfähige Material, das nach Stufe (i) abgeschieden wurde, gekennzeichnet



durch die Verwendung eines Brettes aus Polyarylsulfid und durch das Altern dieses Brettes nach der stromlosen Plattierung von Stufe (i) oder der Elektroplattierung (ii), wodurch die Haftung zwischen dem leitfähigen Metall und dem Polyarylsulfid verbessert wird.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß man das plattierte Brett wenigstens 5 Tage altern läßt, und insbesondere solange bis die Adhäsion zwischen dem leitfähigen Metall und dem Polyarylsulfidbrett so stark ist, daß die dem zugeordnete Abziehfestigkeit zumindest etwa 0,7 kg/cm, vorzugsweise zumindest etwa 0,9 kg/cm, gemessen gemäß ASTM-Testverfahren Teil 9 B 533-79, Verfahrensvariante A, beträgt.

7. Verfahren nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß zur Beschleunigung der Alterungsstufe einer der folgenden Schritte mit dem plattierten Brett durchgeführt wird:

- a) das Polyarylsulfidbrett wird zumindest teilweise getrocknet,
- b) das Polyarylsulfidbrett wird zumindest teilweise gehärtet,
- c) das Polyarylsulfidbrett wird über Umgebungstemperatur hinaus erhitzt.

8. Verfahren nach einem der Ansprüche 5 bis 7, dadurch gekennzeichnet, daß vor der Stufe (i) das Brett einer Behandlung mit einem chemischen Ätzmittel unterzogen wird, insbesondere mit einem starken Oxidationsmittel, besonders mit Salpetersäure, insbesondere wobei das Polyarylsulfidbrett auch mit Flußsäure geätzt wird.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das Polyarylsulfidbrett vor der Behandlung mit einem chemischen Ätzmittel sandgestrahlt wird, um loses Material von der Oberfläche des Brettes zu entfernen.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das Brett nach der Sandstrahlstufe einer Ultraschallreinigung unterzogen wird, um loses Material von der Oberfläche des Brettes zu entfernen.

11. Gedrucktes Schaltbrett mit einer Unterlage aus Polyarylsulfid und herstellbar nach einem Verfahren nach einem der Ansprüche 5 bis 8.

Revendications

1. Plaque de circuits imprimés comprenant une plaque d'une matière polymère et des éléments de circuit d'un métal conducteur déposé sur cette plaque par métallisation non galvanique, et si on le désire du métal conducteur supplémentaire appliqué électrolytiquement sur ce métal conducteur déposé par métallisation non galvanique, caractérisée en ce que cette matière polymère est un poly(sulfure d'arylène) et en ce que la résistance d'arrachement telle que mesurée par la méthode d'essai (ASTM-Partie 9 B 533-79 Mode opératoire A) est d'au moins environ 0,7 kg/cm, plus particulièrement d'au moins environ 0,9 kg/cm.

2. Plaque de circuits imprimés selon la revendication 1, caractérisée en ce que ce poly(sulfure d'arylène) est le poly(sulfure de phénylène).

3. Plaque de circuits imprimés selon les revendications 1 ou 2, caractérisée en ce que ce métal conducteur est le cuivre ou le nickel.

4. Plaque de circuits imprimés selon l'une quelconque des revendications 1 ou 3, caractérisée en ce que cette plaque est constituée de poly(sulfure de phénylène) et de fibres de verre et, si on le désire, de carbonate de calcium.

5. Procédé de production d'une plaque de circuits imprimés consistant (i) à déposer un métal conducteur sur cette plaque par métallisation non galvanique et, si on le désire, (2) à déposer électrolytiquement du métal conducteur supplémentaire sur le métal conducteur déposé conformément au stade (1), caractérisé en ce qu'on utilise une plaque de poly(sulfure d'arylène) et en ce qu'on fait vieillir la plaque après le stade de métallisation non galvanique (1) ou le stade de métallisation électrolytique (2) et en ce qu'on améliore ainsi l'adhérence entre le métal conducteur et le poly(sulfure d'arylène).

6. Procédé selon la revendication 5, caractérisé en ce qu'on laisse la plaque métallisée vieillir pendant au moins 5 jours, et en particulier jusqu'à ce que l'adhérence entre ce métal conducteur et cette plaque de poly(sulfure d'arylène) soit suffisamment forte pour que la force d'arrachement associée à celle-ci soit d'au moins environ 0,7 kg/cm, de préférence d'au moins environ 0,9 kg/cm, telle que mesurée conformément à la méthode d'essai ASTM Partie 9 B 533-79 Mode opératoire A.

7. Procédé selon la revendication 5 ou la revendication 6, caractérisé en ce que pour accélérer ce stade de vieillissement, on effectue un des stades suivants avec la plaque métallisée:

- a) cette plaque de poly(sulfure d'arylène) est au moins partiellement séchée,
- b) cette plaque de poly(sulfure d'arylène) est au moins partiellement durcie;
- c) cette plaque de poly(sulfure d'arylène) est chauffée au-dessus de la température ambiante.

8. Procédé selon l'une quelconque des revendications 5 à 7, caractérisé en ce qu'avant le stade (1), cette plaque est soumise à un traitement par un décapant chimique, en particulier par un agent oxydant fort, plus particulièrement avec de l'acide nitrique, en particulier dans lequel cette plaque de poly(sulfure d'arylène) est également décapée avec de l'acide fluorhydrique.

9. Procédé selon la revendication 8, caractérisé en ce que cette plaque de poly(sulfure d'arylène) est grenillée avec ce traitement par un décapant chimique pour éliminer la matière non adhérente de la surface de cette plaque.



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10. Procédé selon la revendication 9, caractérisé en ce que cette plaquette, après le stade de grenaillage, est soumise à un nettoyage par ultrasons, pour éliminer la matière non adhérente de la surface de cette plaquette.

11. Plaquette de circuits imprimés comprenant un substrat de poly(sulfure d'arylène) et pouvant être produite conformément à un procédé de l'une des revendications 5 à 8.

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