

## **Method and Device for a Forced Wet-Chemical Treatment of Surfaces**

### **TECHNICAL FIELD**

The invention relates to a method and device for a wet-chemical treatment of a surface of material by means of sprayed or sprinkled treatment fluid.

### **BACKGROUND OF THE INVENTION**

Plants for a wet-chemical treatment may be immersion plants or continuous processing plants. In using such plants, a person skilled in the art employs stationary, actuated or oscillating nozzles or nozzle pipes such that treatment fluid flows against the surface of a material to be treated. There is an intention that a sufficient result of the wet-chemical treatment is achieved as quickly as possible. In practice of surface treatment, such an intention is an antagonism since with increasing intensity of surface treatment, i.e. shorter treatment time, achievable results change for the worse.

A typical example for application for the treatment of surfaces is printed circuit technology. There are various processes in this technology where the inventive method and device may be applied favourably. This is for example washing or swilling, developing of a film or a resist, etching of copper, stripping of a film or a resist and metal resist etching. Such methods are usually carried out by means of spraying or sprinkling against a material to be processed. On the surface of the material, the necessary mass transfer occurs in corresponding diffusion layer. Such a mass transfer may be accelerated by means of increased spraying pressure, which results in a reduced amount of treatment time. However, in such a case unwanted side

effects emerge which unfavourably influence the precision of the treatment result. An example is etching of general structures on the surface of a material or etching of a conductive pattern of printed circuit boards. Areas not to be etched are covered by means of a film or resist. The resist is stable against etching fluid. If an etching by means of spraying or sprinkling of nozzles or nozzle pipes is performed such a treatment does not only occur in exposed areas of etching channels between resist covered areas but in flanks of etchings channels, too. The result is undercutting of the resist that can only be tolerated on a very small scale. Thus, with respect to dimensions and cross-sections of conductor tracks, the result of remaining structures is unpredictable. Especially in precision conductor technology (conductor track widths and spacings of approximately 120  $\mu\text{m}$  and less), a higher and reproducible precision of treatment results is required. Therefore, an unpredictable treatment of flanks of structures by means of other methods mentioned above is also not allowed. In general, in order to achieve the necessary precision of etched structures the treatment time is reduced, which, however, is not appreciated.

In DE 195 24 523 A1 a method and a device is described in order to solve such a problem as mentioned above occurring during wet-chemical treatment of surfaces. A fluid jet combined with cavitation bubbles is created at high pressure in specific nozzles. The fluid jet transports the necessary fresh mass to the diffusion layer on the surface of the material. There, the cavitation bubbles implode resulting in a mass transfer. This method is suitable for the above-mentioned applications and especially for the printed circuit technology. However, the technical complexity of the high pressure units is very high.

In DE 31 04 522 A1 an inhibitor for wet-chemical etching of structures is described wherein the inhibitor is added to an etching solution. The inhibitor

creates a protective skin for protection of the flanks of etching channels. It is described that the inhibitor reduces the reaction to the flanks. However, this method requires specific inhibitors for respective processes which restrains a general application of this method.

In DE 199 08 960 a further method for etching of layers of a flat carrier is described, wherein the thickness of the layer of one side is different from the thickness of the layer of the other opposing side. An individual treatment time for each side of the carrier is set and the treatment time is proportional to the thickness of the layer to be etched. This is carried out by temporary interruption of the processing if a shorter time in comparison with longest possible treatment time is necessary. The period for interruption may be zero in case of maximum layer thickness.

In DE 199 08 960 C2 it is described in paragraph [0021] that during each interruption of an etching process a temporary reetching occurs by adhering etching solution. A period of interruption that is shorter than the period where reetching takes place is not reasonable for this application. In general a thin layer may be etched in a reduced etching time. In case of reetching a periodic interruption is meaningful.

In DE 101 54 886 A1 a method for a reduction of etching at flanks of etching channels is described. The removal of metallic material is performed in two method steps. First, the metallic material is electrolytically removed by applying a pulsed electrical field. This etching happens preferably in depth direction of the etching channel wherein the flanks are attacked to a lower extent. After reaching a certain depth of the etching channels the electrical connections of some structures are disconnected. Therefore, the area on the base of such an etching channel has to be reetched in a further process that requires a further technical effort.

## BRIEF SUMMARY OF THE INVENTION

In view of such problems of the prior art, a primary object of the present invention is to provide a method and a device which allow a wet-chemical process for a precise treatment of structures on surfaces thereby achieving a short treatment time.

This and other objects of the invention can be accomplished by providing a method according to claim 1 and a device according to claim 15. Advantageous embodiments are described in the subclaims.

## BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is described in the following with reference to the appended drawings, in which:

Fig. 1 is a sectional view of a first embodiment of the device according to the present invention;

Fig. 2a is a front view of a second embodiment of the device according to the present invention wherein a first rotary interrupt means is illustrated;

Fig. 2b is a top view and side view of the first interrupt means illustrated in Fig. 2;

Fig. 3 is a sectional view of a third embodiment of the device according to the present invention;

Fig. 4 is a developed view of a part of the third embodiment of the device according to the present invention;

Fig. 5a is a side view of a fourth embodiment of the device according to the present invention in a first position;

Fig. 5b is a side view of a fourth embodiment of the device according to the present invention in a second position.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Fig. 1 shows a first embodiment of the device according to the present invention. An intensive stream or spray jet 2 of treatment fluid flows through an opening or nozzle 1 wherein the spray jet 2 is in a repeated manner and preferably regularly interrupted by an interrupt means 3 which is provided with openings. In this embodiment the cyclically interrupted spray jet 2 reaches the surface 5 of a material 6 to be treated wherein according to the invention the spray jet 2 impacts or impinges discontinuously against the surface 5 of the material 6. The spray jet 2 works as an effective jet 4 that is hydrodynamically pulsating. The fluid of the effective jet 4 is called in the following an effective fluid 8. The treatment fluid, which accumulates at the interrupt means 3 during a pulse pause and is not used at the moment, is called in the following a reactive fluid 9. This reactive fluid 9 is kept away largely from the surface 5 of the material 6 to be treated. This reduces adhering of treatment fluid on the surface 5 of the material 6. Thus, the dynamic influence of the interrupted and pulsating effective jet 4 is enhanced significantly during chemical treatment. On the surface 5 of the material 6 to be treated a permanent impact and breaking-through of the surface wetted with treatment fluid is achieved. Such an impact action substantially supports the real wet-chemical process by reducing the thickness of the diffusion layer. This hydrodynamic support is useful for all processes mentioned above including swill process. The treatment time is reduced up to 50 % by means of the impact action. The achieved precision during structure treatment is not influenced in a negative way which is a significant advantage and is very surprising since methods for forcing wet-chemical processes according to prior art have an unfavourable influence to the

quality of treatment results in general and the quality of etching channels in specific.

The cyclic interruption of the treatment jet is performed with a frequency, which is at least 0.5 Hz, favourably 10 Hz to 100 Hz or more. The ratio of impingement pulse time to impingement pause is at least 10:1 to 1:10, favourably 2:1 to 1:2 wherein the ratio is adjusted by means of a control device. The drive of the interrupt means may be performed electromotive, electromagnetic, pneumatic, hydraulic or by means of other actuator devices. The invention may be combined with other known measures for improvement of wet-chemical treatment results, e.g. with inhibitors in a treatment fluid.

The applicant applied the inventive method and device for etching of precision tracks on printed circuit boards. The result was a reduction of treatment time of approximately 33 % wherein no further undercutting of the resist was discovered in comparison with results achieved by methods according to prior art. In spite of the intensive etching process flanks in the etch channels remained unchanged. It is assumed that the impact effect on the base of the etch channel is much greater compared to the effect on the flanks of the structures. Furthermore, it is suspected that during pulse pauses on the one hand the treatment fluid does not flow to the surface of the material and on the other hand the treatment fluid can drain away from the etch channels. During the following etch pulse the treatment fluid remained in etch channels is free from pressure and the effective jet 4 penetrates the thinner diffusion layer up to a greater depth. Especially in precision conductor technology, so called HDI technology, the necessary depth of cutting of an etch channel achieves the width of the track. This is a big challenge for all processes of the printed circuit board technology. Fluid pressure on the flanks caused by the treatment fluid, as it is known in prior

art, is avoided by means of the inventive pulsating treatment of deep structured channels. Consequently, flanks of the structures are less wet-chemically treated compared with the base of the channels. Thus, by applying the inventive method it is possible to enhance significantly the precision of the wet-chemical treatment while significantly reducing the treatment time without loss of quality.

During etch experiments performed by the applicant the distance of the nozzles 1 to the surface 5 of the material 6 amounted to 100 mm. The flow rate of the treatment fluid through each of the taper nozzles having an apex angle of  $30^\circ$  amounted to 1.6 litres per minute at a pressure of 3 bar ( $300.000 \text{ N/m}^2$ ).

Fig. 2a illustrates a cross section of a tubular spraying device 10 that is equipped with several nozzles 1. Instead of nozzles, it is cheaper to provide the device 10 with holes having an opening diameter of e.g. 0.5 mm to 3 mm. The treatment fluid flows pressurized through the inlet 7 into the spraying device 10 and discharges pressurized the device 10 through the nozzles 1. The pressure can vary largely. The pressure can be 1.1 to 100 bar depending on the process, the dimensions of the structures and the positioning of the nozzles in relation to the lower side or the upper side of the material 6. A rotatable interrupt means as perforated disk 11 having holes or recesses is positioned in front of the nozzles 1. The perforated disk is provided with catches 12 that are exposed to a part of the spray jet 2 of the treatment fluid. Thereby, the perforated disk 11 is set in motion. The disk 11 interrupts the spray jet 2 so that the treatment fluid as effective jet 4 reaches in a pulsed manner the surface 5 of the material 6. In Fig. 2b a perforated disk is illustrated for two pairs of nozzles 1. Each pair of nozzle 1 is arranged at the spraying device 10 wherein each pair of nozzles 1 is differently inclined according to predetermined direction of rotation of perforated disk

11. In the perforated disk 11 there are openings 13 as holes or slots, as is illustrated in Fig. 2b.

According to a further embodiment, the interrupt means is a perforated or slotted strip arranged axially in front of the nozzles or holes extending along the whole length of the spraying device. The strip having openings is moved cyclically and in axial direction in order to interrupt the spray jet 2.

The spraying devices can be stationary located in a continuous processing plant with horizontal or vertical transport of the material 6 wherein the spraying devices are spaced 100 mm apart in transport direction. However, they can be movably arranged as is known in wet-chemical machines according to prior art. In this respect, the inventive spraying devices 10 in combination with interrupt means 3 may perform radially and/or axially swivelling or oscillating movements. Thereby, an accumulation of fluid on the surface of the material is reduced.

Fig. 3 illustrates a further embodiment of the invention wherein a spraying device 10 is provided with holes 14 or nozzles. A swivelling or rotary cylinder 15 is coaxially located to the spraying device 10 wherein the cylinder 15 is provided with slots 16 or holes arranged on the circumference of the cylinder and being congruent to the holes of the spraying device 10. The slots 16 or holes each are provided with a collar 17 at both sides thereof. Such a collar 17 serves as a contacting surface for the slightly inclined spray jet 2 whereby the cylinder is set in motion. Furthermore, the collars 17 accumulate the treatment fluid that should not reach the surface 5 of the material 6 during a pulse pause. The treatment fluid is laterally discharged from the cylinder. A slight inclination of the spraying device 10 and the cylinder 15 supports the lateral discharge of the treatment fluid. Therefore, this portion of fluid does not reach the surface 5 of the material 6. Thereby, the wetting of the surface

to be treated is reduced to a minimum so that the impact effect described above is improved. The inventive device is well suited for wet-chemical treatment of a surface of a material if this material is transported horizontally through a continuous processing plant. Treatment fluid that is not necessary is kept away from the surface of the item to be treated.

Bearings of the cylinder may be arranged at the end of the spraying device. For this, rolling bearings 18 can be used wherein such bearings have to be chemically resistant against a respective treatment fluid. Rolling bearings composed of plastics or ceramics are suitable.

The cylindrical interrupt means and other interrupt means may be set in motion by an electric, pneumatic or hydrodynamic drive. Thereby, the rotational speed is independent from the physical properties of the spray jet 2. Especially, high rotational speeds and a high pulse cycle may be adjusted, e.g. 1000 pulses per second. Thereby, the effective jet is transformed in a short cycle of highly accelerated drops of treatment fluid in case of high pressure in the inlet 7. This is particularly effective for the wet-chemical process. Due to the rough atmosphere, air-cooled motors or appropriately protected electric motors are applicable.

Electric and electronic control devices of the wet-chemical plant adjust process parameters depending on required treatment of the material. The same is with the adjustment of the interrupt frequency and the ratio between pulse time and pulse pause of the effective jet 4.

In Fig. 5a and Fig. 5b, a developed view of the cylinder 15 is illustrated in top view and in side view, respectively. A bridge or web 19 may be arranged between nozzle positions in order to stabilize the cylinder 15 provided with slots 16 so that spray jet 2 is not hindered. On the base of an area of the

cylinder 15 where the treatment fluid is accumulated an elastic item as damper 20 may be inserted. This damper 20 reduces an uncontrolled splashing of the treatment fluid when the fluid hits onto the inside wall of the cylinder 15. In addition, this accelerates the lateral discharge of the treatment fluid from the cylinder 15.

In Fig. 5a and Fig. 5b a nozzle 1 and an interrupt means 3 as vibrating lamina 21 is illustrated. This elastic machine element is mounted in a fixed point 23. The interrupt means is arranged in front of the nozzle 1 such that the spray jet 2 hits the upper end of the lamina 21 whereby the spray jet 2 is diverted. Thereby, the lamina 21 is bent in direction to the spray jet 2 so that an outlet 22 in the lamina 21 is positioned in the jet direction, see Fig. 5b. The outlet 22 opens the path to the surface of the material 6 to be treated. The effective jet of the treatment fluid abruptly reaches the material 6. Simultaneously, the dynamic pressure on the lamina 21 is reduced. Thereby, the lamina 21 returns abruptly into its starting position as illustrated in Fig. 5a. In this position, the spray jet 2 of the treatment fluid is diverted as reactive jet and is collected by a collection channel 24. The treatment fluid, which should not reach the surface of the material, is diverted laterally and transversally to the spraying device by the collection channel 24. The collection channel 24 extends parallel to the surface 5. This embodiment of the present invention is suitable for a treatment at both sides of a material horizontally transported. The elastic properties and dimensions of the lamina and the hydrodynamic conditions of the treatment fluid determine the optimum pulse frequency of the wet-chemical treatment.

The interrupt means according to this embodiment is also suited for an accommodation in the nozzle itself in case of respective small dimensions. Using nozzles provided with such an interrupt means or with a similar interrupt means, the discharge of treatment fluid during a pulse pause is

prevented. Therewith, these nozzles are furthermore suited to be placed on upper side of a horizontally transported material.

According to a further embodiment of the invention, an additional suction device is provided for an exhaust of treatment fluid reflecting from the surface 5 of the material 6. Therewith, a fluid accumulation on the surface 5 of the material 6 is prevented and unnecessary residue of fluid is avoided so that undercutting of conductor tracks is further reduced.

The description is given for purposes of illustration and explanation. It will be apparent to those skilled in the relevant art that changes and modifications may be made to the invention described above without departing from its scope or spirit.

## LIST OF REFERENCES

- 1 nozzle, opening
- 2 spray jet of the treatment fluid
- 3 interrupt means
- 4 effective jet, pulsating jet
- 5 surface to be treated
- 6 item
- 7 inlet
- 8 effective fluid
- 9 reactive fluid
- 10 spraying device
- 11 perforated disk
- 12 catch
- 13 opening
- 14 hole
- 15 cylinder
- 16 slot
- 17 collar
- 18 rolling bearing
- 19 bridge
- 20 damper
- 21 lamina
- 22 outlet
- 23 fixed point
- 24 collection channel

## CLAIMS

1. Method for a wet-chemical treatment of a surface (5) of a material (6), especially a printed circuit board, wafer or hybrid material by means of a treatment fluid in an immersion plant or continuous processing plant, wherein the treatment fluid is transported as spray jet (2) towards the material (6), characterized in that a spray jet interrupt means (3) is displaced such that the spray jet (2) impinges discontinuously on the surface (5) of the material (6).
2. Method according to claim 1, characterized in that the spray jet (2) is created by means of a nozzle (1), wherein the treatment fluid hits on the interrupt means (3) that is arranged in front of the nozzle (1), inside of the nozzle (1) or behind the nozzle (1), related to the flow direction of the treatment fluid.
3. Method according to claim 1 or 2, characterized in that the displacement of the interrupt means (3) is achieved by means of rotational, swivelling or linear movement.
4. Method according to any of the claims 1 to 3, characterized in that the discontinuous impingement of the spray jet (2) on the material (6) is performed cyclically, wherein an interrupt frequency of at least 0.5 Hz, especially 10 Hz to 100 Hz is achieved.
5. Method according to any of the claims 1 to 4, characterized in that the spray jet (2) flows with overpressure and with up to 1000 drops per second against the material (6).
6. Method according to any of the claims 1 to 5, characterized in that the discontinuous impingement of the spray jet (2) on the material (6) occurs with a ratio of impingement pulse time to

impingement pulse pause that ranges from 10:1 to 1:10, preferably from 2:1 to 1:2.

7. Method according to any of the claims 1 to 6, characterized in that the interrupt means (3) as rotary, oscillating or vibrating element is set in rotary, oscillating or vibrating motion by the treatment fluid that is discharged with overpressure.
8. Method according to any of the claims 1 to 7, characterized in that the displacement of the interrupt means (3) is performed by an electric, pneumatic or hydrodynamic drive.
9. Method according to any of the claims 1 to 8, characterized in that flat material is treated on one side only or at both sides simultaneously.
10. Method according to any of the claims 1 to 9, characterized in that operating parameters such as a frequency of the discontinuous impingement of the spray jet (2) to the material (6) or the ratio between impingement pulse time and impingement pause of the spray jet (2) to the material (6) is adjusted by means of a control device.
11. Method according to any of the claims 1 to 10, characterized in that the wet-chemical treatment of printed circuit boards is achieved by means of washing, swilling, development of a film or a resist, etching of copper, stripping of a film or a resist and metal resist etching.
12. Method according to any of the claims 2 to 11, characterized in that the nozzles (1) cooperate with swivelling devices or oscillating devices.
13. Method according to any of the claims 1 to 12, characterized in that the interrupt means (3) collects treatment fluid and keeps the fluid away from the surface (5) of the material (6) to be treated.

14. Method according to claim 13, characterized in that the treatment fluid is kept away from the surface (5) of the material (6) by means of a collar (17) or a collection channel (24) or a suction device.
15. Device for wet-chemical treatment of a surface of a material (6) such as a printed circuit board, a wafer or a hybrid material by means of a treatment fluid in an immersion plant or continuous processing plant, wherein by means of the device the treatment fluid is transportable as a spray jet (2) towards the material (6), characterized in that the device comprises at least one spray jet interrupt means (3) that is displaceable such that the spray jet (2) may be discontinuously guided to the material (6).
16. Device according to claim 15, characterized in that the spray jet (2) is achievable by means of a nozzle (1), and the interrupt means (3) is arranged in front of the nozzle (1), inside of the nozzle (1) or behind the nozzle (1), related to the flow direction of the treatment fluid.
17. Device according to any of the claims 15 or 16, characterized in that the displacement of the interrupt means (3) is achievable by means of a rotary, swivelling or linear movement.
18. Device according to any of the claims 15 to 17, characterized in that the displacement of the interrupt means (3) is achievable by means of a force that is exerted by the spray jet of the treatment fluid flowing with overpressure.
19. Device according to any of the claims 15 to 18, characterized in that the displacement of the interrupt means (3) is achievable by means of an electric, pneumatic or hydrodynamic drive.

20. Device according to any of the claims 16 to 19, characterized in that the interrupt means (3) is arranged between the nozzle (1) and the material (6) to be treated and the interrupt means (3) is formed as a cylinder (15) which is rotatable or swivelling.
21. Device according to any of the claims 16 to 20, characterized in that the interrupt means (3) is formed in the nozzles (1) as vibrating or oscillating element.
22. Device according to any of the claims 15 to 21, characterized in that the interrupt means is formed as vibrating lamina (21).
23. Device according to any of the claims 15 to 22, characterized in that the interrupt means (3) is formed as rotary perforated disk (11) having openings.
24. Device according to any of the claims 15 to 23, characterized in that the interrupt means (3) comprises a collection channel (24) extending parallel to the surface to be treated wherein the channel (24) is suited to collect portions of the spray jet (2) which are not necessary.
25. Device according to any of the claims 15 to 24, characterized in that the interrupt means (3) is formed as cyclically moved strip having openings.
26. Device according to any of the claims 15 to 24, characterized in that the interrupt means (3) is formed such that the treatment fluid may be collected and kept away from the surface (5) of the material (6).
27. Device according to claim 26, characterized in that collected treatment fluid may be kept away from the surface (5) of the material (6) by means of a collar (17) or a collection channel (24).

28. Device according to any of the claims 15 to 27, characterized in that the device comprises a suction device for an exhaust of the treatment fluid.