

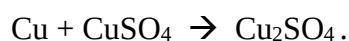
Etching device for the electrolytic etching of copper

The invention relates to an etching device for electrolytic etching of copper on an etching material, for example printed circuitry or circuit boards.

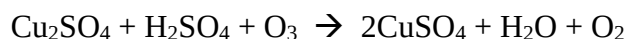
In order to electrolytic etch copper on printed circuitry or a printed circuit board, it is possible to use a copper-containing etching fluid. In that case, the etching fluid comprises, for example, copper(II) chloride, which is reduced in contact with the copper on the circuitry or circuit board to copper(I) chloride. This reaction product hardly attacks the copper at all and has to be regenerated back to copper(II) chloride if the etching fluid is to be reused. Such a regeneration can be achieved by means of hydrochloric acid and hydrogen peroxide, giving chlorine gas. Alternatively, etching of copper can also be achieved on the basis of sulfuric acid electrolytes. For this purpose, a copper(II) sulfate is dissolved in sulfuric acid and is reduced after a reaction with copper to be etched away to give copper(I) sulfate. After addition of hydrogen peroxide, it is possible to generate a copper(II) sulfate again, such that an etching fluid regenerated in this way can be supplied again to the etching material.

It has been found that such etching methods are difficult to manage in practice, since copper acts catalytically on the hydrogen peroxide in the acidic solution and breaks it down, and so the consumption of the hydrogen peroxide is relatively high. In addition, high evolution of heat occurs, and so energy-intensive cooling is required.

Another approach is to use not hydrogen peroxide but ozone gas as the oxidizing agent for copper(I) ions in the electrolyte. Divalent copper reacts with the copper to be etched away in sulfuric acid electrolyte according to the following equation to give copper(I) sulfate:



The copper(I) sulfate obtained is then oxidized with sulfuric acid and ozone gas according to the following equation back to copper(II) sulfate:



Relatively little heat of reaction arises here, and so the expenditure on cooling is considerably lower. Moreover, no chlorine gas is formed, but instead oxygen, which is associated with lower risks in an etching device.

Etching devices working by this method are known. With increasing demands on the miniaturization of the conductor tracks on printed circuitry or circuit boards, however, it has been found that it is difficult to achieve narrow and sharply bounded intermediate spaces between conductor tracks by etching continuously over a prolonged processing time.

It is therefore an object of the invention to provide an etching device with which it is possible to etch a large amount of copper continuously with a small amount of etching fluid, and it is also possible to achieve fine and sharp contours of conductor tracks with high flank steepness.

The object is achieved by the subject matter of independent claim 1. Advantageous developments of the invention are the subject of the dependent claims.

The inventive etching device for electrolytic etching of copper on an etching material comprises:

- a first mixing device set up to receive an acidic electrolyte containing copper ions and an oxygen gas or ozone gas, in order to form a first liquid/gas mixture which can be passed out of a first outlet of the first mixing device into a connecting line coupled thereto,
- a vessel containing a vessel liquid,
- a second mixing device arranged within the vessel and surrounded by the vessel liquid, the second mixing device having a suction orifice in order to suck in the vessel liquid present in the region of the suction orifice, and the second mixing device being connected to the connecting line and set up to pass the first liquid/gas mixture and the vessel liquid sucked in into a constriction zone of the

second mixing device, such that the vessel liquid sucked in can mix with the first liquid/gas mixture and thus form a second liquid/gas mixture, and the second mixing device having a second outlet through which the second liquid/gas mixture can flow out and mix with the vessel liquid present in the region of the second outlet, and

- a vessel outlet line set up to supply the vessel liquid present therein to the etching material provided in an etching module.

The inventor has recognized that it is not sufficient simply to mix an acidic electrolyte containing copper(I) ions and copper(II) ions with oxygen gas, an ozone gas or an oxygen/ozone gas mixture. Although oxidation of copper(I) ions to copper(II) ions does take place theoretically, the amount of divalent copper in the existing etching devices decreases with increasing circulation of the electrolyte. Thereafter, the etching action of the electrolyte decreases to an ever greater degree, until the results of the etching operations are no longer satisfactory. This is the starting point of the invention: in the inventive etching device, there is very intensive mixing of the oxygen gas or ozone gas supplied with the acidic electrolyte, such that a high concentration of gas microbubbles of oxygen gas or ozone gas are formed. The effect of this is that a large amount of copper(I) ions can be oxidized back to copper(II) ions in the electrolyte, this being achieved after only a single run through the etching device. It is thus possible firstly to achieve a high efficiency in the regeneration of the electrolyte. Secondly, with such an etching device having a continuously high concentration of copper(II) ions, it is possible to achieve rapid and sharply contoured etching even in very narrow recesses between copper conductor tracks.

The mixing of the gas with the electrolyte is firstly achieved by means of a first mixing device set up to receive an acidic electrolyte containing copper ions and an oxygen gas or ozone gas, in order to form a first liquid/gas mixture. This results in a first contact between copper(I) ions and oxygen or ozone gas, such that a portion of the copper(I) ions can be oxidized at this early stage.

In order to oxidize a sufficient amount of monovalent copper, by means of the inventive etching device, the first mixing device is connected by a connecting line to a second

mixing device, to which the first liquid/gas mixture is supplied. The second mixing device is arranged within a vessel and is surrounded by a liquid present in this vessel. The second mixing device has a suction orifice in order to suck in the vessel liquid present in the region of the suction orifice. The second mixing device, according to the invention, is set up such that the first liquid/gas mixture and the vessel liquid sucked in are passed into a constriction zone, such that the vessel liquid sucked in comes into intensive contact with the first liquid/gas mixture and the two mix with one another, forming a second liquid/gas mixture.

The second liquid/gas mixture exits the second mixing device at an outlet envisaged therefor, and the second liquid/gas mixture, after passing through the constriction zone, is decompressed and exits at high velocity according to the Bernoulli equation. In doing so, it entrains a portion of the vessel liquid present in the region of the outlet, resulting in mixing between the second liquid/gas mixture and the vessel liquid present there. The vessel liquid is an acidic electrolyte comprising copper ions. The constriction zone in the second mixing device and the decompression in the region of the outlet of the second mixing device again result in significant mixing between electrolyte and gas, such that a large number of gas microbubbles can form. The gas microbubbles achieve oxidation of a large amount of copper(I) ions with the acidic electrolyte to give copper(II) ions.

The liquid/gas mixture which has formed in this way and is enriched with copper(II) ions can then be tapped off at a vessel outlet line and be supplied to the material to be etched.

Preferably, the first mixing device is a Venturi nozzle and more preferably a liquid jet gas compressor. In the case of such a nozzle or such a compressor, the electrolyte can be supplied as the motive stream and the oxygen gas or ozone gas as the suction stream. The mixing is intensive without moving parts, such that a low-maintenance mixing device is possible. A Venturi nozzle or a liquid jet gas compressor is additionally relatively inexpensive as a purchasable component.

In one embodiment of the invention, the second mixing device is arranged in the lower half of the vessel and the vessel outlet line is arranged above the second mixing device. This

achieves the effect that the mixture of second liquid/gas mixture with the vessel liquid present at the outlet of the second mixing device can be sucked in again by the suction orifice of the second mixing device and is mixed once again in the second mixing device. In the case of multiple repetition of this operation, there is very intensive and prolonged mixing of the fluids, such that ever more gas microbubbles of oxygen gas or ozone gas are formed. Only a relatively small portion of the gas then ultimately arrives at the vessel outlet line, which can pass the mixture to a material to be etched.

Preferably, there is a distance of at least 1 meter between the vessel outlet line and the second mixing device. It is thus possible to reliably achieve multiple circulation of the vessel liquid through the second mixing device. More preferably, the vessel has a height of at least 1.5 meters with a volume of at least 400 liters of vessel liquid. The result of this is that the vessel liquid flows repeatedly through the second mixing device and circulates in the vessel for at least two minutes, such that a large number of gas microbubbles is produced.

In a further embodiment, the first mixing device is capable of accommodating at least 100 liters per minute of acidic electrolyte and at least 50 liters per minute of oxygen gas or ozone gas. Thus, given the customary sizes of a circuit board and an etching module, a sufficient amount of copper(I) ions formed therein can be oxidized in a single cycle back to copper(II) ions.

Further advantages and features of the invention are explained with reference to the following figures, which show:

Figure 1 a schematic diagram of one embodiment of the inventive etching device;
and

Figure 2 a schematic diagram of the flow conditions in a vessel of the etching
device according to figure 1.

Figure 1 shows, in greatly simplified form and in schematic view, an etching device 100 according to a preferred embodiment of the invention. The etching device 100 has a first mixing device 1, which has a first inlet 2 to receive an acidic electrolyte 3 containing copper ions. By means of a second inlet 4, a gas 5 in the form of oxygen gas, ozone gas or oxygen/ozone gas mixture can be passed into the first mixing device 1 so as to effect mixing with the electrolyte 3. The result of this mixing operation is a first liquid/gas mixture 6 which can leave the first mixing device 1 at a first outlet 7.

The first liquid/gas mixture 6 is then passed through a connecting line 8 to a second mixing device 10 arranged in a vessel 11. The vessel is filled with a vessel liquid 12, which is an acidic electrolyte comprising copper ions. The second mixing device 10 has at least one suction orifice 13. Through this suction orifice 13, it is possible to suck in a vessel liquid 14 present in the region of the suction orifice. In the second mixing device 10, a zone 15 is provided, in which there is a constriction of the flow cross section, resulting in good mixing of the first liquid/gas mixture 6 and the vessel liquid 14, such that a second liquid/gas mixture 16 is formed. At a second outlet 17 of the second mixing device 10, the second liquid/gas mixture 16 then exits at high velocity. In doing so, it entrains a vessel liquid 18 present in the region of the second outlet 17 and mixes with this liquid.

Figure 2 shows, in a simplified and highly schematic view, a mixing operation of this kind between the second liquid/gas mixture 16 and the vessel liquid 18 present around the second outlet 17. The flow arrows indicate that a majority of the vessel liquid flows several times toward the suction orifice 13 of the second mixing device 10, in order to mix there with the first liquid/gas mixture 6 flowing out of the connecting line 8. This leads to a large amount of gas microbubbles distributed in the vessel liquid 12. Only a relatively small portion of the vessel liquid 12 mixed intensively and provided with gas microbubbles in this way flows upward at the edge of the vessel to a vessel outlet line 19 arranged above the second mixing device 10.

As apparent from Figure 1, the vessel outlet line 19 then passes the liquid/gas mixture to an etching module 30, where an etching material such as a circuit board 31 can be etched. This involves reduction of copper(II) ions to copper(I) ions. The liquid comprising

copper(I) ions and copper(II) ions present in the etching module 30 then passes into a return line 32 in which the liquid, supported by a pump 33, is supplied back to the first mixing device 1, such that the mixing operation and the regeneration of the etching liquid can start again.

List of reference numerals:

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| 1 | first mixing device |
| 2 | first inlet |
| 3 | electrolyte |
| 4 | second inlet |
| 5 | oxygen gas or ozone gas |
| 6 | first liquid/gas mixture |
| 7 | first outlet |
| 8 | connecting line |
| 10 | second mixing device |
| 11 | vessel |
| 12 | vessel liquid |
| 13 | suction orifice |
| 14 | vessel liquid in the region of the suction orifice |
| 15 | constriction zone |
| 16 | second liquid/gas mixture |
| 17 | second outlet |
| 18 | vessel liquid in the region of the outlet |
| 19 | vessel outlet line |
| 30 | etching module |
| 31 | circuit board |
| 32 | return line |
| 33 | pump |
| 100 | etching device |

Claims

1. An etching device for electrolytic etching of copper on an etching material, comprising:
 - a first mixing device set up to receive an acidic electrolyte containing copper ions and an oxygen gas or ozone gas, in order to form a first liquid/gas mixture which can be passed out of a first outlet of the first mixing device into a connecting line coupled thereto,
 - a vessel containing a vessel liquid,
 - a second mixing device arranged within the vessel and surrounded by the vessel liquid, the second mixing device having a suction orifice in order to suck in the vessel liquid present in the region of the suction orifice, and the second mixing device being connected to the connecting line and set up to pass the first liquid/gas mixture and the vessel liquid sucked in into a constriction zone of the second mixing device, such that the vessel liquid sucked in can mix with the first liquid/gas mixture and thus form a second liquid/gas mixture, and the second mixing device having a second outlet through which the second liquid/gas mixture can flow out and mix with the vessel liquid present in the region of the second outlet, and
 - a vessel outlet line set up to supply the vessel liquid present therein to the etching material provided in an etching module.
2. The etching device as claimed in claim 1, wherein the first mixing device is a Venturi nozzle or a liquid jet gas compressor.
3. The etching device as claimed in either of claims 1 and 2, wherein the second mixing device is arranged in the lower half of the vessel and the vessel outlet line is arranged above the second mixing device.
4. The etching device as claimed in any of the preceding claims, wherein there is a distance of at least one meter between the vessel outlet line and the second mixing device.

5. The etching device as claimed in any of the preceding claims, wherein the vessel has a height of at least 1.5 meters with a volume of at least 400 liters of vessel liquid.
6. The etching device as claimed in any of the preceding claims, wherein the first mixing device is capable of accommodating at least 100 liters per minute of acidic electrolyte and at least 50 liters per minute of oxygen gas or ozone gas.