

ETCHANT FORMULATIONS AND USES THEREOF

FIELD

The invention relates to etchant formulations. More particularly but not exclusively it
5 relates to etchant formulations useful in, but not limited to, the manufacture of flexible circuits and to a method of etching.

BACKGROUND

Flexible circuits are pliable alternatives to rigid printed circuit boards. As the electronics
10 industry moves towards requiring thinner, lighter, flexible and more functionally integrated products demand for flexible circuitry increases. These circuits are often used as they allow the more rapid construction of a device in addition to their ability to conform and twist during the assembly and/or operation of the products.

Flexible circuits may be made by a number of suitable methods such as an additive,
15 subtractive, additive-subtractive and semi-additive process. In additive flexible circuit manufacturing, the process may include pretreatment of the substrate (generally a polymeric film such as polyimide) to remove water and to enhance adhesion between the substrate and the circuitry. Following the pretreatment, a tie layer metal or metal alloy is
20 typically deposited on the substrate. Typically the tie layer is subsequently sputtered with a seed metal layer of the circuit metal and then a flash layer of this metal is electroplated. A resist mask is then defined using photolithography. The metal traces of the circuitry are electroplated at areas where the resist has been removed. The resist is then stripped and the exposed portion of the flash metal layer is etched to electrically isolate the traces. Finally
25 the exposed portion of the tie layer is also etched away to provide complete electrical isolation between the metal traces.

The tie layer acts as a bonding medium between the substrate and the metal traces forming the circuit. Copper (hereafter Cu) is a metal commonly used to form the circuitry. The tie
30 layer also has a variety of other functions such as a corrosion resistance medium and a facilitator in flex-chip bonding without affecting the substrate.

During the etching of the tie layer, care is to be taken to remove as much of the tie layer as possible without attacking the metal trace.

An etchant may be tie layer and tie layer-thickness specific. An etchant which works for thinner tie layers may not be suitable for thicker tie layers. A change in the etching parameters or the etchant composition may be required if an etchant that is suitable for thinner tie layer is to be used on thicker tie layers.

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The tie layer thickness may be represented by the optical transmittivity (OT) values, which is a measure of transparency of the substrate. The OT of the tie layer is the difference between the OT of the substrate before and after the tie layer sputtering. While the thinner tie layer will show higher OT values due to the low surface coverage on the substrate, the thicker tie layers will show lower OT values due to the high surface coverage.

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SUMMARY OF THE INVENTION

There are a number of considerations when selecting a tie layer etchant. An etchant with an aqueous chemistry capable of attacking the tie layer with minimal attack on the metal traces is one of them. In general, it is difficult to find an etchant that preferentially attacks the tie layer without etching the metal traces.

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Another consideration is that there should be minimal attack of the substrate, which would otherwise degrade and have an adverse effect on the circuit reliability. Furthermore, in recent years, tie layer thicknesses have increased to optimize bonding and barrier properties. Thus a further consideration is selecting an etchant capable of etching thicker tie layers (such as those of 70% and 50% OT) in an acceptable timeframe.

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According to a first aspect of the invention there is provided an etchant formulation comprising an inorganic acid and an organic compound with at least one carboxylic acid group (-COOH) or its salt.

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Optionally the etchant formulation further includes a source of nitrate ions.

The concentration of the inorganic acid in the etchant formulation is less than about 20 weight % (hereafter wt %), alternatively in the range of about 7 to about 14 wt %, with less than about 10 wt % of the organic compound, alternatively in the range of about 4 to about 8 wt %.

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There is optionally a source of nitrate ions, at less than about 10 wt %, alternatively in the range about 4 to about 8 wt %.

Another embodiment of the etchant formulation comprises sulphuric acid (hereafter H_2SO_4), acetic acid (hereafter CH_3COOH) and potassium nitrate (hereafter KNO_3) with
 5 concentration of H_2SO_4 in the range of about 7 to about 14.5 wt %, CH_3COOH in the range of about 4 to about 9 wt % and KNO_3 in the range of about 4 to about 8 wt %.

According to a second aspect of the invention there is provided a method of etching of a
 10 metal or metal alloy comprising the steps of :

provision of a metal or metal alloy, and
 exposing the metal or metal alloy to an etchant formulation comprising an
 inorganic acid at a concentration less than about 35 wt % and an organic
 compound with carboxylic acid group or the salt thereof at a concentration
 15 less than about 21 wt %, for a period of time t , and at an etchant temperature
 T .

Suitably the etchant formulation comprises H_2SO_4 in the range of about 7 to about 14.5 wt
 %, CH_3COOH in the range of about 4 to about 9 wt % and KNO_3 in the range of about 4 to
 20 about 8 wt %.

In one embodiment the metal or metal alloy is a tie layer, the method comprising the steps
 of:

a) provision of a substrate,
 25 b) formation of a tie layer on the substrate,
 c) provision of a metal on one or more regions on the tie layer,
 d) etching of the tie layer using the etchant formulation of the invention to provide
 an etched product.

30 Suitably the etchant formulation is as previously discussed.

In a preferred embodiment the tie layer is one of nickel chrome (hereafter NiCr) or nickel
 chrome oxide (hereafter NiCrO_x), the metal is Cu and use of the etchant formulation results

in minimal damage to, or dissolution of, the Cu. This may be evidenced by less than around 5% loss in thickness and/or less than 1 micrometer undercut of the metal layer.

The method may be appropriate for tie layer thicknesses generally in the range of 10 to 500 nanometers, and in step (d) the temperature T of the etchant generally in the range of 50 to 90°C (more suitably about 75°C), and with the time taken to etch the tie layer, t less than 90 seconds (more suitably less than around 60 seconds).

In one embodiment step (c) may include a step of providing a layer of metal on one or more regions of the tie layer (by a process selected from, for example, vapour deposition, sputtering, electroplating and electroless plating), followed by a step of patterning the layer of metal using a lithographic technique (such as photolithography).

Suitably the step of patterning the layer of metal may include the steps of applying a photoresist, exposing one or more portions of the photoresist to actinic radiation through a mask and developing either the unexposed portions or the exposed portions of the photoresist with an appropriate solvent (ie both positive and negative are appropriate), and removing the exposed portions of the layer of metal with an appropriate etchant. This step of patterning the layer of metal results in the exposure of one or more regions of the tie layer and one or more of these regions is/are etched in step (d).

In one embodiment the method of the invention may further include a step of treating the etched product with an alkaline solution following the step of etching the tie layer.

According to a further aspect of the invention there is provided a flexible circuit prepared according to a process which includes the method as described above.

According to a further aspect of the invention there is provided a flexible circuit wherein during the preparation of which, a tie layer is etched using an etchant formulation comprising less than about 20 wt %, alternatively about 7 to about 14 wt % of H₂SO₄, less than about 10 wt %, alternatively about 4 to about 9 wt % of CH₃COOH and less than about 10 wt %, alternatively about 4 to about 8 wt % of KNO₃.

According to a further aspect of the invention there is provided a method of preparing an etchant formulation comprising the steps of mixing H₂SO₄, CH₃COOH and KNO₃ to

achieve an etchant formulation with concentrations generally less than about 20 wt %, alternatively about 7 to about 14 wt % of H₂SO₄, less than about 10 wt %, alternatively about 4 to about 9 wt % of CH₃COOH and less than about 10 wt %, alternatively about 4 to about 8 wt % of KNO₃.

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Definitions

As used herein the term “carboxylic acid group” denotes both the aliphatic and aromatic compounds with a -COOH group or its salt.

10 As used herein the phrase “minimal damage to, or dissolution of the metal” when used in reference to attack of an etchant on the metalisation layer or metal traces means no significant or detrimental attack of the metal, allowing the circuitry to perform generally as desired or intended. With reference to Cu metal traces, this is generally loss of trace thickness of less than 10%, more ideally less than 5%.

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As used herein the term “etching time” or “time to etch” or “t” means the time taken for the removal of tie layer (either by dissolution or by de-bonding or both), which results in an increase in the resistance of the substrate to 10¹⁰Hertz or higher when measured using a multimeter.

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As used herein the term “undercut” means the removal of metal (which can include the tie layer and conductive layer) at the interface of the metal trace and the substrate, which can result in weakened attachment of the metal trace to the substrate.

25 As used herein the term “tie layer” means a metal or metal alloy which is used in flexible circuit manufacturing between the substrate and conductive layer and which is etched by the etchant formulation.

As used herein the term “and/or” means “and” or “or”, or both.

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As used herein “(s)” following a noun means the plural and/or singular forms of the noun.

As used herein the term “comprising” means “consisting at least in part of”, that is to say when interpreting independent paragraphs including that term, the features prefaced by that term in each paragraph will need to be present but other features can also be present.

5 To those skilled in the art to which the invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the scope of the invention as defined in the appended claims. The disclosures and the descriptions herein are purely illustrative and are not intended to be in any sense limiting.

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BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will now be further described with reference to the figures in the accompanying drawings in which:

15 Figure 1 is a cube plot of etching times for NiCrO_x tie layers;

Figure 2 is a cube plot of etching times for NiCr tie layers;

Figure 3 is a plot illustrating the etchant constituent composition against etching time;

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Figures 4a and 4b are digital images of scanning electron micrographs (SEMs) of a circuit following etching with different etchant constituent concentrations;

Figure 5 is a plot illustrating the effect of KNO_3 concentration on etching time.

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DETAILED DESCRIPTION

This invention relates to an etchant formulation and method of etching suitable for creating conductive features such as but not limited to flexible circuit manufacturing. Other potential applications as would be recognised in the art are those that include the removal
30 of the NiCr, NiCrO_x , NiCo, NiCrCo, NiCrO_xCo surface coatings and also the oxidised surface layers formed on the NiCr, NiCo and NiCrCo alloys are within the scope of the invention.

The features of the formulation include constituent identity, constituent concentration and the selectivity of the etchant to etching of the tie layer without degrading the integrity of the metal layer.

- 5 Additional features of the method include the etch temperature and speed of etching.

As is known in the art, a typical additive flexible circuit manufacturing process is hereafter described. The etchant formulation of the invention and the etching method of the invention are particularly suited to such a process. However, the etchant and the method
10 may be suitably employed in other etching processes as would be recognized by one skilled in the art.

A typical process starts with the preheating of a substrate (generally a polymeric film such as polyimide) to remove water in a vacuum chamber followed by plasma treatment and
15 chemical cleaning to enhance the adhesion. After this pretreatment, a tie layer metal or metal alloy is deposited by vacuum sputtering or vacuum evaporation in an inert atmosphere. The tie layer acts as the intermediate layer to electro-deposit and bond metal traces to the substrate. The tie layer composition can vary with the incorporation of one or more of the elements such as (but not restricted to) chromium (Cr), nickel (Ni), cobalt
20 (Co), molybdenum (Mo), titanium (Ti), with a thickness variation of 10 to 500 nanometers. The tie layer is subsequently sputtered with a seed metal layer, such as a Cu layer. Then a flash metal layer (Cu again) of 1 to 5 micrometers is electroplated and a resist mask is defined using photolithography. The metal traces are electroplated at areas where the resist has been removed. The resist is then stripped and the exposed flash metal layer is etched.
25 In the subsequent process, the exposed tie layer is etched away to provide complete electrical isolation between the metal traces.

The tie layer etching in flexible circuit manufacturing is usually carried out in a separate step, in order to guarantee its full removal so that a complete electrical resistance between
30 metal traces is achieved.

The dissolution or removal of the tie layer with minimal metal trace dissolution is important. A desirable property for the tie layer etchant is that it does not attack the

interface between the substrate and the base of the metal traces resulting in undercut affecting the bonding of the metal traces.

5 The etchant formulation and method of the invention are suitable for both thicker tie layers (low OT) and thinner tie layers (high OT). Thicker tie layers can be etched within reasonable time frames for such process (such as less than around 60 seconds) whilst the thinner tie layers can be etched at much faster rates. Typically, a thicker NiCrO_x tie layer of 60 % OT would take about 150s or more to etch using a commercially available alkaline etchant such as, but not limited to, potassium permanganate. With the etchant formulation
10 of the invention, the etching time of the 60% OT tie layer could be brought down to about 60s or less, a marked increase in the etching rate.

One suitable specific application of the etchant formulation of the invention relates to the etching of thick NiCrO_x or NiCr tie layers used in flexible circuits. After forming Cu metal
15 traces of the circuit, the tie layer is etched away in order to isolate the traces electrically.

One embodiment of the etchant formulation of the invention includes three constituents namely, H₂SO₄, CH₃COOH and KNO₃.

20 The experimental data (described in detail in the Examples) indicate that in other embodiments, suitable substitution of one or more of these constituents is possible without departing from the scope of the invention. Part, but not all, of the H₂SO₄ may be substituted for by nitric acid (hereafter HNO₃). CH₃COOH may be substituted for by sodium acetate (hereafter CH₃COONa), or other suitable aliphatic or aromatic organic
25 compound with carboxylic acid group (-COOH) or its salt as would be known in the art. Nitrate ions may be totally absent in some embodiments whilst in others, KNO₃ may be substituted for by HNO₃ or other suitable nitrate ion sources as would be known in the art.

The formulation is conveniently prepared by mixing appropriate concentrations of the
30 constituents.

The concentrations of the three constituents of the embodiment have a prominent influence on the etching time and percentage reduction in metallization. We have specifically considered Cu lead thickness as Cu is a common metal employed in flexible circuitry.

However, other suitable metals such as gold (Au), aluminium (Al) or stainless steel alloys may be employed. The concentration of the constituents, when maintained at less than about 35 wt % of H_2SO_4 , about 21 wt % of CH_3COOH and about 20 wt % of KNO_3 results in shorter etching times. More suitably with H_2SO_4 in the concentration range of about 7 to about 14 wt %, CH_3COOH in the concentration range of about 4 to about 9 wt % and KNO_3 in the concentration range of about 4 to about 8 wt %, etching times of about 40 to 60 seconds with less than 5% reduction in Cu trace thickness is observed at 75°C.

The present invention results in no appreciable attack on the side walls of the Cu traces which would otherwise lead to uneven etching and wavy leads. In other words, after etching with suitable etchant concentrations, a generally uniform Cu trace width is obtained.

In general, vertical etching is preferred over horizontal etching. Vertical etching is etching in the direction perpendicular to the substrate and horizontal etching is etching in the direction parallel to the substrate. During tie layer etching, if there is too much horizontal etching, the tie layer below the metal traces would be attacked resulting in undercut. This would weaken the bonding between the substrate and metal traces resulting in reliability issues. The etchant formulation was found to etch vertically with minimum horizontal etching as observed from the undercut measurements.

Features of an etching process of the invention when applied to NiCr or NiCrO_x tie layers with metal traces include that NiCr/ NiCrO_x tie layers of OT values between 75 to 50% can be etched in less than 60 seconds.

In one example, the metal trace dissolution during tie layer etching was found to be less than 5% of the original metal trace thickness which was 8 ± 3 microns. The undercut after tie layer etching was found to be less than 1 micrometer.

The temperature of the etchant has an effect on etching time. An increase in temperature brings down the etching time drastically for all chemical concentrations tested.

The etchant formulation is stable with no appreciable decline in its chemical activity during and after etching of the tie layers.

EXAMPLES

Example 1

Example 1 illustrates the effectiveness of an etchant of the present invention on NiCrO_x and NiCr tie layers. Tie layers of 70% OT were used. The H_2SO_4 concentration was fixed at 17.66 wt %, the CH_3COOH concentration was varied between 10.5 to 21.0% and KNO_3 concentration was varied between 10 to 20 wt %. The temperature effect was studied at low (50°C) and moderate (70°C) temperatures with the center point at 60°C . The example showed that both the NiCrO_x and NiCr tie layers were successfully etched by the etchant formulation of the invention.

Figures 1 and 2 present the results for NiCrO_x and NiCr respectively, as cube plots.

One observation deals with the effect of temperature on etching time. This is further illustrated in Example 6, below. In general, for both NiCrO_x and NiCr tie layers, the etching time was found to decrease by several orders of magnitude with increase in temperature from 50 to 70°C . Figure 1 shows that in the case of NiCrO_x tie layer etching, at 21 wt % of CH_3COOH and 10 wt % of KNO_3 , the etching time decreases from 150 to 15 seconds when the temperature is raised from 50 to 70°C .

Example 2

Example 2 illustrates the ability of the etchant to etch thicker tie layers, and the effect of different constituent concentration on undesirable Cu trace dissolution.

The capability of an etchant of the present invention to etch the NiCrO_x tie layers of 60% OT, (which are thicker than the 70% OT tie layers) was studied. The temperature of the etchant was maintained at 75°C . The concentrations of H_2SO_4 , CH_3COOH and KNO_3 were tested in the concentration range of 6.02 to 20.45 wt %, 3.58 to 12.16 wt % and 3.41 to 11.58 wt % respectively. The results show that the NiCrO_x tie layer etching time can be brought down to a range of 45 to 60 seconds with less than 5% reduction in Cu trace thickness. Figure 3 presents the etching times and the corresponding percentage reduction in Cu trace thickness in the etchant process with the change in the concentration. For most of the chemical compositions tested, the percentage reduction in Cu trace thickness is found to be less than 5% indicating the capability of the etchant to preferably attack the tie layer. The legends for x-axis values are as given (e.g. 8.83, 5.25, 5 indicates 8.83 wt % of

H₂SO₄, 5.25 wt % of CH₃COOH and 5 wt % of KNO₃ respectively). Figure 3 shows that with the concentration of H₂SO₄, CH₃COOH and KNO₃ at 13.25 wt %, 12.16 wt % and 7.5 wt % respectively, the % reduction in Cu trace thickness increases. Similarly, with the concentration of H₂SO₄, CH₃COOH and KNO₃ at 20.45 wt %, 7.88 wt % and 7.5 wt % respectively, the % reduction in Cu trace thickness increases.

Example 3

The role of chemical composition on etching behavior is further clarified by viewing the circuits subjected to the etching treatments.

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Figure 4 presents SEMs (4a and 4b) of a circuit previously having an NiCrO_x tie layer after etching. It shows the influence of chemical composition of the etchant on etching behaviour.

15 In particular, an etchant with 13.25, 7.88, 7.5 chemical composition gives rise to minimum attack on Cu traces (Figure 4a) and an etchant with 20.45, 7.88, 7.5 gives rise to a severe attack on Cu traces (Figure 4b). Note that the legends for chemical composition are as given (e.g. 8.83, 5.25, 5 indicates 8.83 wt % of H₂SO₄, 5.25 wt % of CH₃COOH and 5 wt % of KNO₃ respectively).

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The results of Example 3 should be read together with the results of Example 2. In particular, in this example, it is observed that when the chemical composition of the three chemicals is maintained at 13.25, 7.88, 7.5, the attack on Cu traces is minimal. On the other hand, with the change in concentration to 20.45, 7.88, 7.5, a severe reduction in Cu trace width and thickness is observed (as was the case in Example 2). This indicates that the constituent concentration directly influences the etching behaviour and that using appropriate concentrations can reduce Cu trace dissolution.

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Example 4

30 The role of each of the cations and anions in the etchant formulation was studied by suitably substituting them with other anions and cations. As previously discussed, a preferred embodiment of an etchant of the invention is composed of H₂SO₄, CH₃COOH, and KNO₃. The method and conditions of this Example were the same as discussed in the earlier Examples (100ml of etchant at 75°C).

The ions, which were substituted or removed, are as follow:

1. K^+ by H^+ . (HNO_3 was used instead of KNO_3).
2. H^+ with Na^+ (CH_3COONa was used instead of CH_3COOH).
- 5 3. SO_4^{2-} by NO_3^- (H_2SO_4 was replaced with HNO_3)
4. Complete removal of SO_4^{2-} , NO_3^- and CH_3COO^- ions.

The results on etching time with change in anions and cations are presented in Table 1. The table shows the change in etching time and Cu dissolution tendency with change in constituent concentration and constituent species. The role of individual ions on etching time is discussed in separate sections below.

Table 1

Test No.	Etchant chemical composition (wt%)	Etching time (s)	Observation
1.	$10.6H_2SO_4 + 5.4HNO_3 + 8CH_3COONa$	75	No appreciable Cu dissolution
2.	$10.6H_2SO_4 + 5.4HNO_3 + 6CH_3COONa$	60	
3.	$10.6H_2SO_4 + 5.4HNO_3 + 4CH_3COONa$	60	
4.	$10.6H_2SO_4 + 6KNO_3 + 8CH_3COONa$	80	
5.	$3.53H_2SO_4 + 5.4HNO_3 + 4.2CH_3COOH$	45	
6.	$1.77H_2SO_4 + 5.4HNO_3 + 4.2CH_3COOH$	45	
7.	$5.4HNO_3 + 4.2CH_3COOH$	65	
8.	$5.4HNO_3 + 8.4CH_3COOH$	80	
9.	$7.23HNO_3 + 4.2CH_3COOH$	45	Heavy Cu dissolution
10.	$7.23HNO_3$	-----	Heavy Cu dissolution
11.	$9.04HNO_3 + 10.5CH_3COOH$	120	
12.	$7.23HNO_3 + 4CH_3COONa$	70	
13.	$7.06H_2SO_4 + 4.2CH_3COOH$	90	
14.	$10.6H_2SO_4 + 4.2CH_3COOH$	90	
15.	$10.5CH_3COOH + 10KNO_3$	Not etched	Heavy Cu dissolution
16.	$10.5CH_3COOH + 20KNO_3$	Not etched in 240s	Etching time very high
17.18.	$5.4HNO_3 + 6CH_3COONa$	75	No appreciable Cu dissolution.
	$5.4HNO_3 + 12CH_3COONa$	110	No appreciable Cu dissolution.

- 15 The test conditions which resulted in heavy Cu dissolution are marked in **BOLD** and the normal letters show conditions without appreciable Cu dissolution.

Role of K^+ and CH_3COO^- (acetate) ions

- KNO_3 was replaced with HNO_3 and the results are presented in Table 2. This illustrates the role of K^+ ions and CH_3COO^- ions on the etching time.

Table 2

5 The data tabulated below are extracted from Table 1 provided earlier.

Test No.	Etchant chemical composition (wt%)	Etching time (s)	Observation
1.	$10.6\text{H}_2\text{SO}_4 + 5.4\text{HNO}_3 + 8 \text{CH}_3\text{COONa}$	75	No appreciable Cu dissolution in all the conditions tested.
2.	$10.6\text{H}_2\text{SO}_4 + 5.4\text{HNO}_3 + 6 \text{CH}_3\text{COONa}$	60	
3.	$10.6\text{H}_2\text{SO}_4 + 5.4\text{HNO}_3 + 4 \text{CH}_3\text{COONa}$	60	
4.	$10.6\text{H}_2\text{SO}_4 + 6\text{KNO}_3 + 8 \text{CH}_3\text{COONa}$	80	
5.	$3.53\text{H}_2\text{SO}_4 + 5.4\text{HNO}_3 + 4.2 \text{CH}_3\text{COOH}$	45	
6.	$1.77\text{H}_2\text{SO}_4 + 5.4\text{HNO}_3 + 4.2 \text{CH}_3\text{COOH}$	45	

In Tests 1 to 4, CH_3COONa was used in place of CH_3COOH and in Tests 5 and 6, CH_3COOH was used. The replacement of K^+ by H^+ did not result in any notable change in etching time as observed in Tests 5 and 6. This shows that the effect of K^+ ions on etching time is insignificant.

A similar observation is made, when the etching times of Tests 1 and 4 are compared. The etching times of the etchant with K^+ ions, i.e. $10.6\text{H}_2\text{SO}_4 + 6\text{KNO}_3 + 8\text{CH}_3\text{COONa}$ (Test 4) and that without K^+ ions, i.e. $10.6\text{H}_2\text{SO}_4 + 5.4\text{HNO}_3 + 8\text{CH}_3\text{COONa}$ (Test 1) show similar etching times indicating that the replacement of K^+ ions by H^+ ions does not influence the etching time. From the above results, it can be concluded that the K^+ ion concentration does not have a significant effect on etching time.

As the earlier Examples 1 and 2 show, the CH_3COO^- ions have a prominent effect on etching time and Cu dissolution. Replacement of CH_3COOH by the acetate salt CH_3COONa , however, showed only a small increase in etching time possibly due to the increase in pH with the replacement H^+ ions by Na^+ ions. With the H_2SO_4 and HNO_3 concentrations maintained at their respective concentrations of 10.6 wt % and 5.4 wt %, the increase in CH_3COO^- concentration from 4 to 8 wt % increased the etching time from 60 to 75 seconds. This indicates that the CH_3COO^- ion concentration has a significant influence on the etching time, consistent with the earlier Examples.

Role of SO_4^{2-} and K^+ ions

In order to test the role of sulphate ions, (SO_4^{2-}), the concentration of the SO_4^{2-} ions was lowered from 2 to 1 wt % and then completely replaced by nitrate ions, NO_3^- . The results with respect to etch time are shown in Table 3.

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Table 3

The data tabulated below are extracted from Table 1 provided earlier.

No.	Etchant chemical composition (wt %)	Etching time (s)	Observation
1.	3.53H ₂ SO ₄ + 5.42HNO ₃ + 4.2 CH ₃ COOH	45	No appreciable Cu dissolution in all concentrations tested.
2.	1.77H ₂ SO ₄ + 5.42HNO ₃ + 4.2 CH ₃ COOH	45	
3.	5.4HNO ₃ + 4.2 CH ₃ COOH	65	
4.	5.4HNO ₃ + 8.4 CH ₃ COOH	80	
5.	7.23HNO₃ + 4.2 CH₃COOH	45	Heavy Cu dissolution
6.	7.23HNO₃	-----	Heavy Cu dissolution

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This Example shows that the addition of HNO₃ does not change the etching time to a notable extent. In Tests 1 and 2, the replacement of KNO₃ by HNO₃ and the decrease in H₂SO₄ concentration to 3.53 wt % and 1.77 wt % respectively, did not change the etching time.

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With complete replacement of H₂SO₄ by HNO₃, the etching could take place, but with an increase in etching time possibly due to the decrease in H⁺ ion concentration (lowering of pH).

20 Role of NO_3^- ions and SO_4^{2-} ions.

The role of NO_3^- was studied with the etchant composed of H₂SO₄ and CH₃COOH without KNO₃. The results on etching time are given in Table 4.

25 **Table 4**

The data tabulated below are extracted from Table 1 provided earlier.

No.	Etchant chemical composition (wt %)	Etching time (s)	Observation
1.	7.06H ₂ SO ₄ + 4.2 CH ₃ COOH	90	Heavy Cu dissolution. Etching time very high.
2.	10.6H ₂ SO ₄ + 4.2 CH ₃ COOH	90	
3.	10.5 CH₃COOH + 10KNO₃	Not etched	
4.	10.5 CH ₃ COOH + 20 KNO ₃	Not etched in 240s	

In Tests 1 and 2, the etching was carried out in the absence of NO_3^- ions. The etching time was very high, up to 90 seconds in contrast to the etching times of ≤ 60 seconds observed in the presence of NO_3^- ions. This confirms previous Example results. The increase in etching time with the absence of NO_3^- ions indicates that some degree of NO_3^- ions is important in the etchant.

In Tests 3 and 4, the etching was carried out without H_2SO_4 . The tie layer could not be etched even after an exposure time of 240 seconds. This could be due to the low pH of etchant due to the complete removal of H_2SO_4 . This highlights the role of the inorganic acid in governing the etch rates.

10 *Role of Acetic acid*

The effect of the CH_3COO^- ion from CH_3COOH acid or CH_3COONa on etching behavior was studied and the results are given in Table 5.

Table 5

The data tabulated below are extracted from Table 1 provided earlier.

No.	Etchant chemical composition (wt%)	Etching time (s)	Observation
1.	$5.4\text{HNO}_3 + 6\text{CH}_3\text{COONa}$	75	No appreciable Cu dissolution in all concentrations tested.
2.	$5.4\text{HNO}_3 + 12\text{CH}_3\text{COONa}$	110	
3.	$5.4\text{HNO}_3 + 4.2\text{CH}_3\text{COOH}$	65	
4.	$5.4\text{HNO}_3 + 8.4\text{CH}_3\text{COOH}$	80	

At equivalent concentrations of CH_3COOH and CH_3COONa , the etching time with CH_3COONa was found to be higher than that of CH_3COOH at the same HNO_3 concentration. This could be due to the slight pH increase with the use of CH_3COONa in the place of CH_3COOH .

Example 5

The significance of constituent composition in governing the etching behavior is further studied by using etchant compositions with and without KNO_3 . The studies were carried out at certain specified concentration of the constituent and the results are given in Figure 5. This figure shows the effect of KNO_3 concentration on etching time. The legends for x-axis values are as given (e.g. 8.83, 5.25, 5 indicates 8.83 wt % of H_2SO_4 , 5.25 wt % of CH_3COOH and 5 wt % of KNO_3 respectively).

The example indicates that without KNO_3 , the etching time is high at all chemical concentrations tested. The introduction of KNO_3 decreases the etching time drastically by indicating its strong effect on etching.

5 *Example 6*

This Example deals with the effect of temperature on etching time.

Tests were conducted at the etchant temperatures of 75 °C, 80 °C and 90°C. The results are presented in Figure 6.

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Figure 6 indicates that an increase in solution temperature results in a decrease in etching time. Legends (7.06, 4.2, 4), indicates 7.06 wt % of H_2SO_4 , 4.2 wt % of CH_3COOH and 4 wt % of KNO_3 .

15 Thus, in general, the etching time decreased with an increase in etchant temperature. The etchant is generally effective from room temperature (at 25°C, where the etching time is expected to be very high) to very high temperatures of 90°C or beyond. However, the operating temperature for the etchant is preferred to be less than 90°C due to the relatively low boiling points of water (100°C) and acetic acid (118°C). At higher temperatures,
20 solution loss due to evaporation is observed, as well as attendant safety concerns.

CLAIMS

1. An etchant formulation comprising an inorganic acid and an organic acid, the organic acid comprising an aliphatic or aromatic organic compound having a carboxylic acid group, or the salt thereof.
2. An etchant formulation as claimed in claim 1 wherein the etchant formulation further includes a source of nitrate ions.
3. An etchant formulation as claimed in either of claims 1 or 2 wherein the concentration of inorganic acid is less than 20 wt %, the concentration of organic acid or salt thereof is less than 10 wt %, and the concentration of the source of nitrate ions, when present, is less than 10 wt %.
4. An etchant formulation as claimed in claim 3 wherein the concentration of inorganic acid is in the range of 7 to 14.5 wt %, the concentration of organic acid or the salt thereof is in the range of 4 to 9 wt % and the concentration of the source of nitrate ions, when present, is in the range of 4 to 8 wt %.
5. An etchant formulation as claimed in claim 3 or 4 wherein the inorganic acid is selected from the group consisting of sulphuric acid, nitric acid and a mixture of sulphuric and nitric acids, and wherein the source of nitrate ions is selected from the group consisting of nitric acid, potassium nitrate and sodium nitrate.
6. A method of etching of a metal or metal alloy comprising the steps of:
 - providing a metal or metal alloy, and
 - exposing the metal or metal alloy to an etchant formulation comprising an inorganic acid at a concentration less than 35 wt %, and an organic acid comprising an aliphatic or aromatic compound having a carboxylic acid group, or the salt thereof at a concentration of less than 21 wt %, for a period of time t , at an etchant temperature T .
7. A method as claimed in claim 6 wherein the etchant formulation comprises sulphuric acid, acetic acid and potassium nitrate with concentrations of sulfuric acid

in the range of 7 to 14.5 wt %, acetic acid in the range of 4 to 9 wt % and potassium nitrate in the range of 4 to 8 wt %.

- 5 8. A method as claimed in claim 6 or claim 7 wherein the metal or metal alloy is a tie layer, the method comprising the steps of:
- providing a substrate,
- forming a tie layer on the substrate,
- providing a metal on one or more regions on the tie layer, and
- 10 etching the tie layer with the etchant formulation to provide an etched product.
9. A method as claimed in claim 8 wherein the tie layer is selected from NiCr or NiCrO_x and wherein the tie layer has a thickness generally in the range of 10 to 500 nanometers.
- 15 10. A method as claimed in claim 9 wherein the metal is copper and use of the etchant formulation results in less than 5% reduction in the original copper trace thickness with less than 1 micrometer undercut of the metal.
- 20 11. A method as claimed in any one of claims 8 to 10 wherein in step (d) the etchant temperature T is generally in the range of 50°C to 90°C.
12. A method as claimed in any one of claims 8 to 11 wherein in step (d) the time taken to etch the tie layer, t is less than 90 seconds.
- 25 13. A method as claimed in any one of claims 8 to 12 wherein step (c) of provision of a metal includes a step of providing a layer of metal on one or more regions of the tie layer by a process selected from vapour deposition, sputtering, electroplating and electroless plating, followed by a step of patterning of, or on, the layer of metal
- 30 using a lithographic technique.
14. A method as claimed in claim 13 wherein the step of patterning the layer of metal includes the steps of applying a photoresist, exposing one or more portions of the photoresist to actinic radiation through a mask and developing either the unexposed
- 35 portions or the exposed portions of the photoresist with an appropriate solvent, and

removing the exposed portions of the layer of metal with an appropriate etchant and wherein the step of patterning the layer of metal results in the exposure of one or more regions of the tie layer and one or more of these regions is/are etched in step (d).

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15. A method as claimed in claim 6 or claim 8 wherein the method further includes a step of treating the etched product with an alkaline treatment following the step of etching the tie layer.

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16. A flexible circuit prepared according to a process which includes the method as claimed in any one of claims 8 to 15.

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17. A flexible circuit wherein during the preparation of which, a tie layer was etched using an etchant formulation comprising sulphuric acid of concentration generally less than 20 wt %, acetic acid of concentration generally less than 10 wt % and potassium nitrate of concentration generally less than 10 wt %.

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18. A method of preparing an etchant formulation comprising the steps of mixing sulphuric acid, acetic acid and potassium nitrate to achieve an etchant formulation with concentrations generally less than 20 wt %, 10 wt % and 10 wt % for sulfuric acid, acetic acid and potassium nitrate respectively.