HYDROGEN PEROXIDE/SULPHURIC ACID ETCHING SOLUTION

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Abstract: *Copper dissolution known also as a copper etching is a process essential in the electronics industry, particularly in the fabrication of printed circuit board. Recently the focus of the researchers is on the system ensures high etch rate at a lower consumption of the solution components. In this study, a copper etchant on the base of H_2SO_4/H_2O_2 solution is used and the influence of the various effects on the main etching parameters is investigated. The impact of the etching temperature and different chemical additives to main etchant are examined. The chemical additives with a stabilizing and accelerating effect are tested. The additives independent impact also their synergetic effect on the H_2O_2 decomposition is studied.*

ЕЦВАЩ РАЗТВОР НА ОСНОВАТА НА ВОДОРОДЕН ПРЕКИС/СЯРНА КИСЕЛИНА

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Ключови думи: *Водороден прекис, сярна киселина, ецване, мед*

Резюме: *Разтварянето на мед, известно още като ецване на мед, е съществен процес в електронната индустрия, по-конкретно в производството на печатни платки. Напоследък изследванията са фокусирани върху разработване на разтвори за ецване, осигуряващи висока скорост на процеса при слабо изчерпване на компонентите на разтвора. Представената работа разглежда ецващ разтвор на основата на H_2SO_4/H_2O_2 като описва влиянието на различни фактори (температура на разтвора, добавка на различни съединения към ецващия разтвор) върху параметрите на ецващия процес. Тествано е въсдействието на добавки със стабилизиращ и ускоряващ ефект.*

Introduction

[1] The process of great importance in the manufacture of printed circuit boards for the electronics industry is the etching of the unwanted copper metal the formation of the conductive pattern on the board to be exhibited. One of the efficiently etching copper solutions without material adverse side effects is based on the aqueous ferric chloride. In more recent times its usage become a problem due to environmental and cost perspective. A new approach to the refinement of the etching technologies brings forth new acid and alkaline systems. Each of these etching systems has advantages and disadvantages. Concerning the significance in terms of practice more important considerations are the etching rate, control of the etching solution, stability and efficiency of the etchant, time and temperature conditions, effect of the etchant on the materials forming the printed circuit board, and effect on the equipment and masking material employed in the etching process. Recently an attractive etchant in regard to its relatively low cost and ability to recover copper electrolytically from the etchant solution is aqueous hydrogen peroxide. The problems caused during the copper dissolution at unpredictable rates and the hydrogen peroxide instability resulting in the rapidly solution exhaustion are under consideration by the scientists.

In [1,2] authors provide a new and improved highly efficient hydrogen peroxide etchant capable of dissolving large amounts of metal before effective exhaustion allowing an etch rate to an impractical level in the manufacture of printed circuits. In accordance with the invention it is found that the addition to acid-hydrogen peroxide solutions of a small amount of phenacetin, sulfathiazole, or silver ion, preferably a mixture of phenacetin with sulfathiazole or silver ions, results in the provision of compositions by which metal may be dissolved for constructive purposes in a practical and most efficient manner.

Investigation in [3] is focused on the study of the influence of the undercut inhibitor, added to the a typical formulation of a standard aqueous alkaline ammoniacal cupric etching bath described in [4]. The solution, including cupric ions, an ammonium salt such as chloride, ammonium hydroxide to achieve a pH between about 8 and about 10.5, water, and, if desired, some ammonium phosphate, the organic undercut inhibitor (in the form of be either 5-nitro-1 H indazole or pyrazole) is examined. It is defined a decrease in the amount of undercutting obtained with 5-nitro-1 H indazole between about 13 and about 34% less than the amount of undercutting present when using a conventional bath.

Another aqueous alkaline ammoniacal cupric chloride etching bath [5] is compared with the new one with addition of copper (I) stabilizers leading to increase the etch rate by at least 40 percent. The suitable copper stabilizers are compounds containing an iodide salt, a thiocyanate ion, and a thiosulfate ion. A 90-130% increase in the etch rate is achieved adding potassium iodide, ammonium thiocyanate, and sodium thiosulfate in concentrations up to approximately 600 mg/L of any one of these compounds.

Research of the scientist [6] provides a new and improved etchant of copper based on acid solution of hydrogen peroxide having a total free chloride and bromide ions content less than 2 parts per million. Authors advise to proceed the etching process in water having a total free chloride and bromide ion content less than about 2 parts per million, preferably less than 1 part per million for a constructive purpose.

[7] avoids instability of the etching composition of printed circuit boards in the presence of chloride ions and ensures a uniform and rapid etch rate. The etchant consists of an aqueous solution of sulfuric acid, hydrogen peroxide, a thiosulfate salt to overcome the depressing effect of chloride ion, preferably at a concentration of 0.05% to 0.1%; and a hydrogen peroxide stabilizer system including an amino methylene phosphoric acid and an unsaturated organic hydroxyl compound such as phenol or allyl alcohol.

In [8] O. Cakir underlines the advantages of the application of cupric chloride (CuCl2) as an etchant in the manufacturing process of PCB's. (CuCl2) produces a stable and high etch rate and low undercut. Not only all important factors for efficient process flow are studied, but also the regeneration/recycle and etched metal recovery of waste etchant is determined. It is defined the four times higher etch rate by using (15% NH4Cl) to CuCl2 solution and the same copper dissolve capacity by HCl addition [9]. As etch rate accelerants the other chemical additives such as monomethanol amine, ethanol, acetonitrile, aceton, dimethyl formamide to CuCl2 etchant are also used [10]. Another advantage of the utilization of CuCl2 as an etchant is observation of minimization or elimination of the disposal products influence on the environment, which would also reduce operational costs.

The incorporation of the effective amount of both a triazole compound and either an aliphatic water soluble monoalcohol or a glycol monoether in the solution including a mixture of an acid selected from the group consisting of sulfuric acid, nitric acid, sulfamic acid, and phosphoric acid; hydrogen peroxide; and water provides a faster etching rate[11].. The stabilization of the hydrogen peroxide is performed with a compound selected from the group consisting essentially of a phenol, a phenol phosphoric acid, or a phosphonate. For the initial start-up of the etching process hydrated copper sulfate is included acting as a slight or mild accelerator. Preferably, the monoalcohol is selected from the group consisting of isopropanol, n-butyl alcohol, and t-butyl alcohol and the glycol monoether is selected from the group consisting of diethylene glycol monobutyl ether, and dipropylene glycol monoethyl ether and the triazole compound is mixed with the monoalcohol or the glycol monoether prior to incorporation in the solution.

In this study, copper etching using H_2SO_4/H_2O_2 etchant solution is studied. The effects of etching temperature and different chemical additions to main etchant are investigated. The used chemical additions are stabilizers and accelerants. The additives independent impact also their synergetic effect on the H_2O_2 decomposition is studied.

Experimental and test methods

Commercial circuit board sided glass size 1mm, Copper - foiled of 35 microns thickness samples (2,0x2,5sm) are used as substrates. The specimens are degreased ultrasonically in acetone. The following pretreatments including both degreasing and micro etching in an acid solution

composition 100 ml/l H_2SO_4 and nonionic surfactant 0,1 g/l at room temperature for 2-3 min, and carefully washing with distilled water are performed.

The etchant composition of Hydrogen Peroxide/Sulfuric acid is listed in Table 1.

Table 1. Etchant composition of Hydrogen Peroxide/Sulfuric Acid

Bath components	Quantity	Bath parameters	Quantity
Sulphuric acid	0.3M to 1.0M	Wetting agent	0,1 to 1,0 g/l
Hydrogen peroxide	0.1M to 0.5M		
Stabilizer: sulfosalicylic acid (SS), 8-oxyquinoline (8-OQ), chromotropic acid (CTR), Sulphaminic acid (SA), amino pyridine (AP),	1,0 to 8,0 g/l	Temperature	45°±5°C
Accelerant: Na- molybdate, NH4- molybdate	5 to 25 g/l		

A few etchant solutions of different composition are studied to observe its effect on the etchant performance. Due to instability of Hydrogen Peroxide in the presence of Copper ions a stabilizing effect of organic components (as a sulfonic acid with concentration of 1 to 8 g/l) is investigated to avoid the etchant solution decomposition. To eliminate the stabilizers retarding action accelerants are used (as Mo_2O7_2 ions) with concentration of 5 to 25 g/l. The used wetting agents are anionic or non-ionic compounds with concentration of 0, 1 to 1, 0 g/l.

The influence of the above mentioned on the etchant performance is investigated studying the dependence on the amount of hydrogen peroxide spent from the surface of the dissolved copper.

The weight of dissolved copper is precisely measured by a chemical method by titration with 0, 1 M Titriplex III in the presence of the PAN [1-(2-Pyridylazo)-Naphthol-2] or PAR [4-(2-Pyridylazo)-Resorcinol] indicator. The Hydrogen Peroxide quantity is measured also by titration with 0,1N potassium permanganate.

Results and discussion

The dependence on the etching rate (dissolved amount of the Copper per minute) from the working temperature is shown in the Table 1 and Figure 1. The study is performed in the H_2O_2/H_2SO_4 solution without any additives.

Table 1. Dependence on the dissolved copper from the working temperature

T°C	10	20	30	40	48
Cu, µm/min	0,9	1,8	2,5	3,8	5,3

The tests carried out confirm the dependence on the etch rate by the working temperature. The dissolved copper quantity per unit time is higher at higher temperature. The decomposition of the H_2O_2 is observed at temperature higher than 50°C. The suitable working temperature is defined at 45±5°C.

The influence of different stabilizers and accelerants on the etchant performance defined by investigation of the dependence on the amount of hydrogen peroxide consumption [H_2O_2, ml] from the surface of the dissolved copper [S, dm2] is presented in the Table 2 and in the Figures 2.

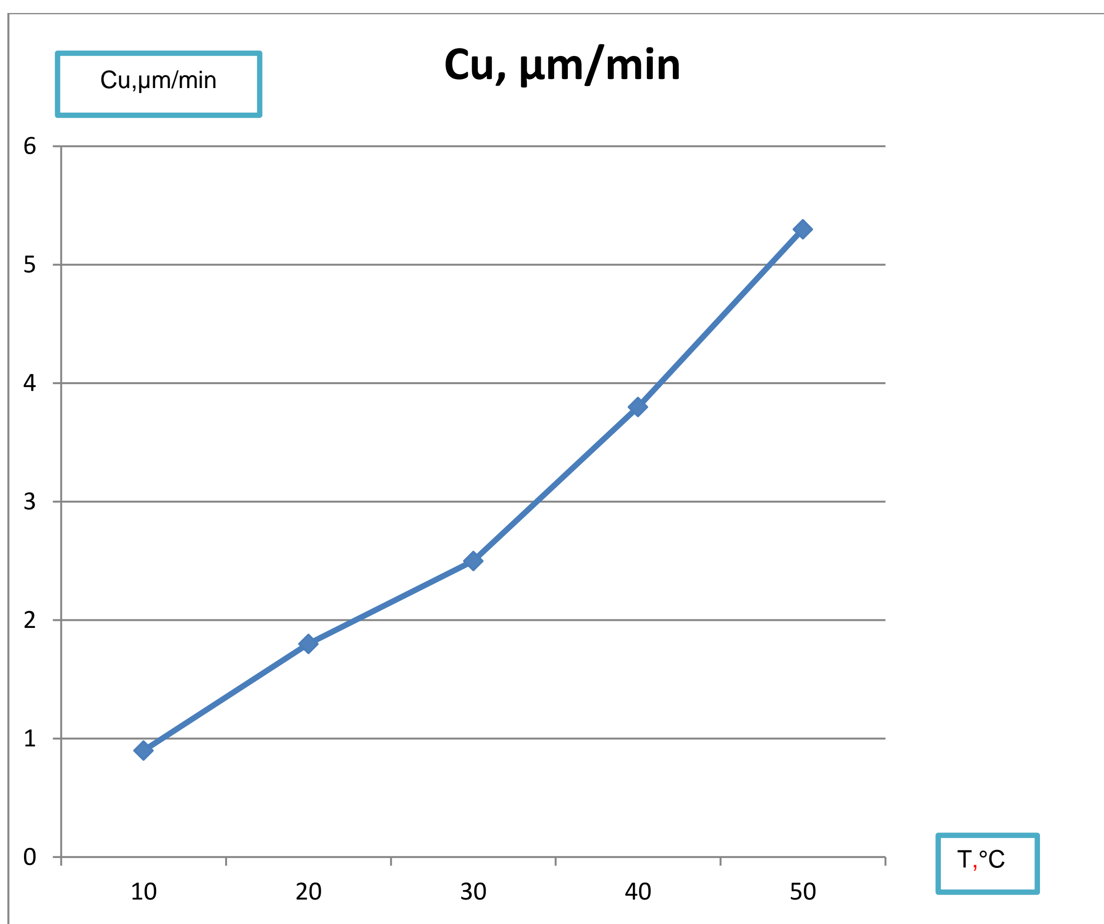

Fig. 1. Dependence on the etching rate (dissolved amount of the Copper per minute) from the working temperature

Table 2. Dependence on the H_2O_2 consumption from the surface of the dissolved copper

S,dm^2	H_2O_2, ml							
	Sulfo-Salicylic acid (SS)	Na-molybdate (Na-Mo)	Sulfosalicylic acid (SS)+ Na-molybdate (Na-Mo)	Sulfosalicylic acid (SS)+ NH_4-Molybdate (NH_4-Mo)	chromotropic acid + NH_4+Molybdate (NH_4-Mo)	amino pyridine+ NH_4-Molybdate (NH_4-Mo)	Sulphaminic acid (SA)+ NH_4-Molybdate (NH_4-Mo)	8-oxyquinoline (8-OQ)+ Na-molybdate (Na-Mo)
5	95	92	32	40	88	38	40	38
10	155	188	66	80	176	80	168	80
15	302	264	184	140	264	208	206	121
20	358	362	260	268	352	248	238	162
25	432	446	444	344	452	292	272	200
30	511	525	468	430	518	336	308	332

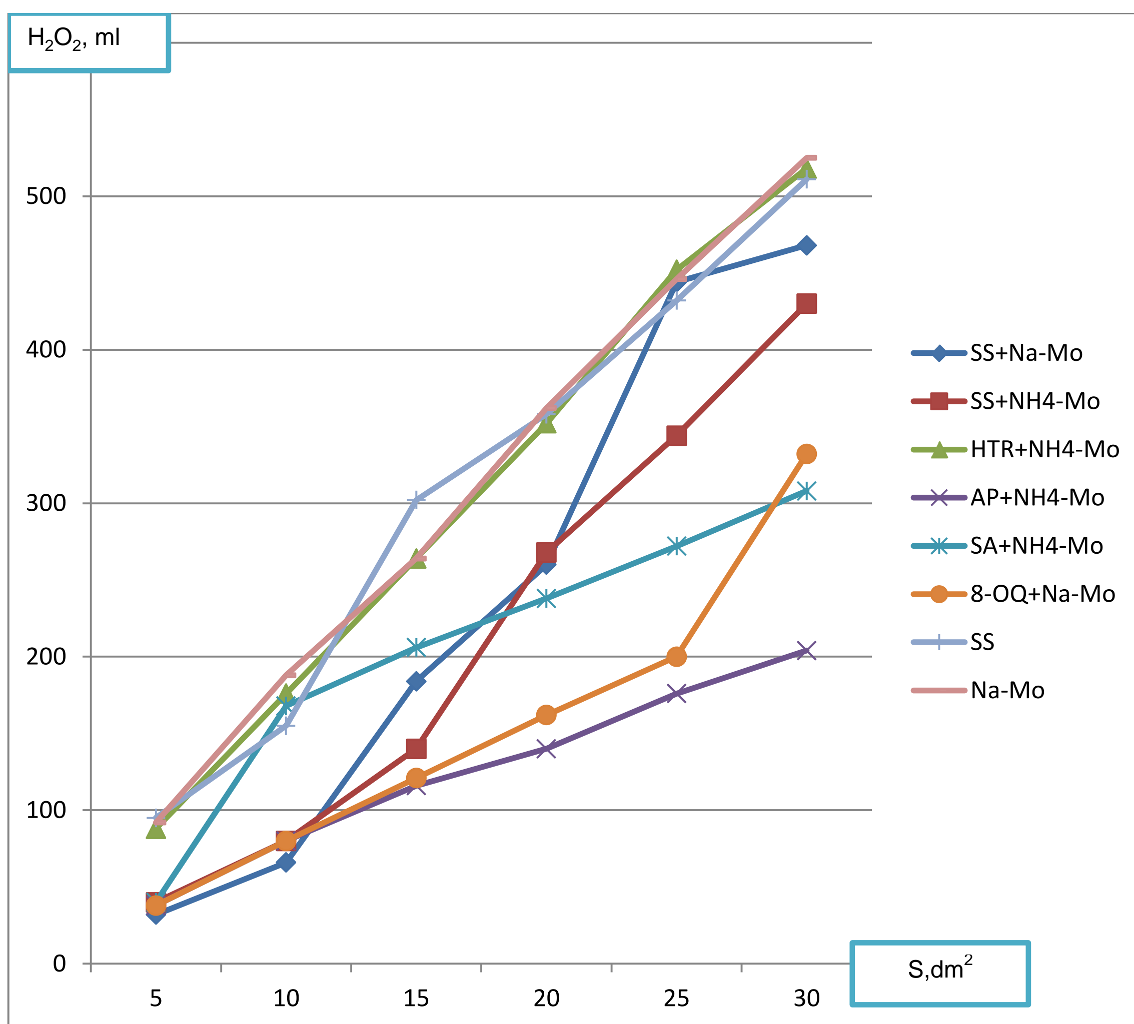

Fig. 2. Dependence on the H_2O_2 consumption from the surface of the dissolved copper

The H_2O_2 consumption during etching process by addition of different stabilizers and accelerants also their mixing shows a correlation with the amount of dissolved copper. Some of the curves represented in the Figure….. are steeper. This suggests that the H_2O_2 consumption is different in the presence of different additives. It is evident that the H_2O_2 consumption is highest in the etchant comprising only accelerant or stabilizer. The combined effect of mixing two different systems – stabilizer and accelerant is studied with the suggestion to exceed the effects of the individual impact of the used stabilizer or accelerant. The mixture of additives comprising accelerant and stabilizer leads to a positive effect to the quantity of the copper dissolution.

The result of the present study shows that between the used additions the higher impact on the copper dissolution and on the acceptable rate of the Hydrogen Peroxide decomposition possess the mixtures of amino pyridine with ammonium molybdate or 8-oxyquinoline with Na-molybdate.

Conclusions

A novel etching solution is developed on the base of H_2O_2 and H_2SO_4.

The increase of the etching rate at higher working temperature is determined. Decomposition of the etching solution is found out at 50°C.

Investigation of the effect of addition of stabilizers and accelerators on the Hydrogen Peroxide dissolution in the etchant is performed.

The results achieved show higher H_2O_2 decomposition in the presence only of the stabilizers or accelerants.

A synergistic effect is achieved using the mixing system composition of a stabilizer and accelerant.

Between the used additives the higher impact on the copper dissolution and on the acceptable rate of the Hydrogen Peroxide decomposition is observed by the system composition of amino pyridine with ammonium molybdate or 8-oxyquinoline with Na-molybdate.

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