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Copper etching with cupric chloride and regeneration of waste etchant

O. Cakir

Department of Mechanical Engineering, Dicle University, 21280, Diyarbakir, Turkey

Copper etching is considerably important process in electronics industry, particularly in the fabrication of printed circuit board. Various etchants can be used for this purpose, but nowadays cupric chloride is more accepted etchant, because of its high etch rate and easy regeneration properties. In the present study, copper etching process with cupric chloride etchant was investigated. In the etching of copper, the most important etching parameter is etch rate, therefore the investigation was based on the various effects on etch rate. The influence of etchant concentration, additives and etching temperature were examined. It is also important to regeneration/recycle of waste etchant from environmental point of view. Thus, various cupric chloride etchant regeneration processes were investigated.

1. INTRODUCTION

Etching is one of the important non-traditional machining processes to produce geometrically complex machine parts from thin and flat sheets. This process is widely used in electronics, aerospace and precision engineering industries. Etching is the main machining step in chemical and photochemical machining processes [1-3].

Copper etching is the main process in the printed circuit board (PCB) manufacturing for electronics application. Historically, the first etchant in PCB fabrication was ferric chloride (FeCl_3) and it is still used as an etchant for small scale production lines. However, last two decades, new etchants have been introduced for copper etching. One of them was cupric chloride (CuCl_2). Nowadays, it has been major etchant in copper etching industry [4].

In this study, copper etching with CuCl_2 was investigated. The effects of etchant concentration, additives and etching temperature on etch rate of copper were examined. It is also important that the regeneration/recycle etchant should be available because of environmental restrictions. The regeneration processes for waste CuCl_2 have been determined.

1. ETCHANTS IN COPPER ETCHING

The ideal etchant for copper should have some properties such as high etch rate, minimum undercut, high dissolved copper capacity, easy control, economic regeneration of waste etchant and copper recovery [5-8]. Basically, there have been widely accepted three etchants for copper etching. These were CuCl_2 , FeCl_3 and alkaline etchants. There are other etchants can be mentioned, but their use have been very limited or unused due to their environmental hazardous properties.

CuCl_2 is a suitable etchant in etching “print and etch” type PCB at a larger scale. These PCBs are single sided board and requires economical etchant. CuCl_2 provides high etch rate when compared with FeCl_3 and produces low undercut. The copper dissolve capacity of CuCl_2 is three times higher than FeCl_3 . The full regeneration advantage of CuCl_2 makes it attractive etchant to etching industry. It is also used as an etchant for copper alloys such as brass, bronze, beryllium copper, etc. Alkaline etchants are only used for copper. These etchants are provided by supplier and the supplier takes waste etchant back for regeneration/recovery of etchant and copper. Alkaline etchants are expensive, therefore they are used for bulk production processes. Table 1 presents some characteristics of CuCl_2 , FeCl_3 and alkaline etchants [8,9].

Table 1. Some etchants characteristics in PCB fabrication [9]

Etchant	Corrosiveness	Neutralisation and Disposal problems	Toxicity	Operational Cost*
Cupric Chloride	High	Low	Medium	Low
Ferric Chloride	High	Medium	Low	Medium
Alkaline Etchants	High	Medium	Medium	High

(*) Include disposal cost.

3. COPPER ETCHING

CuCl_2 is a rather messy, yellow-brown, hygroscopic solid, usually sold as the green crystalline dihydrate salt, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. It is commonly used acidic and comprises the copper salt, water and hydrochloric acid (HCl) [1].

The etching of copper with CuCl_2 can be expressed by the following chemical equation;



The copper surface gets attacked by CuCl_2 while cuprous chloride (CuCl) is formed. One copper atom with one cupric ion produces two cuprous ions. Copper etching with CuCl_2 solution is controlled strongly during the etching process [10].

The molarity of cupric chloride etchant solution is important characteristic. It is represented by Baumé and 32-33 °Bé (2.33-2.5 Mol) gives high and stable etch rate for copper etching. Lower of this degree gives low etch rate with poor line resolution and higher Bé degrees produces slow etch rate with a smooth line resolution [11].

The etching temperature considerably affects etching process. Using higher etching temperature increases the etch rate for copper etching with cupric chloride. It is obtained low etch rate by using low etching temperature. However, the temperature of etching is maintained around 50°C. This is due to etching machine, because etchant affects metallic parts of machine at higher temperatures. The etch rate of copper at 32 °Bé (2.33 Mol) and 50 °C (± 2 °C) etching temperature is around 10 $\mu\text{m}/\text{min}$ [12].

Basically, when CuCl_2 solution is prepared, small amount HCl is added to solution. The effect of HCl addition to CuCl_2 maintains high etch rate that is shown in Table 2. It is also known that the copper dissolve capacity increases by additional HCl [13].

Table 2. HCl addition effect on the etch rate [13]

CuCl_2	Etching Temperature ($^{\circ}\text{C}$)	HCl Addition	Etch Rate ($\mu\text{m}/\text{min}$)
33 $^{\circ}\text{Bé}$ (2.5 Mol)	49	1 N (1 Mol)	25
33 $^{\circ}\text{Bé}$ (2.5 Mol)	49	2 N (2 Mol)	31
33 $^{\circ}\text{Bé}$ (2.5 Mol)	49	3 N (3 Mol)	38

(The calculation of Baumé is done as follows: $\text{Bé}=145 [(sg-1)/sg]$ where sg: specific gravity)

The additions of various chemical additives to CuCl_2 produces better etching properties. The addition of ammonium chloride (NH_4Cl) to CuCl_2 provides high etch rate and increases copper dissolved as the same level of HCl addition. CuCl_2 with 15% ammonium chloride could give four times higher etch rate than CuCl_2 [5]. Some chemical additives such as monomethanol amine, ethanol, acetonitrile, acetone, dimethyl formamide to CuCl_2 also increase the etch rate of copper [14].

This positive effect causes some difficulties on the regeneration of waste etchant. Therefore, it is general approach to keep etchant as simple as possible.

4. REGENERATION OF WASTE ETCHANT

The regeneration/recycle is the most important advantage of CuCl_2 . It is noticed that waste CuCl_2 can completely be regenerated. There are various regeneration processes available for CuCl_2 . Chemical regeneration basically is being used by etching companies, due to of pure CuCl_2 price. After regeneration, surplus CuCl_2 can sell to chemical companies for further utilising. A recovery copper from spent solution by electrolytic method can be more available for companies. This would cause no disposal problem and to sell obtained pure copper from solution [15-17].

The chemical regeneration of waste CuCl_2 is completed by adding one of the following chemicals to spent solution [17]:

1. Chlorine Gas



2. Hydrogen Peroxide and Hydrochloric Acid



3. Sodium Chlorate and Hydrochloric Acid



5. CONCLUSION

As an etchant, CuCl_2 is commonly used in the manufacture of PCBs. It has a stable etch quality rate under uniform process conditions. The copper etching process should be completed at the highest possible etching temperature. The Baumé of etchant should be chosen around 32-33° Bé (2.33-2.5 Mol). These etching parameters would produce stable etch rate and low undercut in copper etching.

Also, environmental regulations push manufacturers to be more careful about environmental pollution occurred during/after etching process. The full regeneration of waste CuCl_2 eliminates pollution. Surplus CuCl_2 , after regeneration process, can be sold to companies which are interested in further using for etching or recovering copper from solution.

REFERENCES

1. D.M. Allen, *The Principle and Practices of Photochemical Machining and Photoetching*, Adam Hilger Publication, 1986
2. W.T. Harris, *Chemical Milling*, Oxford University Press, 1976
3. J.W. Dini, *American Machinist (Special Report)*, 128, (1984), 113-128
4. C.F. Coombs, Jr., (Ed), *Printed Circuit Boards*, McGraw-Hill, 1995
5. J.O.E.Clark, *The Marconi Review*, 26 (1961), 135-152
6. S. Gowri, K.S. Indira, B.A. Shenoi, *Metal Finishing*, 64 (1966), 54-59
7. E.C. Jubb, *Plating*, 139 (1964), 2202-2211
8. M.J. Thomas, "Etching", *Technical Note (MacDermid (GB) Ltd.)*, 28 pages
9. W.C. Bosshart, *Printed Circuit Boards- Design and Technology*", Tata McGraw-Hill Publ., 1985
10. A. Batham, *Electronic Production*, 11 (1988), 101,103,107
11. R.E. Markle, *Industrial Finishing*, May 1982, 47-49
12. O. Çakir, *Proc. of the First Mechanical Engineering Congress (Istanbul, Turkey)*, June 4-6, 1997, 464-468
13. Kenneth Mirski, *Proc. Tech. Prog. Nat. Electronic Pack. And Prod. Conf., USA*, 1981, 196-207
14. E.B. Khobotova, S.D. Gorobels, V.I. Larin, *Zashchita Metallov*, 23 (1987), 980-982
15. D.G. Barrett, *PCMI Journal*, Issue No:46 (1991), 15-17
16. D.M. Allen, O. Çakir, *PCMI Journal*, Issue No:52 (1993), 4-7
17. O.Çakir, *Proc. of the Int. Symposium on Municipal and Industrial Wastes and Their Treatment in 2000 (Treatment 2000) (Istanbul, Turkey)*, May 17-20, 2000, 396-401