1. Introduction

The Hong Kong printed circuit industry has played an important part in Hong Kong manufacturing industry, which supplies printed circuit boards (PCB) for various industries, from high tech electronics to domestic appliances. Currently, the PCB industry produces more than 26 million square meters of PCBs and generating estimated sales of US$1.1 billion per year. According to a recent PCB industry research report, it is forecasted that the HK/China PCB production will grow continually with an annual growth rate of 16.3% from the year 2003 to 2005 despite the global economic downturn. To cope with this increasing market demand, the Hong Kong PCB industry has to upgrade her manufacturing capability and simultaneously to tackle the generic manufacturing difficulties especially on the production efficiency and environmental issues.

Etching is an important process in the PCB manufacturing industry. Every year, approximately 7 million liter of etchant is being used by the PCB factories and generates a huge volume of waste. A total amount of HK$24 million is being spent for waste treatment on top of the HK$9 million chemical cost. Therefore, the regeneration of spent etchant and recovery of the copper is essential to minimize the operating cost of the etching process. Over years, in-situ method uses hazardous chemicals to oxidize the etchant. The etchant is treated through vigorous reactions for reuse; this requires high cost in chemical replenishment and safety measures. Due to the huge operating cost and enormous operating difficulties in maintaining the stable copper etching performance, PCB manufacturers are skeptical to incorporate their on-line etchant regeneration/recovery system with their etching line. We had investigated and established a new and innovative High Precision and Re-circulate Copper Etching System by employing the Hydroxyl Free Radical Oxidation techniques through the use of doped synthetic diamond electrodes. This system incorporates both the etching and regenerating processes in one unit and the etchant

1. 簡介

香港線路板工業，為各高新電子技術和家電等行業提供所必須的線路板，於香港製造業佔著舉足輕重的地位。香港的線路板生產商每天生產大約二千六百萬平方米線路板，總值約十億美元。據業內人士透露，縱然世界經濟正處於不明朗的因子，但香港和華南地區的生產商均估計2003至2005年度，線路板每年的生產量將持續有16.3%的增長。隨著市場環境正慢慢好轉，各港商都積極地裝備自己，不單著焦於技術水平，同時更針算效率的提升以及致力於環保生產以提高競爭能力。

在線路板的生產過程中，蝕銅是一個十分重要的流程。每年，香港線路板生產商大約消耗七百萬公升的蝕銅劑，同時製造出大量廢液。要有效地處理這些大量廢液需要動用約三千四百萬元、另再加九百萬元的蝕銅劑費用。所以，循環再用鈷的蝕銅劑和回收金屬價值的金屬銅，是減低生產成本其中一個最有效的方法。

直至目前為止，線路板生產商對蝕銅器的循環技術仍然存疑，主要因為一般蝕銅器的循環技術少不了使用一些具危險性的化學物來氧化蝕銅器，再經不同化的化學流程，始能有效地轉化鈷和的蝕銅器、再生成為有用之化學物料。由於轉化過程耗資巨大及涉及安全問題，是故，泰半的線路板製造商均不願採用傳統的鈷鋼器循環技術。

有見及此，香港線路板協會聯同香港生产力促進局，在得到香港特區政府創新科技基金的資助下，研發出一個創新的、高精密的，採用了塗上人造鑽石的電極極基氧化銅循環系統技術。此創新系統揉合了蝕銅和循環再用兩個功能，並更精密地控制整個蝕銅流程以及減少回收銅等問題。由於電極基自由基電解方法會把有用的銅回收，整個回收過程
performance is being precisely controlled with minimal fluctuation. Indeed, the key competitive edge with the named system would be its easy-to-manage and more precise controllable manner. Cuprous ions will be removed electrolytically by the hydroxyl free radical, which minimizes the uncertainties and the adverse effect of the chemical reaction. Therefore, the electrolytic regeneration of etchants and recovery of copper serves as a more economical alternative in saving replenishment chemicals. Besides, additional revenue comes from the by-product, the recovered copper.

2. Experimental
The pilot scale continuous copper regeneration and recover system was built and tested.

The experimental setup of this continuous system is shown in Fig. 1. The total volume of the system is 550 liters (anode compartment = 240 L and cathode compartment = 310 L).

The fresh etchant solution was prepared by the following recipe: CuCl₂ = 36.4 g/L, HCl = 0.01 M.

Copper coil was etched by the fresh etchant until the concentration reached to 1.52 g/L.

In this system, the spent copper etchant solution was continuously fed into the anode and cathode compartments by two metering pumps both at various flow rates. Boron doped diamond (BDD) and stainless steel (SS) served as the anode and cathode respectively. The effective areas of the two electrodes were both 4300 cm². After residing in the reactor for certain process time controlled by flow rate, the regenerated etchant solution exited from the reactor and flew back into the etching tank.

The regeneration test was conducted under constant voltage of 6.0V and current of 20A, corresponding to constant current density of 2.33 mA/cm².
3. Results and Discussions

3.1. Dependence of cuprous ion concentration on ORP value

To measure the cuprous ion concentration in the solution containing both cupric (Cu\(^{+2}\)) and cuprous (Cu\(^{+} \)) ions, first we measured the dependence of cuprous ion concentration on the ORP value of the solution as below. From the curve (Fig. 2) the concentration of cuprous ion during the regeneration process can then be obtained by measuring the ORP value of the regenerated solution.

3.2. Etchant regeneration and copper recovery

We measured the change of ORP value in the anolyte and catholyte at various process time. In addition, the change of specific gravity in the catholyte in terms of Baume degree was also measured. The results were shown in the below figures (Fig. 3).

From the above figure, the copper etchant regeneration and copper recovery can be calculated in Fig. 4.

![Fig. 2 Dependence of cuprous (Cu\(^{+} \)) concentration on ORP value](image)

![Fig. 3(a) The change of ORP value in the anolyte (a) and catholyte (b) against process time](image)

![Fig. 3(a) The change of Baume degree in the catholyte against process time](image)

![Fig. 4(a) The change of cuprous ion concentration in the anolyte (a) and catholyte (b) against process time](image)

![Fig. 4(b) The change of copper recovered in the cathode compartment against process time](image)
It can be seen from Fig. 4 (a) that after regeneration, cuprous ion concentration was considerably reduced in the anode compartment. When the process time reached to 3 hr, nearly 90% of initial cuprous ion has been oxidized into cupric ion.

It was also observed that although there was negligible copper metal recovered when the process time was less than 1 hour, the copper recovered in the cathode compartment started to increase when the process time exceeded 1 hour.

3.3. Electricity utilization efficiency

It can be calculated from the process time between 2-3hr that the electricity utilization efficiency of anode and cathode compartments is about 100%. Due to the co-existence of both Cu⁺ and Cu²⁺ in the solution which both contributed to the copper recovery, the current efficiency in the cathode cannot be measured directly. Despite this, the current efficiency in a typical cathode compartments can be generally considered 98%. Under such circumstance, the electricity utilization is summarized in Table 1 (according to constant current of 20 A).

<table>
<thead>
<tr>
<th></th>
<th>Change rate in the anode compartment after 20 Ahr of power input</th>
<th>Change rate in the cathode compartment after 20 Ahr of power input</th>
<th>Net change rate after 20 Ahr of power input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺</td>
<td>+ 2.4 g/Ahr</td>
<td>- 0.5 g/Ahr</td>
<td>+ 1.9 g/Ahr</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>- 2.4 g/Ahr</td>
<td>- 1.4 g/Ahr</td>
<td>- 3.8 g/Ahr</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>+ 1.8 g/Ahr</td>
<td>+ 1.8 g/Ahr</td>
</tr>
<tr>
<td>Cu²⁺/Cu⁺</td>
<td>1.0</td>
<td>2.8</td>
<td>1.9 (theoretical value = 2) (理論值 = 2)</td>
</tr>
</tbody>
</table>

Table 1 Electricity Utilization of the Copper Etchant Regeneration System

By balancing the ratio of Cu⁺ generated to Cu²⁺ consumed, it is possible to maintain the concentration ratio of Cu⁺ to Cu²⁺ in the solution by the above set up. An application example is shown in the Appendix.

4. Conclusions

The continuous cupric regeneration system by means of BDD electrode proved to generate hydroxyl radicals which efficiently oxidized cuprous ions and regenerated copper etchant.

By balancing the ratio of Cu⁺ generated to Cu²⁺ consumed, it is possible to maintain the concentration ratio of Cu⁺ to Cu²⁺ in the solution by the above set up. An application example is shown in the Appendix.

5. Appendix: Application Example

Here is an example for the application of the above system. Supposing that a PCB factory uses CuCl₂ (initial Cu²⁺=71g/L) as copper etchant. The copper coil with a thickness of 0.1mm is etched at 1 m/min (the copper forwarding speed is 2m/min and the width of the etching machine is 0.5m) and the etching tank has a volume of 1 m³ (or 1000L). A regeneration
system can be designed as below to stabilize the etching rate.

Fig. 5 shows the schematic setup of the regeneration system.

The calculation of operating parameters is as follows:

a) Copper etching rate: Given the area of copper coil to be etched is $1\text{m}^2/\text{min}$, the total copper to be etched is $53.5\text{kg/hr}$ [$= 8.92 \times 10^3 \text{g/m}^3 \times 1 \text{ m}^2 / \text{min} \times 0.1 \times 10^{-3} \text{m} \times 60 \text{ min}$]. This copper etching rate corresponds to the reduction of cupric ion at $53.5\text{kg/hr}$ and accumulation of cuprous ion at $107.0\text{kg/hr}$.

b) Regeneration current: The regeneration tank aims to regenerate cupric ion and recover copper both at $53.5\text{kg/hr}$ in order to make balance. Table 1 shows that $1\text{Ahr}$ of power input can resume $1.9\text{g}$ of cupric ion and recover $1.8\text{g}$ of copper metal. Therefore, it requires $28.2\text{kA}$ [$= 53.5 \times 10^3 \text{g/hr} / 1.9\text{g(Ahr)}$] and $29.7\text{kA}$ [$= 53.5 \times 10^3 \text{g/hr} / 1.8\text{g(Ahr)}$] of power input rate to resume cupric ion and recover copper metal at the expected rate. If the regeneration tank operates at constant current of $29\text{kA}$, the cupric ion can be regenerated at $55.1\text{kg/hr}$ [$= 29\text{kA} \times 1.9\text{g(Ahr)}$] and copper recovery rate at $52.2\text{kg/hr}$ [$= 29\text{A} \times 1.8\text{g(Ahr)}$], respectively.

c) Flow rate of etchant circulation: It has been estimated from literature (Processing and Economic Aspects of Etchant Regeneration, R. E. Markle, 1983, Plating and Surface Finishing, 59-62) that the specific gravity of the copper etchant has to be controlled between 1.280 and 1.295$g/mL$ so that the copper etching rate is maintained at $25\text{m/min}$. The increase in specific gravity is due to the increase of total copper ions in the solution (cupric ion + cuprous ion). Therefore, when the total copper ion has been increased by 15$kg$ [$= (1.295 - 1.280g/mL) \times 1000\text{L}$], the etchant has to be disposed and regenerated. As the net change of total copper ion is $53.5\text{kg/hr}$ (=increase of cuprous ion at 107.0$kg/hr$ decrease of cupric ion at 53.5$kg/hr$), as calculated in step (a), the maximum turnover time of the etchant is $0.28\text{hr}$ [$= 15\text{kg} / 53.5\text{(kg/hr)}$]. As the total volume of the etching tank is $2\text{m/min}$, the regeneration system should be designed to achieve the above etching condition.
tank is 1000L, the flow rate is 3571L/hr (= 1000L / 0.28hr).

Table 2 shows the summary of the above system.

<table>
<thead>
<tr>
<th>Change</th>
<th>Cu⁺</th>
<th>Cu²⁺</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching Tank</td>
<td>+107.0kg/hr</td>
<td>-53.5kg/hr</td>
<td>-53.5kg/hr</td>
</tr>
<tr>
<td>Regeneration Tank</td>
<td>-110.2kg/hr</td>
<td>+55.1kg/hr</td>
<td>+52.2kg/hr</td>
</tr>
</tbody>
</table>

Table 2 Summary of the regeneration system

It can be seen from the above table that after 1 hour of running, 97% of etched copper can be recovered and 100% of the Cu²⁺ can be refreshed.

After regeneration, the system runs as below figure.

Fig. 6 Summary of the Operation of the Regeneration System

6. 鳴謝

《發展一個再循環銅氧化系統來增加HDI線路板生產過程的精密度》獲香港特區政府創新科技基金撥款資助，特此鳴謝。