Pertanika J. Sci. & Technol. 21 (2): 375 - 386 (2013)

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

Recovery of Heavy Metals from Spent Etching Waste Solution of Printed Circuit Board (PCB) Manufacturing

A. H. M. Ali*, S. Sobri, Salmiaton. A. and Faizah M. Y.

Department of Chemical and Environmental Engineering, Faculty of Engineering,
Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

ABSTRACT

The process of etching is the most crucial part of the work of manufacturing printed circuit boards (PCB). In the etching process by nitric acid, a spent etching waste solution of composition 250 g/L HNO_3, 30-40 g/L Cu, 30-40 g/L Sn, 30-40 g/L Pb and 20-25 g/L Fe is produced. High metal concentrations in the spent etching waste solution make it a viable candidate for the recovery of metals. Recovery of metals from spent etching waste solution is a significant concern as the recent growth in production of printed circuit boards has generated a drastic increase of spent etching waste solution each year. This study concerns itself with the recovery of metals from spent etching waste. In this study a dilution was made in order to increase the pH of the solution as spent etching waste solution has high acidity, and the electrowinning method was performed to recover metals from the spent etching waste solution. Glassy carbon and platinum were used as cathode and anode in order to investigate the electrodeposition of metals and cyclic voltammetry investigation suggests that the deposition of metals on glassy carbon electrodes occurs at four different overpotentials mainly at -0.15 V, -0.35 V, -0.45 V and -0.75 V. Microscopy observation demonstrates that there is a deposition of metals by applying the potentials in a set of current-time transient study for a duration of 60 seconds and the metals recovered formed as aggregates.

Keywords: PCB etching solution, electrowinning, linear sweep voltammetry, cyclic voltammetry

INTRODUCTION

Etching waste solution produced in the process of printed circuit board manufacturing contains tin, copper, iron and lead as by-products. In the etching process by nitric acid, spent etching waste solution of composition 250 g/L HNO_3, 30-40 g/L Cu, 30-40 g/L Sn, 30-40 g/L Pb and 20-25 g/L Fe is produced (Man-Seung *et al.,* 2003). In recent years, it

Article history:
Received: 28 February 2011
Accepted: 10 September 2012

E-mail addresses:
halim_6985@yahoo.com (A. H. M. Ali),
shafreeza@upm.edu.my (S. Sobri),
mie@upm.edu.my (Salmiaton. A.),
fmy@upm.edu.my (Faizah M. Y.)
*Corresponding Author

ISSN: 0128-7680

has been reported that the average rate of worldwide printed circuit board (PCBs) manufacturing increases by 8.7% with total value of 51.5 billion USD worldwide and this number is higher in Southeast Asia by 10.8% (Kui *et al*., 2009; WEEC, 2009). Technological innovation and intense marketing are factors accelerating the production rate of electric electronic equipment (EEE) and shortening the lifespan of EEE.[4] As the demand for production of EEE increases, the discharge of etching waste solution has become a major economic as well as environmental concern as it contains significant amounts of heavy metals and acid and has to be treated as hazardous waste.

Conventionally, etching waste solution resulting from the etching process is neutralised by adding sodium hydroxide, resulting in metal-bearing sludge. The neutralised sludge is incinerated and the residues dumped in special landfills (Man-Seung *et al*., 2003; Chang-Hoon *et al.,* 2009). Due to the emission of nitrogen monoxide during the incineration and leaching of heavy metals from the dumped residues, the disposal of etching waste solution by neutralisation fails to solve the waste problem; in addition, the sludge contains a lot of valuable components that should be recovered economically (Man-Seung *et al*., 2003; Tiina *et al.,* 2007).

At present, several methods exist for the treating and regenerating of etching waste such as solvent extraction (Man-Seung *et al.,* 2003; Chang-Hoon *et al.,* 2009), evaporation (Man-Seung *et al.,* 2003), membrane technology and electrowinning (Tiina *et al.,* 2007; Department of Environmental Protection, Florida, 2006). A comparison of the existing current treatments shows that electrowinning is the most well established technology for metal deposition from solution. Electrowinning can recover element metals directly from aqueous solutions in a single-stage process without the addition of reagents (Shafreeza, 2006; Walsh, 2001; Juttner *et al*., 2000). Electrowinning technologies are more efficient, green, compact and economical compared with existing technologies in terms of efficiency in metals recovery and clean technologies that help to prevent the production of unwanted by-products which in many cases have to be treated as waste.

In this study, we focus on recovery of heavy metals in etching waste solution produced in PCB manufacturing by electrowinning as an initial investigation for metal recovery from etching waste solution.

THEORY OF ELECTROWINNING

Electrowinning is a process where metals are deposited at the cathode from an electrolyte by the process of reduction. The term ‘electrowinning’ is often used in many technologies such as electroplating, electrodeposition and electrorefining**.** The process usually features as a process that is usually carried out in three electrode electrochemical cells that consist of a working electrode, a counter electrode and a reference electrode. Both working and counter electrodes are connected to a power supply.

The deposition of metals is achieved by applying a negative charge on the working electrode, and the metallic ions which carry a positive charge will be attracted to the cathode. When the positive charge of the metallic ions reaches the cathode, it receives an electron to reduce the positive-charged ions to their metallic form and causes them to be deposited on the electrode surface as a thin layer. The electrodepositing mechanism for metal recovery on an electrode surface is very simple. It is basically a simple electron transfer and may be represented as:

$$M^{n+} + n\bar{e} \rightarrow M$$

MATERIALS AND METHODS

Reagents

Experiments were conducted using a synthetic etching solution and prepared in the ratio shown in Table 1. A 3.5 M HNO_3 solution was prepared by diluting 240.6 mL of 14.545 M HNO_3 in distilled water and diluting it to 1000 mL. The final concentration of nitric acid in the synthetic etching solution was 250 g/L. 30 g/L Cu, 40 g/L Pb, 40 g/L Sn and 20 g/L Fe, dissolved in nitric acid (HNO_3). The mixtures were stirred using a magnetic stirrer at 250 rpm for 30 minutes. The concentration of the synthetic spent nitric etching solution was analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) Optima 7300 from Perkin Elmer.

TABLE 1
Chemical composition of the synthetic spent nitric etching solution

Element	Copper (g/L)	Lead (g/L)	Tin (g/L)	Iron (g/L)	HNO_3 N
Concentration	30	40	40	20	3.5

Due to the high acidity of the etching waste solution, a dilution was made to increase the pH of the solution to pH > 2 in order to meet the requirements of the potentiometer to work at its optimum condition. The initial pH of the etching solution was -1.67 and a dilution of 100 times was made of the solution to increase the pH to 2.1.

Electrochemical experiments

Linear sweep voltammetry

Linear sweep voltammetry was performed to measure the current at the working electrode while the potential between the working electrode and a reference electrode was swept linearly in time. The linear sweep experiments were carried out at 0 to -1.0 V at scan rates ranging from 5-50 mVs^{-1}. In linear sweep voltammetry experiment, reduction of species is registered as a peak in the current signal at the potential at which the species begins to reduce.

Cyclic Voltammetry

Cyclic voltammetry was performed to determine the potential for metal nucleation on glassy carbon electrodes. The voltammetry experiments were carried out from -1 to 1 V at scan rates ranging from 5-50 mVs^{-1}. Surface area available for the deposition was 1.0 cm^2.

Current-time transient

Current-time transient for studying the deposition of metals in spent etching waste solution was accomplished by applying the potential voltage of each reduction peak gained in linear sweep voltammetry for 60 seconds. Metals deposited on the electrode were analysed by scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS).

Electrochemical system

Flat cell system

A Princeton Applied Research Model K0235 Flat Cell was used to study the electrochemical characteristic of the synthetic etching waste as well as the growth mechanism of the metals. K0235 Flat Cell is a cylindrical cell and consists of a glass cylinder clamped horizontally between two end plates. One end plate houses the working electrode and the other houses the counter electrode. The placement of the counter electrode is directly opposite to the working electrode. The reference electrode is housed in a luggin well, with a fixed Teflon luggin capillary protruding from the bottom of the well.

Electrochemical Instrumentation

All electrochemical experiments performed with flat cell, such as linear sweep, cyclic voltammetry and chronoamperometry were carried out using a potentiostat VersaSTAT 4 from Princeton Applied Research and operated by a PC using VersaStudio software. Two-electrode electrolytic cells were set up using a glassy carbon as cathode and platinum as anode. Experiments were conducted at room temperature. Current-potential data on the experiment were collected and interpreted using Microsoft Excel.

Microscopy imaging

Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectrometry (EDS)

Microstructural properties of the deposited particles and the microscopy images of metal deposits were analysed using a S-3400N SEM model from Hitachi High-Technology Corporation and Thermo Scientific NORAN System Six (NSS) Energy Dispersive Spectrometry (EDS) system. SEM analysis for metals deposits were recorded at 3000 magnification and at an acceleration voltage of 15kV and the deposit characterisation was performed to investigate the influence of deposition overpotential over time and used to characterise elemental constituents of the metal deposited on the electrode.

RESULTS AND DISCUSSION

Electrowinning experiments

Linear Sweep Voltammetry

Linear sweep voltammetry was performed to measure the current at the working electrode while the potential between the working electrode and a reference electrode was swept linearly in time. The linear sweep experiments were carried out at 0 to -1.0 V at scan rates ranging from 5-50 mVs^{-1}.

Reduction of species was registered to peak in the current signal at the potential at which the species began to be reduced. Fig.1 shows the linear sweep voltammetry for the glassy carbon at scan rate of 50 mVs^{-1}. It can be seen that the voltammograms are characterised by 4 peaks; first peak at -0.15V, second peak at –0.40V, third peak at -0.55 V and followed by the fourth peak at –0.75 V. The peaks are labelled A, B, C and D.

Cyclic voltammetry

Cyclic voltammetry was performed to determine the potential for metal nucleation on glassy carbon electrodes. The voltammetry experiments were carried out from -1 to 1 V at scan rates ranging from 5-50 mVs^{-1}. Surface area available for the deposition was 1.0 cm^2. Fig.2 shows the polarisation curves for etching waste solution when polarised from -1.0 to 1.0 V at scan rates of 5, 10 and 50 mVs^{-1}.

Fig.2 shows that as the scan rate increased, the total current also increased and the reduction peak shifts to more negative overpotentials. This could be due to slow electron transfer kinetics on the electrode surface, ohmic drop in the solution or the kinetics of the nucleation and growth process (Shafreeza, 2006; Chrzanowski & Lasia, 1996).

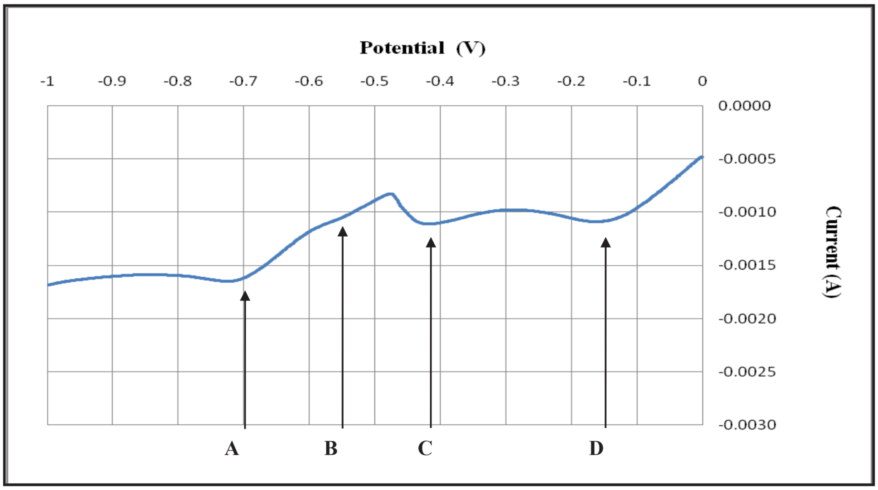

Fig.1: Linear sweep voltammetry of spent etching solution at 50 mVs^{-1}

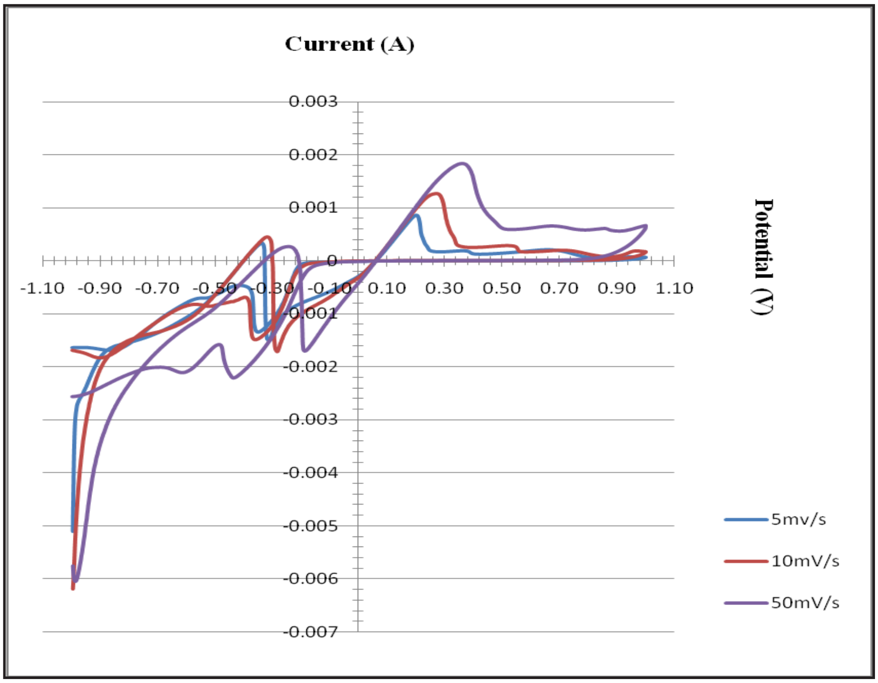

Fig.2: Cyclic voltammetry of spent etching solution at 5 mVs^{-1}, 0 mVs^{-1}and 50 mVs^{-1}10 mVs^{-1}and 50 mVs^{-1}

Fig.3 shows that the reduction of metals occurs between -0.15 V and -0.75 V and no peaks were observed for the anodic cycle for cyclic voltammetry at 5 mVs^{-1}. Fig.3 also shows four peaks. The first hump was observed at -0.75 V followed by a peak observed at potential -0.55 V. The third peak was observed at -0.35 V and exhibits a higher peak compared to the earlier two peaks. The final peak was observed at -0.15 V.

Current-time transients

Current-time transient for studying the deposition of metals in spent etching waste solution was accomplished by applying the potential voltage of each reduction peak gained in linear sweep voltammetry for 60 seconds. Metals deposited on the electrode were analysed by SEM and EDS.

Fig.4 shows the current-time transient for nucleation of metals on the glassy carbon at -0.45 V; the graph comprises two regions of interest, A and B. In region A, there was a sharp decay in the first two seconds mainly due to the capacitive charging and decay of local currents (Shafreeza, 2006; Walsh, 2001). After the initial decay, the maximum current can be observed from the transient; the transient exhibited a hump at region B.

Between points A and B, the electroactive area on the substrate surface increased due to the continuous formation of new nuclei as well as the increase in the size of the existing nuclei. Diffusion zones were developed during this stage, and as the radius of each nuclei increased, the diffusion zones began to overlap (Shafreeza, 2006).

In region B, the cluster of nuclei continuously grew and the formation of new nuclei occurred on the metal being deposited rather than the substrate which led to large particle

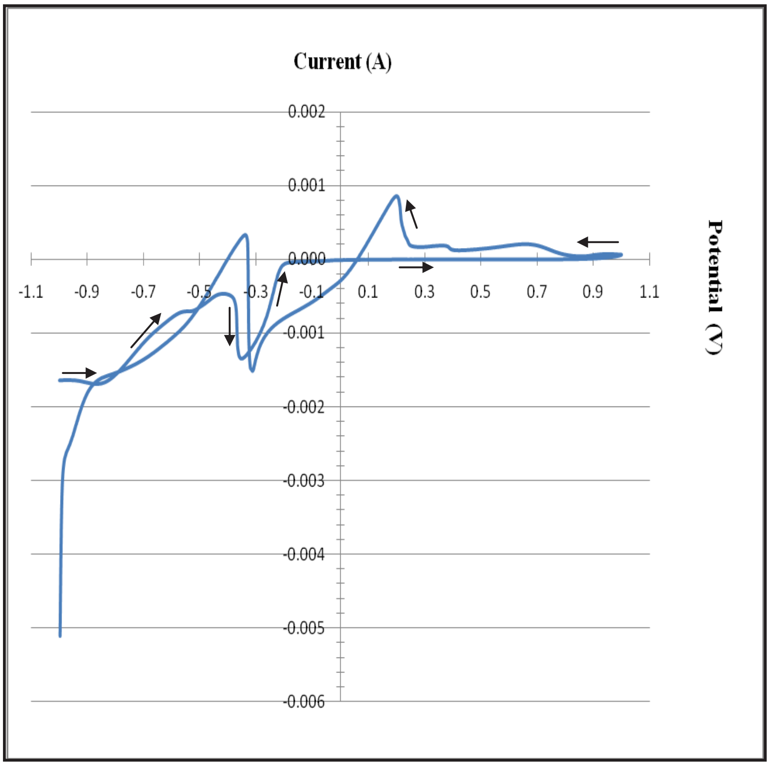

Fig.3: Cyclic voltammetry of spent etching solution at 5 mVs^{-1}

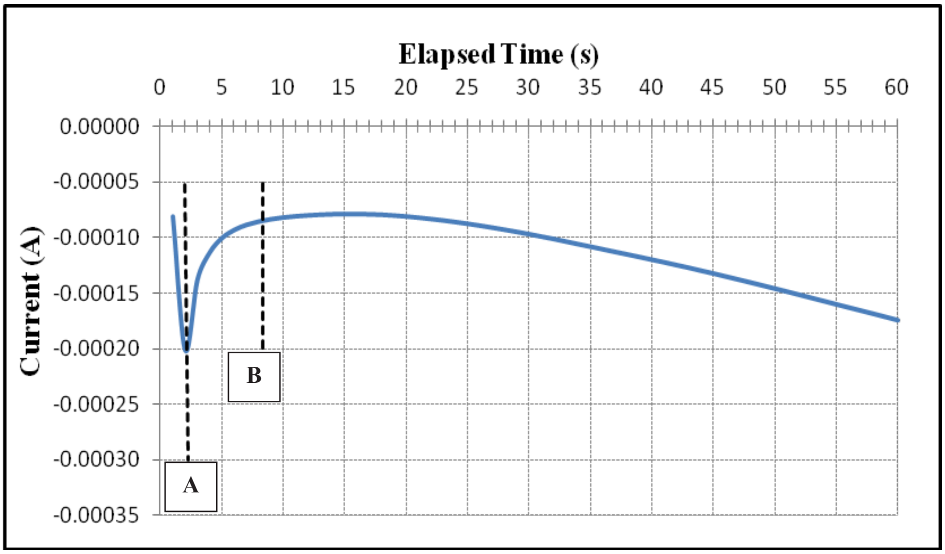

Fig.4: Current-time transient for nucleation of metals on glassy carbon at -0.45 V

aggregations. The decreasing of the current is mainly due to the combined effects of the depletion of the diffusion layer as well as the coagulation of nuclei.

The deposited metals on glassy carbon were analysed using SEM. As shown in Fig.5, deposition at -0.45 V formed in large aggregates and the distribution of the aggregates on the surface of the electrode was not even. Electrode surface was still visible as shown in Fig.5. X-ray diffraction patterns of metals deposited on the glassy carbon at -0.45 V were analysed using Energy Dispersive Spectrometry (EDS). Based on the weight percentage from EDS analysis, Pb dominated with 62.29% by weight while Sn with 3.61% and Fe with 2.40%. In order to determine the average particle size of metals nuclei, 6 areas were chosen at random from the micrographs of the substrate surface with each area being 100 µm^2. Based on Fig.5, the average particle size of metals deposited on the glassy carbon at -0.45 V overpotentials was 20.6 x 10^{-12} m^2.

Fig.6 shows the current-time transient for nucleation of metals on glassy carbon at -0.75 V. A sharp decay was observed in the first three seconds as in region A. After the initial decay, the current transient exhibited a hump at region B.

Comparing Fig.4 and Fig.6, as the applied potential is lowered, the maximum current became more pronounced and its height and position increased as the applied potential

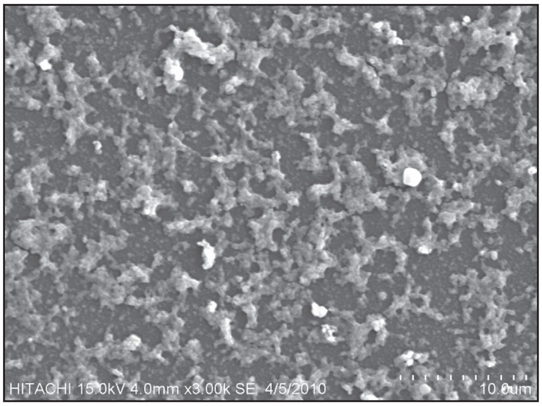

Fig.5: SEM images of metals on glassy carbon at -0.45 V deposition over potentials with 3K magnification

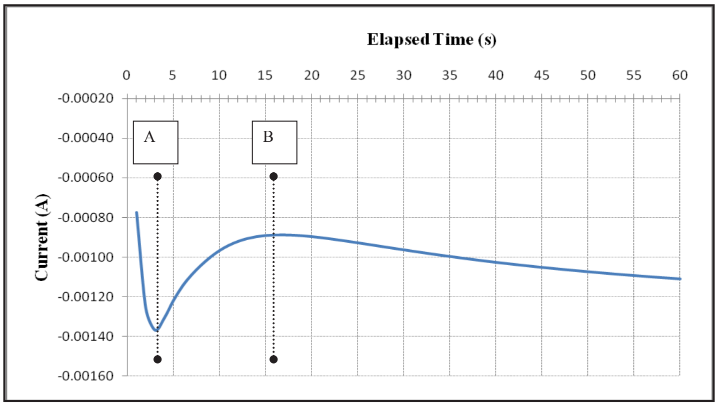

Fig.6: Current-time transient for nucleation of metals on glassy carbon at -0.75 V

became more cathodic. The SEM image of metals deposited on the glassy carbon at -0.75 V overpotential is shown in Fig.7.

As shown in Fig.7, deposition at -0.75 V formed aggregates and the distribution of the aggregates on the surface of the electrode was even. The size of the aggregates deposited was smaller compared to the size of the aggregates deposited at -0.45 V. The average particle density of metals deposited on the glassy carbon at -0.75 V overpotentials was 18.1 x 10^{-12} m^2. Based on the EDS analysis, Cu deposited with 38.53% by weight, O with 51.87% and C with 2.76%.

Fig.8 contains representatives scanning electron micrographs of metals deposited on glassy carbon electrodes of each potential voltage. The figure shows the deposits after 60 seconds of each potential application. Based on Fig.8, as the applied potential is lowered, deposited metals started to form as aggregates and the deposition on the surface of the electrodes was even.

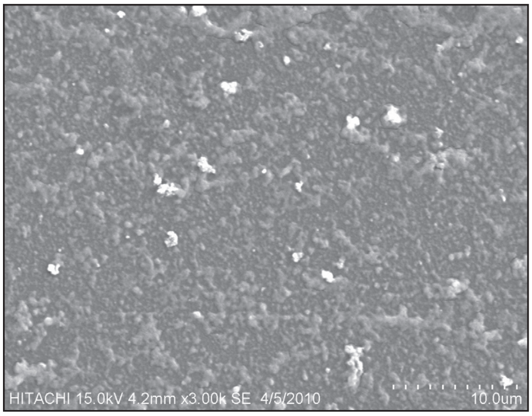

Fig.7: SEM images of metals on glassy carbon at -0.75V deposition overpotentials at 3K magnification

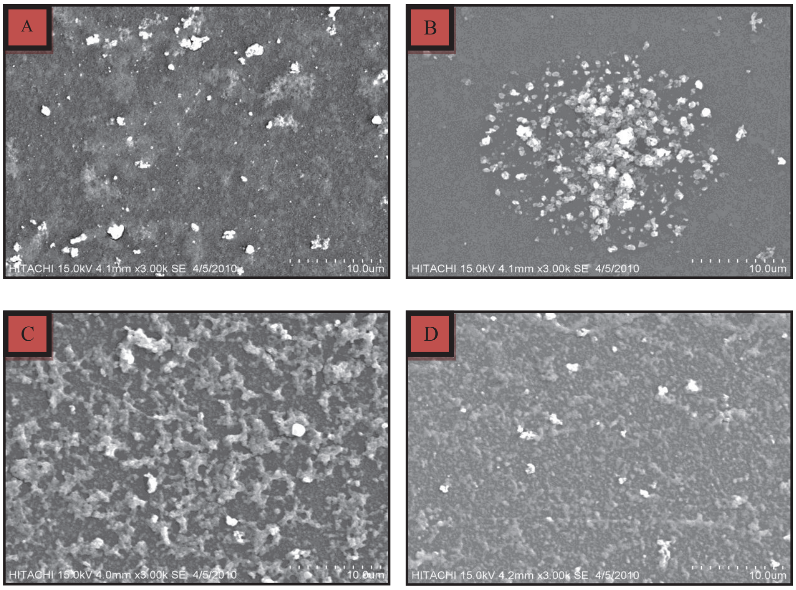

Fig.8: SEM images of metals on glassy carbon at deposition overpotentials at 3K maginification :
(A) -0.15 V (B) -0.45 V (C) -0.55 V (D) -0.75 V

CONCLUSION

Spent etching waste solution contains a significant amount of heavy metals such as copper, iron, lead and tin. Since the discharge of etching waste is a major economic as well as environmental concern, this paper aimed to investigate if the heavy metals in spent etching waste solution can be recovered.

Due to the high acidity of the etching waste solution, a dilution was made to increase the pH to pH > 2. The initial pH of the etching solution was -1.67 and a dilution of 100 times was made to the solution to increase the pH to 2.1.

Glassy carbon and platinum were used as cathode and anode in order to investigate the electrodeposition of the metals. Cyclic voltammetry investigation suggests that the deposition of metals on the glassy carbon electrodes occurs at four different overpotentials mainly at -0.15 V, -0.35 V, -0.45 V and -0.75 V. Microscopy observation demonstrates that there is a deposition of metals by applying the potentials in a set of current-time transient studies for a duration of 60 seconds where the metals recovered formed as aggregates.

Based on this study, we can conclude that heavy metals in spent etching waste solution can be recovered by electrowinning methods. Unfortunately, selective recovery cannot be done as the metals recovered formed as aggregates and not as a single element. Due to the high acidity of etching waste solution, a future work with respect to eliminating acid in etching waste by solvent extraction can be done in order to increase the pH of the solution to replace the dilution method as acids and metals concentration in etching waste solution is relatively high and with effective recovery, acids and metals from the waste stream can be recycled to the main process and, thus, would greatly simplify any further treatment of the wastewater.

REFERENCES

Chang-Hoon, S., Ju-Yup, K., Jun-Young, K., Hyun-Sang, K., Hyang-Sook, L., Debasish, M., Jae-woo, A., Jong-Gwan, A., & Wookeun, B. (2009). Recovery of nitric acid from waste etching solution using solvent extraction. *Journal of Hazardous Materials, 163*, 729-734

Chrzanowski, Y. G. W., & Lasia, A.(1996). Nucleation and crystal growth in gold electrodeposition from acid solution Part I: Soft gold. *Journal of Applied Electrochemistry, 26*, 843.

Department of Environmental Protection, Florida, USA. (2006). *Recovery and Recycling of Bath Chemicals; Electroplatingy tip sheet, Pollution prevention program 2006*. Department of Environmental Protection, Florida, USA.

Juttner, K., Galla, U., & Schmieder, H. (2000). Electrochemical approaches to environmental problems in the process industry. *Electrochimica Acta, 45*, 2575.

Kui, H., Jie, G., Zhenming, X. (2009). Recycling of waste printed circuit board: A review of current technologies and treatment status in China. *Journal of Hazardous Materials, 164*, 399-408.

Man-Seung, L., Jong-Gwan, A., & Jae-Woo, A. (2003). Recovery of copper, tin and lead from the spent nitric etching solution of printed circuit board and regeneration of the etching solution. *Hydrometallurgy,70*, 23-29.

Shafreeza, S. (2006). *Electrocrystallisation and Recovery of Gold from Thiosulphate-sulphite Aged Electrolyte.* (Unpublished doctoral dissertation). University of Newcastle Upon Tyne, UK.

Tiina, K., Juha, T., & Toivo, K. (2007). Analysis of key patents of the regeneration of acidic cupric chloride etchant waste and tin stripping waste. *Resource, Conservation and Recycling, 49*, 217-243.

Walsh, F. C. (2001). Electrochemical technology for environmental treatment and clean energy conversion. *Pure and Applied Chemistry, 73*, 1819

World Electronic Circuit Council. (2008, July). *WECC Global PCB Production Report for 2008*. (July 2009). World Electronic Circuit Council.

Young, J. P., & Derek, J. F.. (2009). Recovery of high purity precious metals from printed circuit boards. *Journal of Hazardous Materials, 164*, 1152-1158.