



## **Detection of Organic Additives in Copper Plating Bath Using Voltammetric Methods That Involve a Screen-printed Nano-Au Electrode**

**Yu-Ching Weng<sup>1\*</sup>, Jhih-Jie Huang<sup>1</sup>, Chih-Yao Wang<sup>2</sup> and Miao-Zhen Hong<sup>2</sup>**

<sup>1</sup>*Department of Chemical Engineering, Feng Chia University, Taichung 40724, Taiwan.*

<sup>2</sup>*Electronic and Optoelectronic System Research Laboratories, Industrial Technology Research Institute, Hsinchu, 31040, Taiwan.*

### **Authors' contributions**

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

### **Article Information**

DOI: 10.9734/CSJI/2021/v30i730241

#### Editor(s):

(1) Prof. Pradip K. Bhowmik, University of Nevada Las Vegas, USA.

#### Reviewers:

(1) Suja Mathai, University of Kerala, India.

(2) Muthanna Jaafar Abbas, Babylon University, Iraq.

Complete Peer review History: <https://www.sdiarticle4.com/review-history/73291>

**Original Research Article**

**Received 19 June 2021**  
**Accepted 27 August 2021**  
**Published 01 September 2021**

### **ABSTRACT**

Three electrochemical methods used to detect organic additives, A, B and C, in acidic plating baths. Cyclic voltammetric stripping (CVS) is used in industry to detect the concentration of organic additives indirectly by measuring the effect of commercial organic additives on the rate of copper deposition. This study directly determines the concentration of organic additives on a screen-printed nano-Au electrode at high potential using three different electrochemical methods: linear scanning voltammetry (LSV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV). The results show that the response currents for the three electrochemical methods exhibit a linear relationship with the concentration of organic additives. The nano-Au electrode is the most sensitive device for the detection of organic additive B using LSV.

**Keywords:** *Copper electroplating additives; sensor; nano-Au electrode; concentration detection.*

\*Corresponding author: E-mail: [ycweng@fcu.edu.tw](mailto:ycweng@fcu.edu.tw);

## 1. INTRODUCTION

The printed circuit board (PCB) industry produces a small number of products and has diverse production patterns. The industry is actively leading the way in the development of smart factories to evolve from an automated production pattern of large-scale batch production to intelligent and flexible adjustment of production. The wet process for a PCB production line, including electroplating, stamping, exposure and etching, is a key element of the entire PCB process. An electroplating production line involves the most important process. A traditional plating production line uses a basic plating solution, to which a variety of organic additives is added [1]. The copper electroplating solution is mainly composed of copper sulfate, sulfuric acid, hydrochloric acid and organic additives. The organic additives consist of accelerators [2-3], suppressors [4-5] and levelers [6-7]. Three types of organic additives enhance chemical reactions, improve surface deposition increase the uniformity of thickness and enhance filling with high aspect ratio features and improve the overall plating [8-11]. Sulfuric acid is used as a highly conductive electrolyte and chloride ions improve the performance of additives. The organic additives are added to the plating solution at a low concentration, which is usually calculated in parts per million (ppm). It is necessary to maintain a low concentration of organic additives to achieve the desired deposition behavior and the required metal properties [12-15].

Industry usually measures the concentration of organic additives offline and then adjusts the process parameters for a product using this measurement data to meet product quality requirements. However, the measurement process is time-consuming and cannot be monitored and fed back in real time so production line machines are used to add and adjust the concentration of additives. This time-consuming and inconvenient measurement means that PCB manufacturers use loose upper and lower limits for statistical process control and experience is used to adjust the plating current and plating time for production control.

This study develops a highly sensitive sensor for the detection of organic additives to allow the detection of organic additives for plating production lines. Currently, cyclic voltammetric stripping (CVS) is used to measure the

oxidation peak of copper indirectly to detect the concentration of organic additives [16-17]. Xie et al. [18] used CVS with a microelectrode and found that the microelectrode can replace a traditional rotating electrode to monitor the concentration of copper ions and organic additives in metal plating solutions. Ellis et al. [19] developed a new set of analysis methods using a reduced number of steps and artificial neural networks. This study respectively predicts the concentrations of accelerator, suppressor and leveler to within 0.5%, 2.7% and 0.12% [19]. Choe et al. [20] devised a modified CVS method to measure the concentration of bis-(sulfopropyl) disulfide (SPS) and 3-mercaptopropane sulfonate (MPS) in Cu plating solutions. A two-step CVS analysis determines the total accelerator concentration and conversion ratio. The modified method allows measurement of the SPS concentration with less than 10% error [20]. Iodine ions are used as a leveling agent in the copper plating process. Yoon et al. [21] conducted a responsive curve RC-CVS analysis under optimized conditions and determined that there is a linear relationship between the real and measured concentration of I<sup>-</sup>.

Detecting the concentration of organic additives in the plating solution quickly and accurately is a challenging problem for industry. Some methods accurately quantify the concentration of organic additives on the production line, so this study develops a method to directly measure the concentration of organic additives. To avoid the potential window range for copper ion deposition or stripping, a high potential is used to directly oxidize the organic additives. This study uses three electrochemical methods (LSV, DPV and SWV) to measure the concentration of organic additives in copper plating at high potential. The nano-gold electrode is a highly sensitive device for the detection of organic additives A, B and C.

## 2. MATERIALS AND METHODS

### 2.1 Electrode Preparation

The screen-printed nano-Au electrode was purchased from Vida BioTechnology Co and was used as the working electrode. The surface morphology of the nano-Au electrode was determined using a scanning electron microscope (SEM, HITACHI S-4800). X-ray diffraction (XRD, Bruker D8 Discover) was used to identify the structure of the nano-Au electrode.

## 2.2 Electrochemical Analyses

A cyclic voltammogram (CV) performed using an electrochemical analyzer system (SP-240, Bio-Logic Science Instruments, CH) was used to determine the electrochemical behavior of the nano-Au electrode in the presence and absence of organic additives in a 50-mL vessel with an electrolyte consisting of 2.14 M H<sub>2</sub>SO<sub>4</sub>, 4.6×10<sup>-4</sup> M HCl and 0.395 M CuSO<sub>4</sub>. The organic additives, A, B and C were provided by Unitech Company and are inhibitors, accelerators and levelers, respectively. A three-electrode cell used a Pt counter electrode (CE), an Ag/AgCl reference electrode (3.5 M NaCl) and a working electrode (WE) with an exposed area of 0.196 cm<sup>2</sup>. The solution was composed of 2.14 M H<sub>2</sub>SO<sub>4</sub>, 4.6×10<sup>-4</sup> M HCl and 0.395 M CuSO<sub>4</sub>·5H<sub>2</sub>O. The concentration of the organic additives A, B, C that was added to the solution was determined evaluated using LSV, DPV and SWV. A scan rate of 10 mV/s was used for the LSV measurement. The DPV measurement parameters were: 50 mV modulation amplitude, 0.2 s modulation time and a scan rate of 10 mV/s. The SWV was recorded using a frequency of 10 Hz, a potential increment of 4 mV and an amplitude of 50 mV.

## 3. RESULTS AND DISCUSSION

### 3.1 CVs for the Nano-Au electrodes in the Absence and Presence of Organic Additives

Fig. 1 shows CVs for nano-Au electrodes at potentials from 0.4 to 1.6 V vs Ag/AgCl in different electrolytes. To confirm the potential for copper ion deposition and copper metal stripping, the CVs for nano-Au electrodes in the presence and absence of 0.395 M CuSO<sub>4</sub>·5H<sub>2</sub>O are shown in Fig. 1(a). In the absence of copper ions, there are two oxidation peaks at about 1.25 and 1.45 V vs Ag/AgCl, which correspond to gold (hydr)oxides formation, which is consistent with previous reports [22]. There are two reduction peaks in the reverse scan at 1.05 and 0.83 V vs Ag/AgCl, which correspond to the reduction of gold (hydr)oxides to Au [22]. In the presence of 0.4 M copper ions, copper ions are deposited at a potential of 0.65 to 0.45 V vs Ag/AgCl and copper stripping peaks are observed at a potential of 0.45 to 0.65 V vs Ag/AgCl. The presence of copper ions does not affect the electrochemical (EC) behavior of the nano-Au electrode at a potential of more than 0.65 V vs Ag/AgCl.

Fig. 1(b) shows CVs for a nano-Au electrode in the presence and absence of 375 μL of organic additive A. The current increases significantly at a potential of 1.15 V and 1.45 V vs Ag/AgCl, indicating that the organic additive A is adsorbed and oxidized on the surface of the nano-gold electrode at a high potential. When the potential is scan reversed, the reduction peak current also increases, which shows that the oxidation product of the additive A is reduced. The CVs for a nano-Au electrode in the presence and absence of 12.5 μL of organic additive B are shown in Fig. 1(c). The electrochemical behavior of organic additive B is similar to that for organic additive A. The oxidation current increases significantly at 1.15 V and 1.45 V vs Ag/AgCl.

Fig. 1(d) shows CVs for a nano-Au electrode in the presence and absence of 30 μL of organic additive C. If organic additive C is added to the solution, there is an obvious oxidation current at 1.15 V and 1.45 V vs Ag/AgCl so a high applied potential range is used for the detection of organic additives. In the following discussion, LSV, DPV and SWV are used to detect organic additives separately.

### 3.2 LSVs for the nano-Au Electrodes for the Detection of Organic Additives

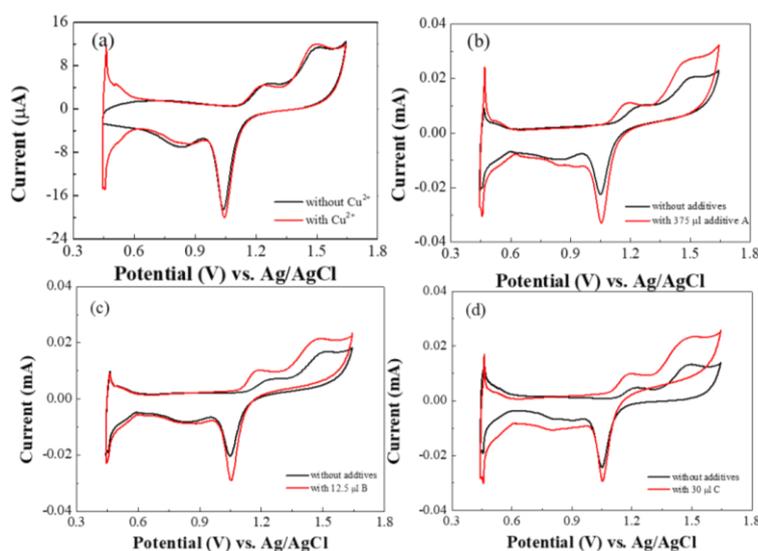
LSVs were used to detect the organic additives A, B, and C and the results are shown in Fig. 2. The range of concentrations of organic additives for this study is determined according to the real operating conditions for the copper plating plant of the Unitech Company in Taiwan. Fig. 2(a) shows LSVs for a nano-Au electrode in the presence of organic additive A at a concentration from 0 to 300 μL. 50 μL of organic additive A was added to the electrolyte for each experiment. The oxidation peak at 1.45 V vs Ag/AgCl is obvious. The oxidation current increases as concentration of organic additive A increases.

There is a linear relationship between the concentration of organic additive A and the response current, as shown in Fig. 2(d) (black line). The gradient represents the sensitivity. The sensitivity for the detection of organic additive A is 0.0046 μA/μL·cm<sup>2</sup> (R<sup>2</sup> = 0.98). Fig. 2(b) shows LSVs in the presence of organic additive B for a concentration from 0 to 24 μL. 4 μL of organic additive B was added to the electrolyte for each experiment. There are two oxidation peaks at 1.15 and 1.35 V vs Ag/AgCl. The peak current is proportional to the concentration of organic

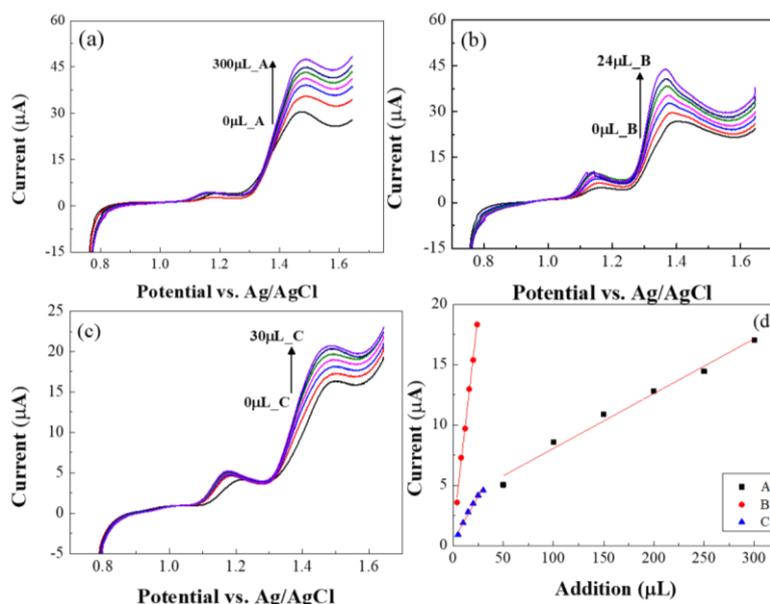
additive B. The sensitivity for the detection of organic additive B at 1.35 V vs Ag/AgCl is  $0.92 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.996$ , red line).

Fig. 2(c) shows LSVs in the presence of organic additive C at a concentration from 0 to 30  $\mu\text{L}$ . 5  $\mu\text{L}$  of organic additive C was added to the electrolyte for each experiment. The oxidation peak current at 1.45 V vs Ag/AgCl increases

significantly if the concentration of organic additive C increases. The sensitivity for the detection of organic additive C is  $0.15 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.98$ , blue line). A comparison of the concentration calibration curves for the detection of organic additives A, B, and C is shown in Fig. 2(d). The order of sensitivity for the detection of organic additives is  $B > C > A$ .



**Fig. 1. Cyclic Voltammograms for nano-Au electrodes in the presence and absence of (a) 0.395 M copper ions, (b) 375  $\mu\text{L}$  A, (c) 12.5  $\mu\text{L}$  B and (d) 30  $\mu\text{L}$  C in 2.14 M  $\text{H}_2\text{SO}_4$ ,  $4.6 \times 10^{-4}$  M HCl and 0.395 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solutions**



**Fig. 2. The Linear Sweep Voltammetry curves for nano-Au electrodes in electrolyte with (a) 0 ~ 300  $\mu\text{L}$  A (b) 0 ~ 24  $\mu\text{L}$  B (c) 0 ~ 30  $\mu\text{L}$  C and (d) a comparison of the sensitivity linearity of three additives, A, B and C, in 2.14 M  $\text{H}_2\text{SO}_4$ ,  $4.6 \times 10^{-4}$  M HCl and 0.395 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solutions**

### 3.3 DPVs for Nano-Au electrodes for the Detection of Organic Additives

DPVs were used to detect organic additives A, B, and C and the results are shown in Fig. 3. Fig. 3(a) shows the DPVs for the detection of organic additive A at a concentration from 0 to 300  $\mu\text{L}$ . There are two obvious oxidation peaks at 1.15 and 1.31 V vs. Ag/AgCl. The oxidation peak current increases as the concentration of organic additive A increases. The second oxidation peak current varies more significantly with the concentration of organic additive A than the first oxidation peak current.

The plot of peak current at 1.31 V vs. Ag/AgCl against the concentration of organic additive A is shown in Fig. 3(d) (black line). The sensitivity for the detection of organic additive A is  $0.0008 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.93$ ). Fig. 3 (b) shows DPVs for the detection concentrations of organic additive B from 0 to 24  $\mu\text{L}$ . 4  $\mu\text{L}$  of organic additive B was added each time. The results are similar to those for the detection of organic additive A. At 1.31 V vs. Ag / AgCl, there is a linear relationship between the oxidation peak and the concentration of organic additive B, as shown in Fig. 3(d) (red line). The sensitivity for the detection of organic additive B is  $0.2636 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.988$ ).

Fig. 3 (c) shows DPVs for the detection of organic additive C at a concentration from 0 to 30  $\mu\text{L}$ . 5  $\mu\text{L}$  of organic additive C was added each time. The sensitivity for the detection of organic additive C at 1.31 V vs. Ag/AgCl is  $0.065 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.902$ ). Fig. 3(d) compares the concentration calibration curves for the detection of organic additives A, B and C. The sensitivity for the detection of organic additive B is highest. Compared with the LSV in Fig. 2, the first oxidation peak for the detection of organic additives is higher for DPV. However, the sensitivity for the detection of organic additives at 1.31 V is higher for LSV than for DPV.

### 3.4 SWVs for Nano-Au electrodes for the Detection of Organic Additives

SWVs were used to detect organic additives A, B, and C and results are shown in Fig. 4. Fig. 4(a) shows SWVs for the detection of organic additive A at a concentration from 0 to 300  $\mu\text{L}$ . 50  $\mu\text{L}$  of A was added to the electrolyte each time. There are two obvious oxidation peaks at

1.06 V and 1.31 V vs. Ag/AgCl. At these two applied potentials, there is a linear relationship between the concentration of organic additive A and the response current. The concentration calibration curves these two oxidation peaks are shown in Fig. 4(d) (black lines). The sensitivity for the detection of organic additive A is  $0.0014$  ( $R^2 = 0.97$ ) and  $0.0014 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.961$ ) at applied potentials of 1.06 V and 1.31 V vs Ag/AgCl, respectively.

Fig. 4 (b) shows SWVs for the detection of organic additive B at a concentration from 0 to 24  $\mu\text{L}$ . 4  $\mu\text{L}$  of organic additive B was added each time. There are two obvious oxidation peaks at 1.06 V and 1.26 V vs Ag/AgCl. The concentration calibration curves for the two oxidation peaks for the detection of organic additive B are plotted in Fig. 4(d) (red lines). The sensitivity is  $0.3923 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.97$ ),  $0.3936 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.99$ ) at 1.06 V and 1.26 V vs Ag/AgCl, respectively.

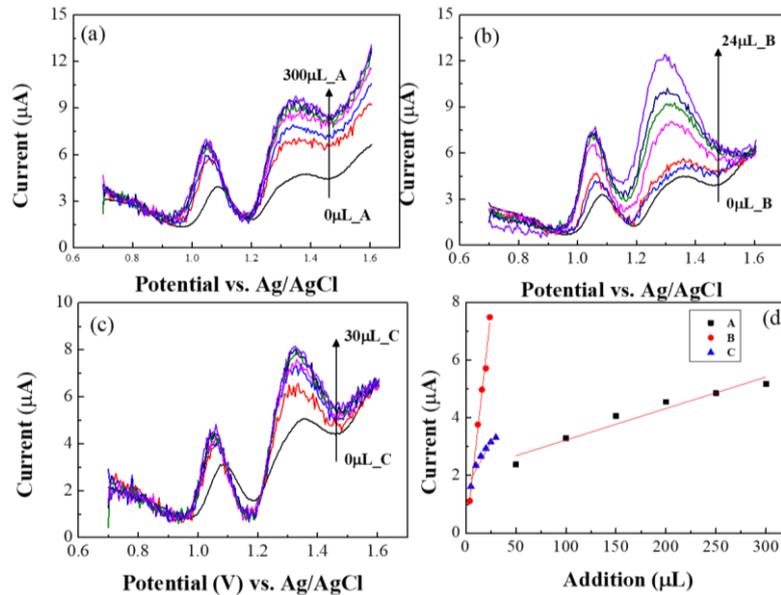
Fig. 4(c) shows SWVs for the detection of organic additive C at a concentration from 0 to 30  $\mu\text{L}$ . 5  $\mu\text{L}$  of organic additive C was added each time. There are two obvious oxidation peaks at 1.06 V and 1.31 V vs Ag/AgCl. The concentration calibration curves for the detection of organic additive C at the two oxidation peaks are shown in Fig. 4(d) (blue lines). The sensitivity is  $0.0935 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.98$ ) and  $0.1453 \mu\text{A}/\mu\text{L}\cdot\text{cm}^2$  ( $R^2 = 0.97$ ) at 1.06 V and 1.31 V vs Ag/AgCl, respectively. Fig. 4(d) compares the concentration calibration curves for the detection of organic additives A, B and C. Using the SWV method, organic additives are detected at two potentials. There is a linear relationship between the concentration of organic additives and the response current. The nano-Au electrode has the highest sensitivity for the detection of organic additive B.

### 3.5 Comparison of the Sensitivity for the Detection of Organic Additives using the three Electrochemical Methods

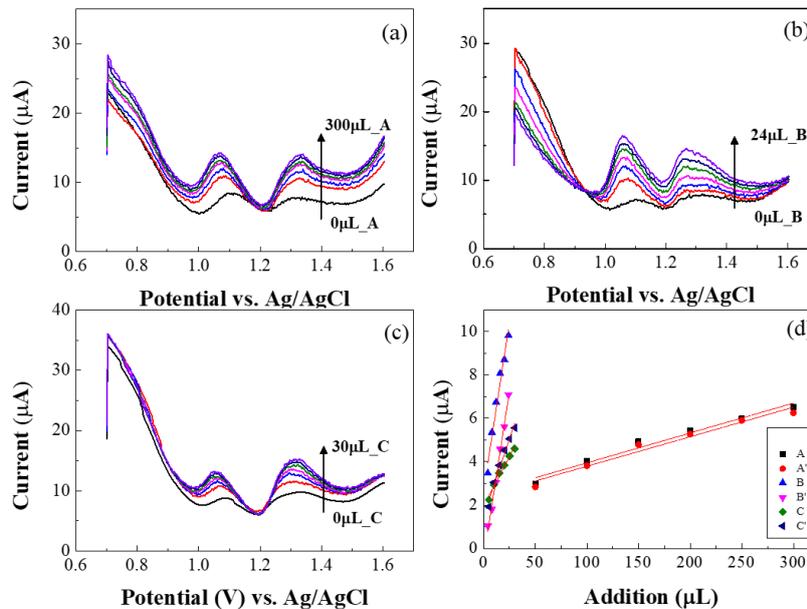
Figs. 5(a-c) respectively compare the sensitivity of the nano-gold electrodes for the detection of organic additives A, B, and C using LSV, DPV and SWV. Regardless of the electrochemical method used, the best sensitivity for the nano-gold electrode is for the detection of organic additive B. Using LSV as shown in Fig. 5(a), the best sensitivity for the detection of B is 200 times and 6 times the sensitivity for A and C, respectively.

Fig. 5 (b) shows that the sensitivity of nano-gold for the detection of B using DPV is 330 times and 4 times that for A and C, respectively. The SWV has a sensitivity for the detection of B at 1.06 V vs Ag/AgCl that is 280 times and 4 times that of A and C, respectively and the sensitivity for the

detection of B at 1.3 V vs Ag/AgCl is 280 times and 3 times that for A and C. It is concluded that the sensitivity of the nano-gold electrodes for the detection of organic additives is: B > C > A. The sensitivity for the detection of organic additives is: LSV > SWV > DPV.



**Fig. 3. The Differential Pulse Voltammetry curves for nano-Au electrodes in electrolyte with (a) 0~300 μL A (b) 0~24 μL B (c) 0~30 μL C and (d) a comparison of the sensitivity linearity of three additives A, B and C, in 2.14 M H<sub>2</sub>SO<sub>4</sub>, 4.6×10<sup>-4</sup> M HCl and 0.395 M CuSO<sub>4</sub>·5H<sub>2</sub>O solutions**



**Fig. 4. The Square Wave Voltammetry curves for the nano-Au electrodes in electrolyte with (a) 0 ~ 300 μL A (b) 0 ~ 24 μL B (c) 0 ~ 30 μL C and (d) a comparison of the sensitivity linear relationship for the three additives (where A, B, and C are at 1.05 V and A', B', C' are at 1.3 V) in 2.14 M H<sub>2</sub>SO<sub>4</sub>, 4.6×10<sup>-4</sup> M HCl and 0.395 M CuSO<sub>4</sub>·5H<sub>2</sub>O solutions**

### 3.6 Morphology and Structure of the Nano-Au Electrodes

Fig. 6 shows the X-ray diffraction (XRD) spectrum for the nano-Au electrode. The XRD pattern shows the typical face-centered cubic (fcc) structure of the nano-Au electrode. Peaks at 38.18, 44.39, 64.57, and 55.54 correspond to the (111), (200), (220), and (311) crystal planes of Au metal. The diffraction pattern is consistent with JCPDS 04-0784.

Fig. 7 shows SEM images of the nano-Au electrodes before and after the electrochemical

experiments. Close-packed round particles of 350-450 nm sized are seen on the fresh nano-Au electrode, as shown in Fig. 7(a). Smaller particles (less than 20 nm) and cracks exist at each round particle. Fig. 7(b) shows the surface morphology of the nano-Au electrode after the electrochemical experiments. The surface structure is similar but the cracks are deeper and significantly larger. The sensitivity of the nano-Au electrode gradually decreases as the number of uses increases. This phenomenon is presumed to be related to the change of the surface morphology of the electrode with the electrochemical reaction.

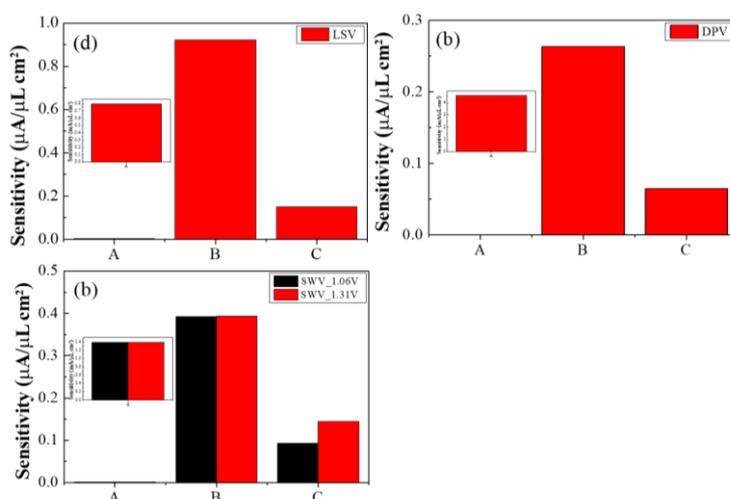


Fig. 5. Comparison of the sensitivity of nano-Au electrodes (a) LSV (b) DPV and (c) SWV for the detection of organic additives A, B and C in 2.14 M H<sub>2</sub>SO<sub>4</sub> + 16.94 ppm HCl + 0.395 M CuSO<sub>4</sub>•5H<sub>2</sub>O solutions

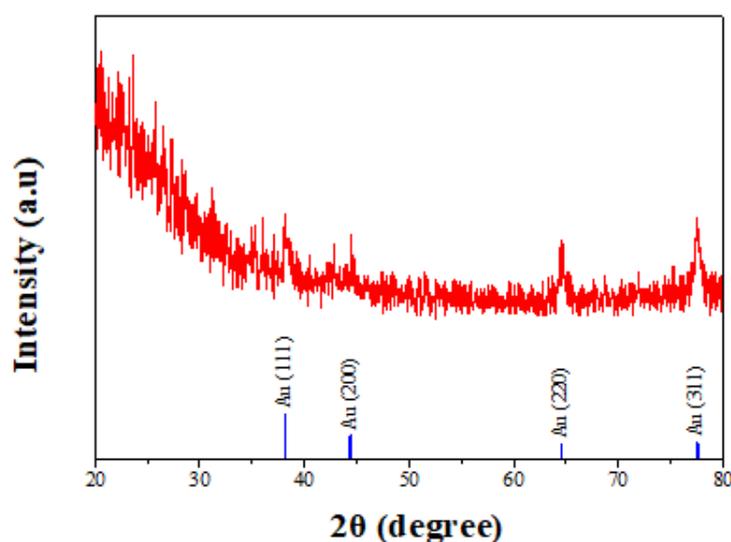
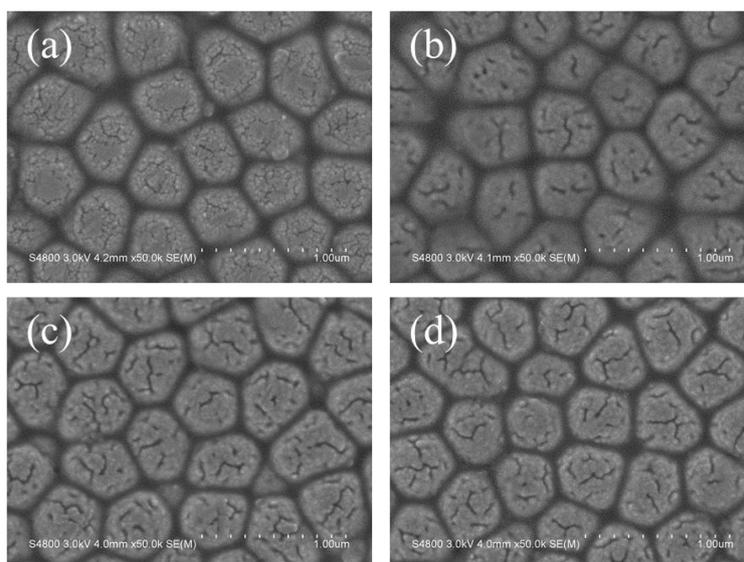


Fig. 6. XRD diffraction patterns for the nano-Au electrode



**Fig. 7. SEM images of the nano-Au electrode (a) before the experiment, (b) after the detection of organic additive A, (c) after the detection of organic additive B and (d) after the detection of organic additive C**

#### 4. CONCLUSION

Organic additives, A, B, and C are detected using nano-gold electrodes and LSV, DPV and SWV methods. The organic additives are detected at a more positive potential window to avoid interference of the potential window for copper ion deposition and stripping. The response currents for all three methods exhibit a linear relationship with the concentration of the additive. The sensitivity of the nano-gold electrodes for the detection of organic additives is:  $B > C > A$ . The order of sensitivity to the same organic additive is:  $LSV > SWV > DPV$ .

#### DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

#### ACKNOWLEDGEMENTS

Support from the Industrial Research Institute Innovative Foresight Technology Research Project (J301ARY118), the Ministry of Science

and Technology (MOST109-2221-E-035-024-MY3) and Feng Chia University is gratefully appreciated. The authors also appreciate the help of the Precision Instrument Support Center of Feng Chia University in providing fabrication and measurement facilities.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

1. Dow WP, Yena MY, Liao SZ, Chiu YD, Huang HC. Filling mechanism in microvia metallization by copper electroplating. *Electrochim. Acta.* 2008;53:8228-8237.
2. Li Z, Tan B, Shi M, Luo J, Hao Z, He J, Yang G, Cui C. Bis-(sodium sulfoethyl)-disulfide: A Promising Accelerator for Super-conformal Copper Electrodeposition with Wide Operating Concentration Ranges. *J. Electrochem. Soc.* 2020;167:042508.
3. Chan PF, Chiu YD, Dow WP, Krug K, Lee YL, Yau SL. Use of 3,3-Thiobis(1-propanesulfonate) to Accelerate Microvia Filling by Copper Electroplating. *J. Electrochem. Soc.* 2013;160:D3217.
4. Xiao N, Li N, Cui G, Tian D, Yu S, Li Q, Wu G. Triblock Copolymers as Suppressors for Microvia Filling via Copper Electroplating.

- J. Electrochem. Soc. 2013;160:D188-D195.
5. Yang L, Radisic A, Deconinck J, Vereecken PM. Modeling the Bottom-Up Filling of Through-Silicon vias Through Suppressor Adsorption/Desorption Mechanism. J. Electrochem. Soc. 2013; 160:D3051-D3056.
  6. Dow WP, Li CC, Lin MW, Su GW, Huang CC. Copper Fill of Microvia Using a Thiol-Modified Cu Seed Layer and Various Levelers. J. Electrochem. Soc. 2009;156:D314-D320.
  7. Ren S, Lei Z, Wang Z. Investigation of Nitrogen Heterocyclic Compounds as Levelers for Electroplating Cu Filling by Electrochemical Method and Quantum Chemical Calculation. J. Electrochem. Soc. 2015;162:D509-D514.
  8. Haba T, Ikeda K, Uosaki K. Electrochemical and in situ SERS study of the role of an inhibiting additive in selective electrodeposition of copper in sulfuric acid. Electrochemistry Communications. 2019; 98:19-22.
  9. Wang X, Yang Z, Li N, Liu Z, Yang Z, Wang Z. First Synergy Effects of SPS and PEG-4000 on the Bottom-Up Filling in Electroless Copper Plating. J. Electrochem. Soc. 2010;157:D546-D549.
  10. Wang X, Zhang S, Chen S, Tan B, Guo H, Wang Y, Qiang Y, Fu S, Wen Y. Effects of 2,2-Dithiodipyridine as a Leveler for Through-Holes Filling by Copper Electroplating. J. Electrochem. Soc. 2019;166:D660.
  11. Lin GY, Yan JJ, Yen MY, Dow WP, Huang SM. Characterization of Through-Hole Filling by Copper Electroplating Using a Tetrazolium Salt Inhibitor. J. Electrochem. Soc. 2013;160:D3028.
  12. Tan M, Harb JN. Additive Behavior during Copper Electrodeposition in Solutions Containing Cl<sup>-</sup>, PEG, and SPS. J. Electrochem. Soc. 2003;150:C420.
  13. Lin CC, Yen CH, Hu CC. The Degradation Behavior of Brightener on Dimensionally Stable Anodes during the Copper Electrodeposition. J. Electrochem. Soc. 2019;166: D626-D634.
  14. Li LL, Yang CJ. Size Control of Copper Grains by Optimization of Additives to Achieve Flat-Top Copper Pillars through Electroplating, J. Electrochem. Soc. 2017;164:D315-D320.
  15. Hung CC, Lee WH, Chang SC, Chen KW, Wang YL. Suppression Effect of Low-Concentration Bis-(3-sodiumsulfopropyl disulfide) on Copper Electroplating. J. Electrochem. Soc. 2007;155:D133.
  16. Tran A, Hoang H, Hirato T, Kondo K. Monitoring of SPS Concentration by the Ring Current Using a Rotating Ring-Disk Electrode with Dissolving Disk Copper to Refresh a Void Free Solution, J. Electrochem. Soc. 2019;166:D742.
  17. Luo J, Li Z, Tan B, Cui C, Shi M, Hao Z. Communication—Triphenylmethane-Based Leveler for Microvia Filling in Copper Super-Conformal Electroplating, J. Electrochem. Soc. 2019;166:D603.
  18. Xie BG, Sun JJ, Chen XB, Chen JH, Xiang TL, Chen GN. In Situ Monitoring of Additives in Copper Plating Baths by Cyclic Voltammetric Stripping with a Microelectrode. J. Electrochem. Soc. 2007;154:D516-D519.
  19. Ellis CD, Hamilton MC, Nakamura JR, Wilamowski BM. Efficient determination of copper electroplating chemistry additives IEEE Transactions on Components, Packaging and Manufacturing Technology. 2014;4:1380-1390.
  20. Choe S, Kim M, Kim K, Kim H, Jeon Y, Kim T, Kim S, Kim J. High Accuracy Concentration Analysis of Accelerator Components in Acidic Cu Superfilling Bath. J. Electrochem. Soc. 2016; 163(2):D33.
  21. Yoon Y, Ham Y, Kim T, Choe S, Kim J. Cyclic Voltammetry Stripping Analysis to Determine Iodide Ion Concentration in Cu Plating Bath. J. Electrochem. Soc. 2018;165(5):H213.
  22. Aranzales D, Wijenberg JHOJ, Koper MTM, Voltammetric Study of Tin Electrodeposition on Polycrystalline Gold from Sulfuric and Methanesulfonic Acid J. Electrochem. Soc. 2019;166(8):D283-289.

© 2021 Weng et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:

<https://www.sdiarticle4.com/review-history/73291>