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Corrosion study of electrodeposited Co-Ni-Fe protective coating on Electroless Nickel Immersion Gold (ENIG) flexible printed circuit

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Abstract

Flexible Printed Circuits (FPCs) have been vastly used in electronic devices such as mobile phones and sensors. This multi-layer polymer is used in electronic packaging to interconnect high performance devices. Electroless Nickel Immersion Gold (ENIG) is the final finishing method commonly applied on FPCs due to its excellent planarity, wear or abrasion resistance and electrical contact performance. However, corrosion problem on FPCs surface may influence the electrical conductivity, performance and thus affect the functionality of the end product. Previous published literature showed that Co-Ni-Fe enhanced the corrosion behavior of metals. Therefore, ternary Cobalt alloys (Co-Ni-Fe) have been synthesized as the protective coating on ENIG FPCs in this research. A low cost electrodeposition method is applied to produce a Co-Ni-Fe protective coating to improve the corrosion resistance of ENIG FPCs. The result will be compared between FPCs with and without protective coating. Co-Ni-Fe solution for electrodeposition process was prepared at pH 1. The current applied to coat the FPCs is 0.6 ± 0.05 A. The experiment conducted at 50^{0}C ± 0.5 and performed at 30s and 60s of deposition time. Irregular shape of microstructure with grain size range from 46 nm to 88 nm was observed under FESEM micrographs. Corrosion test was performed by using Potentiodynamic Polarization technique under acidic environment. The corrosion rate per year of the FPCs after coated with electrodeposited Co-Ni-Fe showed lower corrosion rate than ENIG FPC. The corrosion behavior and surface morphology studies have shown that the electrodeposited Co-Ni-Fe coating improved the corrosion rate of ENIG FPCs.

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1. Introduction

The needs of multifunctional components in electronic industry encourage researchers to improve several features such as low resistance interconnects, high electrical conductivity [1, 2, 3, 4] and develop new formulation for coating [5] to enhance performance and reduce cost maintenance. However, electronic devices in real application will be exposed directly on corrosion element such as air, moisture and corrosive environment. Therefore, to retain its reliability is one of the biggest challenges [1]. Recently, it has been found that corrosion was visible on the surface of ENIG FPCs. Corrosion on FPCs surface can affect the electrical conductivity, performance and thus affect the functionality of the end product [5].

Electrodeposition is a low cost and easy installment process used to produce coatings on various samples with free porosity. It can be applied to polymers, metals, alloys and composites [6]. Ternary Cobalt alloys (Co-Ni-Fe) have been synthesized onto FPCs by using electrodeposition process to produce a protective coating on its gold surface. Previous published literature showed that the addition of Nickel in Co-Fe alloys enhanced the corrosion behavior of metals [7]. The Co-Ni-Fe synthesized by electrodeposition was able to produce nanocrystalline with grain size less than 100 nm [7]. Youssef *et. al* [8] reported that smaller grain size will improve the protection performance of passive film and thus improve the corrosion resistance. In order to improve the corrosion problem of ENIG FPCs by applying Co-Ni-Fe coating, it is important to study the effect of the electrodeposition process on FPCs. Hence, the investigation on the effect of electrodeposited Co-Ni-Fe towards corrosion behavior, surface morphology and grain size of the protective coating on ENIG FPCs is reported in this paper.

Nomenclature

ENIG	Electroless Nickel Immersion Gold
FPC	Flexible Printed Circuit
Co-Ni-Fe	Cobalt-Nickel-Iron
$CoSO_4$	Cobalt Sulfate
XRD	X-Ray Diffractrometry
FESEM	Field Emission Scanning Electron Microscope

2. Experimental

2.1. FPC Preparation

Flexible Printed Circuit area was sprayed with pneumatic air gun to remove dust and contamination on its surface. The surface was dried and not expose to water before begin the electrodeposition process. The purpose is to avoid moisture entrapped in the coating during the electrodeposition. The interconnection areas were covered with copper tape to enhance the conductivity of FPC so that top to bottom of ENIG area can be fully deposited. A copper plate was used to support the FPC and to ensure it is static at its position during the deposition process. The static position is essential as the distance between FPC and electrode will affect the current density and finally results in poor coating appearance. The copper plate immersion area has been covered with Gamry PortHoles Electrochemical Sample Mask. This action is to avoid current flow and coating form on the copper plate. The coating shall only form on the FPCs during the electrodeposition process.

2.2. Bath Preparation & Electrodeposition Process

The electrolyte composition bath was firstly prepared for the electrodeposition process. The bath is a mixture of Cobalt Sulfate, Nickel Sulfate, Iron Sulfate, Boric Acid, Saccharine and Ascorbic Acid. Table 1 shows the molar concentration of the precursors for bath composition. According to the previous study [9], the electrodeposited Cobalt and its alloy prepared by 0.075M $CoSO_4$ of bath concentration had smaller grain size and thus increased its corrosion resistant [9]. Boric Acid and Saccharine were added in the composition as pH buffer and grain refinement

agent. All the precursors were mixed in a basic beaker cell with 500 ml distilled water. The temperature was controlled at 50^0C ± 0.5 and 6ml nitric acid was added to get pH 1 of the bath. The Co-Ni-Fe protective coatings were deposited by immersing prepared FPC into the bath (cathode) parallel with graphite electrode (anode). The current for this study was 0.6 ± 0.05 A. The deposition time took place for 30s and 60s. After the process completed, the FPC was rinsed with distilled water and dried at room temperature. Crystallographic structures analysis of the Co-Ni-Fe protective coating was carried out by using Ultima IV FD 3668N X-Ray Diffractrometry (XRD) machine with Cu-Ka (λ= 0.7093 Å) radiation. Surface morphology characterization was observed by Carl Zeiss SMT Field Emission Scanning Electron Microscope (FESEM). Corrosion behavior study was conducted by using GAMRY Potentiodynamic Polarization. Alicona Infinite Microscope was used to measure the thickness of the coating.

Table 1. Bath composition of Co-Ni-Fe electrodeposition.

Bath composition	**Concentration (M)**
Cobalt Sulfate	0.075
Nickel Sulfate	0.2
Iron Sulfate	0.03
Boric Acid	0.4
Saccharine	0.01
Ascorbic Acid	0.1

3. Results and Discussion

Phase and Crystallographic Structure Characterization. The phase and crystal structure of Co-Ni-Fe coating were determined by XRD analysis from 35º to 100º with 2θ angle. Figure 1 shows the XRD patterns of Co-Ni-Fe coating in 30s and 60s of deposition time.

Peaks of Au, CoFe, CoNiO and FeNi were observed at both 30s and 60s of deposition time. All the phases exhibited the cubic crystal structure. The CoFe, CoNiO and FeNi phases were formed from the electrodeposited Co-Ni-Fe coating while the Au from the ENIG FPC. From this observation, the Co-Ni-Fe coating of 30s deposition time may be predicted to adhere on the ENIC FPC surface but not reacted with the base substrate. The crystallite size can be measured by using Debye Scherrers's equation [10]. From the XRD result, the crystallite size for 30s deposition is estimated to be 39.94 nm in average. As for 60s deposition time, it is 50.14 nm in average. There was no other contamination from electrolyte observed.

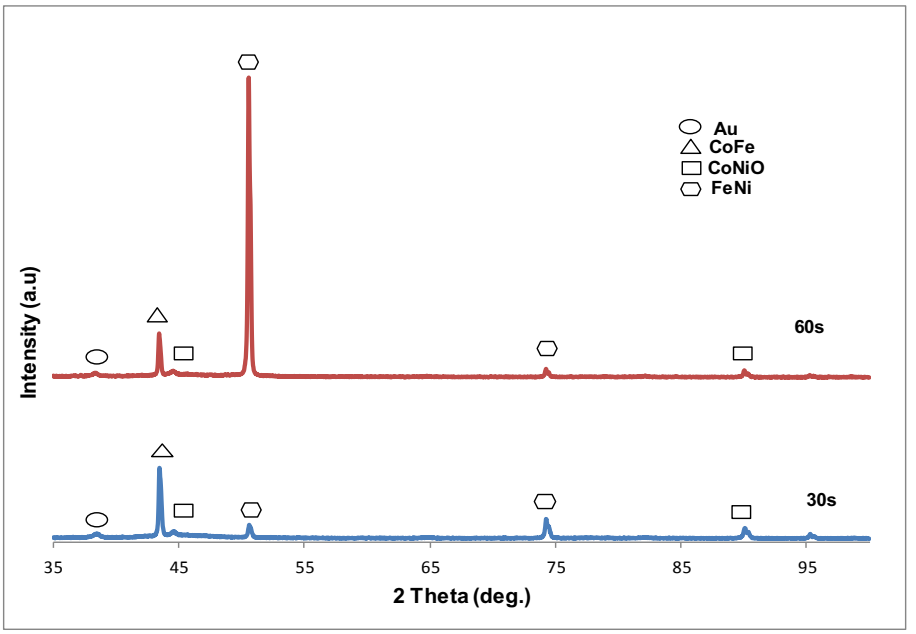

Fig. 1. XRD patterns of electrodeposited Co-Ni-Fe at 30s and 60s deposition time.

Surface Morphology Study. Structural and morphological characterization was observed by using FESEM. The granular structure of ENIG and Co-Ni-Fe coating in 30s deposition time are shown in Figure 2. All the microstructures were identified as irregular shape. The existence of voids was identified in ENIG microstructure. These voids might be due to formation of oxide occurred in the spaces between of grains. Co-Ni-Fe coating showed a stacking grain covering the FPC surface. The bottom layer of the grain consisted of small and compact grains.

The grain sizes for Co-Ni-Fe coating in 30s and 60s deposition time are 46 nm and 88 nm, respectively. This measurement was taken from the average grain size of at least 8 grains. The smallest grain size was found in the sample prepared at 30s deposition time. This result showed that the grain size decreases with the increment of deposition time. In the case of 30s deposition time, there might be insufficient time for the grain to growth. This irregular structure was formed because Co-Ni-Fe atoms distributed mostly inside the grains instead of at the grain boundaries [11]. However, the average grain size for both deposition time of Co-Ni-Fe coating is still in nano-size, which the grain size is less than 100 nm [12]. A coating with nanocrystalline grain size has excellent chemical, mechanical and physical properties. These characteristics are resulted from the reduction in its grain size in addition to the existence of a huge numbers of grain boundaries in the grain structures. The thickness of the coating was measured by Infinite Focus Microscope (Alicona). From the measurement, the thickness of Co-Ni-Fe coating at 30s deposition time is about 7.7 µm.

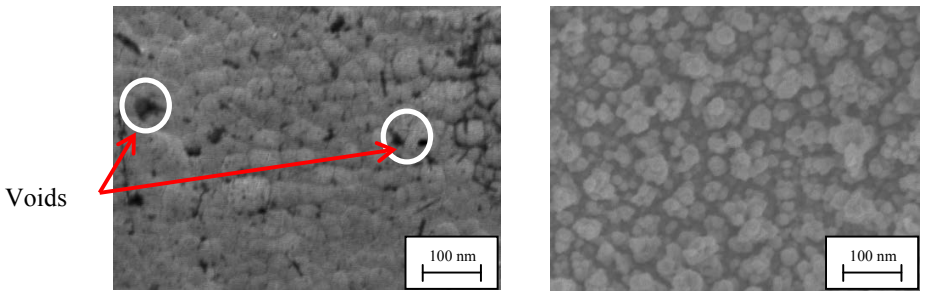

Fig. 2. Co-Ni-Fe coatings microstructure under FESEM micrographs in (a) 30s deposition time (b) 60s deposition time.

Potentiodynamic Polarization Analysis. The electrolyte applied for the testing is 200ml of 0.25M Sodium Sulfate (Na_2SO_4) to accelerate oxidation of the coating [13]. The electrolyte solution has a pH of 5 (acidic) and performed at room temperature. This study is to identify the corrosion behavior between Co-Ni-Fe with protective coating and without coating (ENIG). The corrosion rate of Co-Ni-Fe coatings showed a smaller value than ENIG FPC. The lowest corrosion rate of Co-Ni-Fe coatings is due to the smallest grain size and the compactness of microstructure [8]. This was supported by the FESEM micrograph analysis. The E_{corr} value of Co-Ni-Fe coating at 30s and 60s deposition time showed more cathodic potential than the ENIG FPC. Cathodic potential of E_{corr} exhibited the highest corrosion resistance than the anodic potential. The comparison of corrosion rate of these flexible circuits can be seen in Table 2.

Table 2. E_{corr} and corrosion rate for FPCs.

FPC Type	Deposition time (s)	E_{corr}, mV (SCE)	Corrosion Rate, mmpy
ENIG	0	-301.0	463 e^{-3}
FPC With Co-Ni-Fe	30	-523.0	160 e^{-3}
FPC With Co-Ni-Fe	60	-622.0	208 e^{-9}

Referring to Table 2, the corrosion rate for FPC with Co-Ni-Fe coating of 30s deposition time showed the lowest corrosion rate per year with $160e^{-3}$. Both the FPC with Co-Ni-Fe coating of 30s and 60s deposition time showed better corrosion rate as compared to ENIG FPC.

4. Conclusion

Co-Ni-Fe protective coatings were successfully produced by electrodeposition method on ENIG FPCs. Surface and morphology studies revealed that the granular structure of Co-Ni-Fe coatings has irregular shapes. The grain sizes for both Co-Ni-Fe coatings at 30s and 60s deposition time are 46 nm and 88 nm, respectively. FESEM result showed that the grain size decreased as the deposition time increased. The corrosion rate values decreased with the increment of deposition times. The lowest corrosion rate showed in the coated ENIG FPC prepared at 30s deposition time. In fact, the Co-Ni-Fe coating shows improvement in corrosion behavior as compared to ENIG FPCs without Co-Ni-Fe coating.

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References

[1] Bui QV, Nam ND, Choi DH, Lee JB, Lee CY, Kar A, Kim JG, Jung SB. Corrosion protection of ENIG surface finishing using electrochemical methods. Materials Research Bulletin 2010;45/3:305-308.
[2] Merchant HD, Wang JT, Florida C, Liu YL. Metallurgy and performance of electrodeposited copper for flexible circuits. Circuit World 2000; 26:7-14.
[3] Ptchelintsev A. Automated Modeling and Fatigue Analysis of Flexible Printed Circuits. 7th. Int. Conference on Thermal, Mechanical and Multiphysics Simulation and Experiments in Micro-Electronics and Micro-Systems 2006:1-6.
[4] Tan CW, Chiu YW, Chan YC. Corrosion study of anisotropic conductive joints on polyimide flexible circuits. Materials Science and Engineering: B 2003;98/3:255-264.
[5] Lai W, Wong P, Hsu K. Development of novel electroless nickel for Selective electroless nickel immersion gold applications. IMPACT 2012:80-85.
[6] Gurrappa I, Binder L. Electrodeposition of nanostructured coatings and their characterization – a review. Science and Technology of Advanced Materials 2008;9/4.
[7] Hyie KM, Resali NA, Abdullah WNR. Study of Alloys Addition to the Electrodeposited Nanocrystalline Cobalt. Advanced Materials Research 2012;486:108-113.
[8] Youssef KM, Koch C, Fedkiw P. Improved corrosion behavior of nanocrystalline zinc produced by pulse-current electrodeposition. Corrosion Science 2004;46/1:51-64.
[9] Resali NA, Abdullah WNR, Hyie KM, Kalam A, Nik Roselina NR, Mardziah CM. The Influence of Bath Concentration on Particle Size of Cobalt Nanoparticles. Applied Mechanics and Materials 2013;393:140-145.
[10] Abdullah WNR, Hyie KM, Resali NA, Chong WT. Effect of Deposition times on Electrodeposited Cobalt-Iron Nanocoating. Advanced Materials Research 2012;576:565-568.
[11] Hyie KM, Normimi W, Abdullah R, Resali NA, Chong WT, Salleh Z, Ghani MAA. The Physical and Magnetic Properties of Electrodeposited Co-Fe Nanocoating with Different Deposition Times. Journal of nanomaterials 2013;2013:1-6.
[12] Tjong SC, Chen H. Nanocrystalline materials and coatings. Materials Science and Engineering: R: Reports 2004;45/1-2:1-88.
[13] Hussain SPA, Pandurangadu V, Reddy SSK. Investigations on the Effect of Sodium Chloride in Low Temperature Hot Corrosion of Mar-M 509 AT 750˚C. International Journal of Engineering and Science 2013;2/7:31-34.