Effects of Complexing Reagent on Electroless Nickel Iron Alloy Plating for the Diffusion Barrier of UBM

Ja-Kyung Koo and Jae-Ho Lee*
Department of Materials Science and Engineering, Hongik University, 94 Wausan-ro, Mapo-gu, Seoul 04066, Korea

Electro and electroless nickel platings have been extensively used as a diffusion barrier in under bump metallization (UBM) or as a surface finish on printed circuit boards (PCB). Even though a thin Ni layer on top of Cu can reduce the interfacial reactions with Sn-rich solders at a low reflow temperature, it may not be so effective when a reflow process is performed at a higher temperature and for a longer period. To provide a more robust diffusion barrier layer than electrodes Ni, electroless NiFe alloy system has been proposed. Since the electroless Ni-Fe plating bath has been rarely studied, the proper baths were not available commercially. In this research, the electroless plating of Ni-Fe alloys was investigated on the basis of complexing reagent. The stability of complexing reagent was studied. The compositions of electroplating layers were analyzed with EDS. The desired Ni-Fe alloy were obtained by controlling the chemical composition of the bath and its operating parameters. [doi:10.2320/matertrans.MA201606]

(Received November 14, 2016; Accepted December 1, 2016; Published January 16, 2017)

Keywords: electroless, nickel iron alloy, complexing agent, under bump metallization (UBM), stability

1. Introduction

Copper substrate has been mainly used in under bump metallization (UBM) with Pb solder. Copper layer has excellent solderability, electrical conductivity properties with solder. However, Pb containing solder has a harmful effect on the human health and the environment. Therefore, lead free solders were studied to replace Pb containing solder. In particular, Sn-3.5Ag or Sn-3.0Ag-0.5Cu (SAC) solder has been widely studied. Sn-rich solder has low melting point, good solderability and good diffusion barrier with adsorption layer.1−3) Copper layer makes intermetallic compound (IMC) rapidly with Sn-rich solder where the mechanical and metallurgical failure occurred. Therefore, electroless NiP plating has been widely used in UBM between copper layer and solder. NiP layer has various desirable properties, such as good solderability, corrosion resistance, uniformity and selective deposition. However, NiP between Sn-rich solder made larger and brittle fracture induced by IMC. NiP layer is dissolved with time and into the molten solder and then it is spalled the Ni-Sn IMC layer. IMC spalling phenomena occurred when the layer contained high contents of P, longer period of reflow time, larger solder size and higher crystallization in the NiP layer. Furthermore, when NiP layer was completely dissolved, the molten solder contacted with copper substrate and made Cu-Sn IMC rapidly.4−6) Recently, alternative materials such as NiFe, NiWP and NiReP to compensate the disadvantage of NiP have been studied. Among them, NiFe layer has the most effective reaction barrier layer with Sn-rich solder. Electroless plating of Ni and Fe are difficult since they had different reduction potential in simple salt bath. The complexing reagents can reduce the difference of reduction potentials and then to fabricate NiFe alloy.7−10) Since the complexing reagent has an important part in the stability of electroless plating bath, citrate and tartrate were used as the complexing reagent in this study. The effects of both citrate and tartrate complex on electroless NiFe alloy plating were investigated. In addition, NH₃·OH and additive were added in the bath to improve the layer properties. Finally the optimum electroless NiFe plating bath composition and conditions were obtained.

2. Experimental Procedure

Electroless NiFe plating layers were deposited on silicon wafer substrate where TiW/Ni/Cu or Ti/Cu were sputtered. Nickel sulfate and iron (II) sulfate were used as metal sources. Sodium citrate and sodium tartrate were used as a complexing reagent. Sodium hypophosphite was used as a reducing agent. The composition of electroless NiFe bath is presented in Table 1.

During the electroless NiFe plating, bath temperature was fixed at 75°C and solution was stirred with magnetic stirrer at 200 rpm. Sn-3.0Ag-0.5Cu (SAC) solder was used on NiFe layer that was reflowed on the hot plate at 250°C. The IMC growth were investigated at different time intervals. The composition of plating layers were analyzed with energy-dispersive X-ray spectroscopy (EDS). The surface morphologies and cross sectional images of plating layer were observed with field emission scanning microscopy (FESEM).

![Table 1](image-url)
3. Results and Discussion

Complexing reagent is an important part of electroless plating bath. Because complexing reagent helps to maintain pH and reduces the reduction potential difference between alloy metal sources so as to fabricate NiFe alloy. The effects of complexing reagents were investigated using surface morphologies, deposits composition, deposition rate and activation energy. In Fig. 1, the surface morphologies were investigated with two different complexing reagent citrate and tartrate at various concentrations. Two complexing reagents made NiFe bath stable. When the concentration was high, grain size was reduced and the amount of pore was increased. The composition of deposits were analyzed and shown in Fig. 2. The content of Fe was higher in citrate bath than that in tartrate bath at all concentration. The concentration of complexing agent did not affect much on the composition of deposits. The deposition rate of NiFe alloy with complexing agent were analyzed and shown in Fig. 3. The deposition rate in citrate bath was much higher than that in tartrate bath. The tartrate bath had slower deposition rate and lower Fe content of plating layer. However, unstable self-decomposition was observed in the citrate bath with time. The baths with the same concentration of complex were unstable and the stable NiFe deposit could not be obtained. Therefore, tartrate bath was investigated afterwards regardless of low deposition rate and low Fe contents.

The effects of ammonia water (NH₄OH) on the NiFe plating layer of tartrate bath were also investigated to improve the property of NiFe. The surface morphologies were investigated. In the Fig. 4, the morphology of NiFe at pH 8 showed the small grains since it had a very low deposition rate. The sur-
face morphologies were improved as pH increased. However nodular type grains were observed at pH 11.5. The deposition rate and the composition of the NiFe layers were analyzed and shown in Fig. 5. In the Fig. 5 (a), as pH was increased, the deposition rate was increased. It can be explained by the following electroless Ni plating reaction.\(^{11}\) As pH was increased, the reaction was proceeded to forward.

\[
\text{Ni}^{2+} + 2\text{H}_2\text{PO}_2^- + 4\text{OH}^- \rightarrow \text{Ni}^{2+} + 2\text{HPO}_3^- + \text{H}_2 + 2\text{H}_2\text{O} \tag{1}
\]

Considering the nodular type deposits at pH 11.5, higher than pH 11 was not desired. The contents of Fe in the deposits were not sensitively increased with pH, however the higher pH gave the higher composition of Fe in the deposits. The effects of temperature on the NiFe deposits were investigated. The growth rates were analyzed at 3 different temperature (65, 75, and 85°C) and shown in Fig. 6. Since the growth rate were depend on the activation energy, the activation energy can be obtained from Arrhenius equation and the slope of Fig. 6 plot. The activation energy was calculated as 37 kJ/mol.

The effects of the additives was also studied. Lead nitrate was used as additive and its effects on the surface morphologies and deposition rate were analyzed and shown in Fig. 7 and Fig. 8. The concentration of lead nitrate did not have significant effects on the surface morphology and the deposition rate. However it affected on the IMC growth. The solder was reflowed for 5 min at 250°C and the cross sections were analyzed in shown in Fig. 9. The NiFe layers before and after reflow were analyzed. The remaining NiFe layer after reflow was thicker with lead nitrate increased. NiFe consumption was low with higher lead nitrate concentration in the bath. IMC growth rate with time was investigated and shown in Fig. 10. The growth of IMC was linearly dependent on square root of time since it is diffusion controlled.\(^{12}\) The IMC growth rate with time was evaluated and shown in Fig. 10.
growth was suppressed at 2 and 5 ppm lead nitrate added bath. As a result, the optimum concentration of lead nitrate is 2 ppm since it showed lowest IMC growth rate.

4. Conclusions

Tartrate is better complexing agent than citrate. Even though the deposition rate of NiFe layer in citrate bath was higher than that in tartrate bath, the self-decomposition behaviors were observed in citrate bath. Ammonia addition can improve the stability of tartrate bath. Lead nitrate can suppress the IMC growth and lowest IMC growth was observed at 2 ppm lead nitrate added bath. Electroless NiFe bath and conditions were obtained and feasibility of electroless NiFe alloy to replace electroless NiP was confirmed.

Acknowledgements

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education (Grant No. 2013051967).

REFERENCES