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Investigation of Eco-friendly Electroless Copper Coating by Sodium-phosphinate

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ABSTRACT

Cu films were plated in an eco-friendly electroless bath (No-Formaldehyde) on Ni/screen printed Ag pattern/PET substrate. For electroless Cu plating, we used sodium-phosphinate ($NaH_2PO_2 \cdot H_2O$) as reducing agent instead of Formaldehyde. All processes were carried out in electroless solution of pH 7 to minimize damage to the PET substrate. According to the increase of sodium-phosphinate, the deposition rate, the granule size, and *rms* roughness of the electroless Cu film increased and the Ni content also increased. The electroless Cu films plated using 0.280 M and 0.575 M solutions of sodium-phosphinate were made with Cu of 94 at.% and 82 at.%, respectively, with Ni and a small amount P. All electroless Cu plated films had typical FCC crystal structures, although the amount of co-deposited Ni changed according to the variation of the sodium-phosphinate contents. From these results, we concluded that a formation of higher purity Cu film without surface damage to the PET is possible by use of sodium-phosphinate at pH 7.

Key words : FPCB, Copper, Electroless plating

Introduction

As the application ratio of portable instruments is increased with introduction of flexible electronics technology having a light weight and excellent flexibility, the use of flexible electronic device technology is also being applied to diversified areas such as military, industrial and medical uses, etc. Flexible printed circuit board (also known as FPCB) is a foundation part of such flexible electronic devices and is the area where much research and development is being conducted in relation to various new technologies and applied product development such as mobile phone, flexible lighting substrate, high-efficiency LED substrate, etc.[1-3)]

In general FPCB manufacturing processes, a method of adhering rough copper foil and PET substrate material with an adhesive and a method of printing conductive paste such as Ag paste have been universally applied for the technique of forming wiring on inexpensive polyethylene terephthalate(PET) films.[3)] However, as the width of a circuit transmitting electricity or signals is reduced according to the trends of rapid implementation of convergence with complex functions loaded as well as high performance, a metal constituting the wiring with lower resistivity is required. Since copper is a material with reasonable prices, excellent thermal conductivity and electrical conductivity so as to allow improvement of operating speeds of devices by reducing RC delay times, it is being studied often as a wiring material for FPCB.[4)]

For metal wiring in FPCB, electroless copper (Cu) plating technique is being applied frequently. Commercial electroless Cu plating solutions in general use consist of a strong acid of pH 13 ~ pH 14 containing formaldehyde as a reducing agent. As manufacturing methods with consideration of environments such as European Restriction of Hazardous Substances guide (RoHS), etc. are emerging as a great issue for the global electronic industry, lead, cadmium, formaldehyde, etc. are restricted as regulated substances, according to which eco-friendly processes are being increased. Under such circumstances, FPCB or PCB industry is also making efforts for development of diversified processes which support eco-friendly new processes and are capable of reducing costs as well.

In the present study, sodium phosphinate instead of formaldehyde was employed as a reducing agent for electroless Cu plating, and development of eco-friendly electroless Cu plating processes was aimed at attempting plating in a neutral condition to minimize damages to substrates.

2. Experimental Procedure

Substrates were employed where a nickel (Ni) thin film was selectively coated on Ag electrode by electroless plating method on a PET substrate material which formed Ag electrode (about 10 μm) by using the screen printing method

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(Fig. 1). For Cu plating film to be selectively formed on this substrate only on the Ag electrode with Ni plating, substrates were processed with a catalyst for 30 minutes at 65 °C by using Pd catalyst solution ($SnCl_2$, $PdCl_2/HCl$, pH 6.9), and dried with N_2 gas after cleaning again to remove impurities, etc. produced upon catalyst processing. For the substrates having completed catalyst processing, plating was enforced for 1 hour by dipping them in an electroless plating bath of pH 7 at 70°C. The Cu plating solution used was a metal salt, which consisted of Copper(II) sulfate pentahydrate($CuSO_4 \cdot 5H_2O$), Sodium phosphinate($NaH_2PO_2H_2O$) as a reducing agent, Sodium citrate tribasic dehydrate($C_6H_5Na_3O_7 \cdot 2H_2O$) and Ammonium chloride($NH_4Cl$) as a complex agent. To supplement the nonconformance aspect of oxidation promotion by sodium phosphinate for copper sulfate as a reducing agent, Nickel (II) sulfate hexahydrate($NiSO_4 \cdot 6H_2O$) was employed as an oxidation promotion agent for the reducing agent to enable smooth electroless Cu plating even in the plating bath near neutral condition.[5-7] The pH was controlled by using NH_4OH. Reduction process of Cu is as follows.[8]

$$Ni^{2+} + 2H_2PO_2^- + 2OH^- \rightarrow Ni + 2H_2PO_3^- + H_2 + 2e$$
$$Cu^{2+} + Ni \rightarrow Cu + Ni^{2+}$$

In the present study, growth rate, purity (Cu composition ratio), surface morphology, etc. of electroless plated Cu films that had been formed were measured as shown in Fig. 1 by controlling the amounts of sodium phosphinate as a reducing agent upon formation of the electroless Cu plating bath. For measurement of changes in the surface morphology of Cu films as a function of added amounts of sodium phosphinate, Scanning Electron Microscope (SEM : Sirion, Nanofab) was employed, while X-ray Diffraction (XRD) and Cu K-edge X-ray Absorption Spectrum(1D XRS KIST beamline, Pohang Accelerator Laboratory) were analyzed to check for changes in crystallinity. Compositional changes in the growth film as a function of amounts of sodium phosphinate were measured by X-ray photoelectron spectroscopy (XPS :VersaProbe PHI-5700, Ulvac PHI, Inc, Japan).

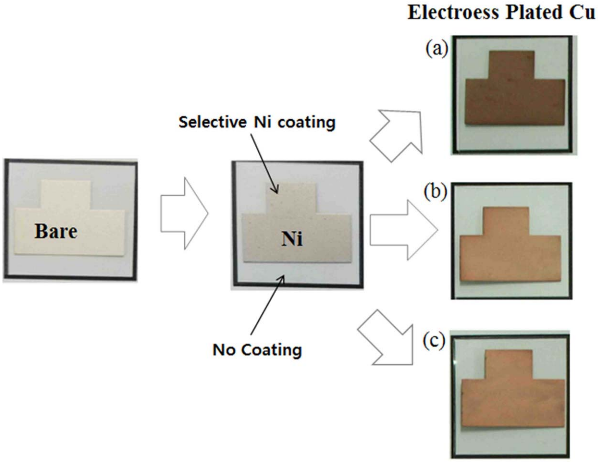


Fig. 1. Digital camera images of bare (Ag printed PET) substrate film and electroless plated Ni film on bare substrate, and electroless Cu plated films (Cu/Ni/Ag printed PET) by (a) 0.280 M, (b) 0.427 M, and (c) 0.575 M of sodium phosphinate.

3. Results and Discussion

In addition to the Ni layer being electroless plated on Ag paste layer patterned on a PET substrate, it may be affirmed in Fig. 1 that eco-friendly electroless plated Cu film was not plated on PET substrate at all but selectively plated only on the pattern coated with Ni. Based on this, it may be seen that Cu is also selectively plated on Ni film by Pd catalyst treatment for Ni plated fim in the same way as Ni being selectively plated only on Ag electrode by Pd ctalyst teatment. According to an examination of electroless Cu films formed on the Ni coated substrate (Ni/Ag paste/PET) (Fig. 1(b) - (d)), having Cu color can be clearly seen unlike Ni color of Fig. 1(a). As some color differences are observed depending on the amounts of sodium phosphinate used upon electroless Cu plating, it may be seen to exhibit darker colors as the amount of sodium phosphinate is increased. To find a deposition rate for the plated Cu films, mass of the plated Cu film was obtained. In Fig. 2, the mass differences before and after Cu plating are shown by the graph. In Fig. 2, the mass of the plated Cu film can be seen to be increased also as the added amounts of sodium phosphinate in the electroless Cu plating bath are increased. In terms of a deposition rate, it was 0.008 mg/min in the case of 0.280 M of sodium phosphinate, 0.013 mg/min in the case of 0.427 M, and 0.017 mg/min in the case of 0.575 M, indicating that the deposition rate was the higher, the larger the added amounts of sodium phosphinate. Since the deposition rate was also increased by almost twice when the number of moles of the added sodium phosphinate was increased by about twice (0.280 M vs 0.575 M), it could be seen that the deposition

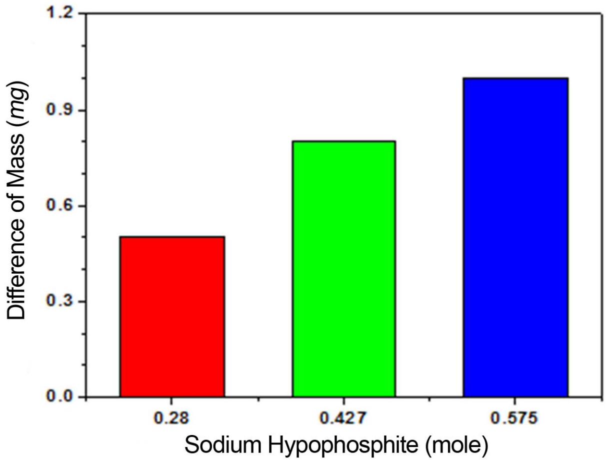
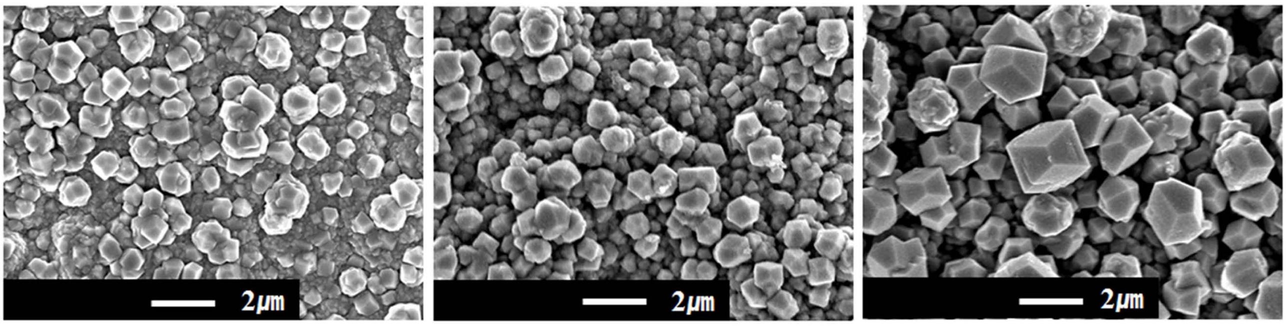


Fig. 2. Mass difference of electroless Cu plated films (Cu/Ni/Ag printed PET) according to variation of sodium phosphinate.



(a) (b) (c)

Fig. 3. FE-SEM images of electroless Cu plated films (Cu/Ni/Ag printed PET) by (a) 0.280 M, (b) 0.427 M, and (c) 0.575 M of sodium phosphinate.

rate was increased almost linearly with the number of moles of the added sodium phosphinate. Since sodium phosphinate can reduce more Ni ions although it cannot directly reduce Cu ions, it could be seen that more Cu ions could be reduced.

In general, colors of films could be changed by composition and structure of substances constituting the formed films, while they could also be changed by thickness of the film or surface roughness. Considering FE-SEM images of Fig. 3 in terms of granule size and shape of the plated Cu film, the largest granule size was observed when the added amount of sodium phosphinate was 0.575 M (Fig. 3(c)), and surfaces appeared relatively very rough as compared with other films. Consequently, for the least amount of sodium phosphinate of 0.280 M (Fig. 3(a)), it could be seen that electroless Cu plating films exhibiting the flattest surfaces consisted of the smallest granules.

Surface roughness of these Cu films was measured by using AFM. The *rms* roughness obtained when the scan domain was made to be 5 μm × 5 μm upon AFM measurement is indicated in Fig. 4. As could be predicted from the FESEM images of Fig. 3, the *rms* roughness could be seen to almost linearly increase with the added amounts of sodium phosphinate. When considered in association with deposition rates, surface roughness of electroless Cu plated film could be seen to increase also, the higher the deposition rates.

To examine the compositions of electroless plated Cu film, XPS was used. As a result, as shown in the XPS spectrum (Fig. 5), not only Cu composition but also Ni composition were clearly detected from electroless Cu plated film, a small amount of phosphor was also detected together. Upon addition of 0.575 M of sodium phosphinate, an increase in the Ni peak could be seen relatively more clearly than upon addition of 0.280 M.

Relative atomic concentrations (at%) were obtained for Cu, Ni and phosphor detected from the XPS core level spectra. Relative atomic concentrations of Cu : Ni : P in electroless copper plated film with addition of 0.280 M of sodium phosphinate were 93.95 : 6 : 0.05 (at%), while those with addition of 0.575 M were 82.27 : 17.33 : 0.4 (at%). Based on this result, the contents of Ni and phosphor as impurities could be seen to increase together, the higher the added amounts of sodium phosphinate. From this result, it could

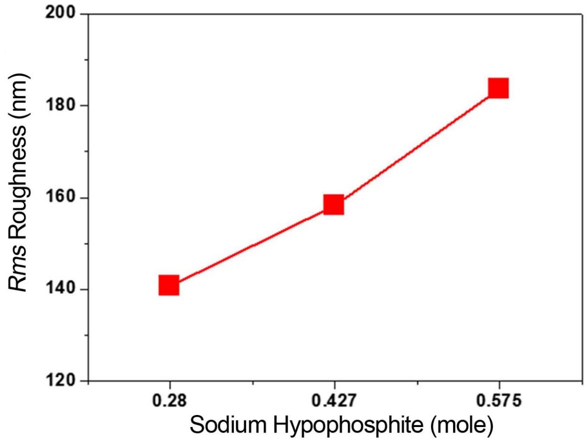


Fig. 4. *Rms* roughness by AFM for electroless Cu plated films (Cu/Ni/Ag printed PET) according to variation of sodium phosphinate.

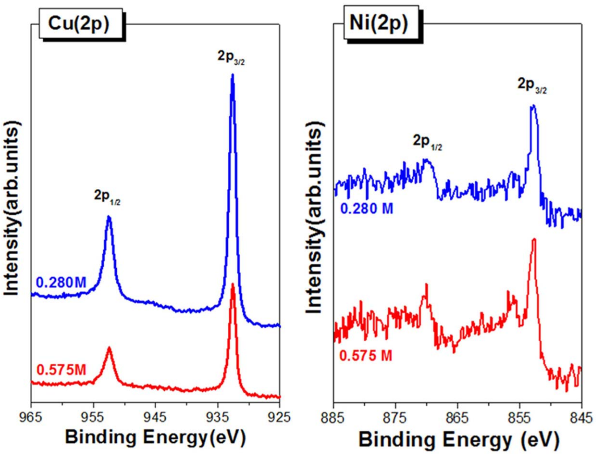


Fig. 5. XPS Cu(2p) and Ni(2p) core level spectra for electroless Cu plated films (Cu/Ni/Ag printed PET by 0.280 M and 0.575 M of for copper, nickel and phosphor detected from XPS core level spectrum.

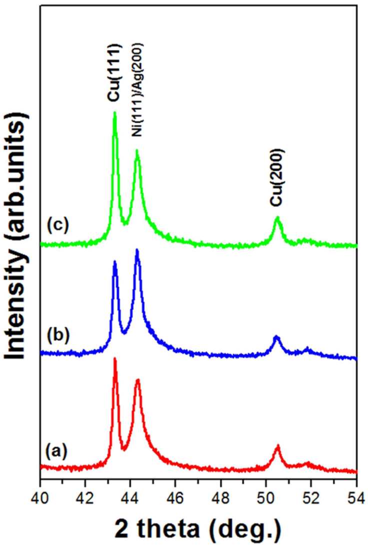


Fig. 6. XRD spectra for electroless Cu plated films (Cu/Ni/Ag printed PET) by (a) 0.280 M, (b) 0.427 M, and (c) 0.575 M of sodium phosphinate.

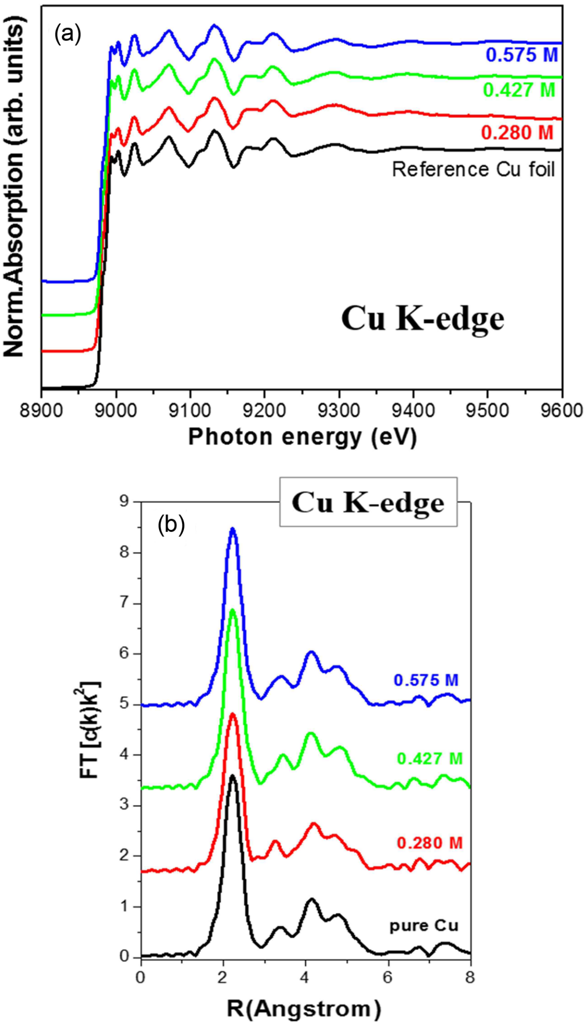


Fig. 7. Cu K-edge (a) X-ray absorption spectra and (b) Fourier transforms of $k^2\chi(k)$ X-ray absorption FS spectra for pure Cu (Cu foil) and electroless Cu plated films (Cu/Ni/Ag printed PET) by 0.280 M, 0.427 M, and 0.575 M of sodium or sodium phosphinate.

be seen that an increase in sodium phosphinate had ill effects on the purity of Cu film since the reduced Ni remaining in the plating bath was also plated together at this time, although more sodium phosphinate reduced more Ni ions and much of the reduced Ni reduced more Cu ions to increase the deposition rates of plated Cu films.

In view of chemical states of XPS core level peaks, the Cu(2p) peak detected together with Ni shows that it is the typical pure metallic Cu (932.6 eV) without changes in peak positions irrespective of impurity contents. This results suggest that the plated Cu exists in films in the condition of not forming compounds with the impurities. In other words, it means that Cu and Ni compositions compose the film in the form of a mixture.

From the X-ray diffraction pattern (Fig. 6) of electroless Cu plated film formed on Ag/PET substrate with Ni coating, Cu(111) and Cu(200) peaks obtained from a typical FCC structure can be seen along with Ag and Ni peaks. Based on this result, all electroless Cu plated film can be seen to have a FCC polycrystalline structure. Ag and Ni peaks detected in Fig. 6 were the peaks detected from the substrate (Ni/Ag paste/PET) prior to plating, where Ni peaks, in particular, are considered to include information on a small amount of Ni contained in Cu plated film.

Since XRD patterns are generally a measurement method showing all structures composing the measured thin film at one go, Cu K-edge X-ray absorption spectrum using synchrotron radiation was obtained, which allowed detailed observation of the structures per element. As shown in Fig. 7(a), the appearance of Cu K-edge absorption spectrum of electroless Cu plated film can be seen to be almost the same as that of a Cu foil. In the spectrum of Fig. 7(b) seen through Fourier transform, it may be affirmed to have the typical FCC structure just as all pure Cu does when compared with FCC structure of the foil. This result is in a very good agreement with the XPS results that the chemical states of Cu in electroless Cu plated film exists as a typical metallic Cu rather than in a compound form. As a result, it could be seen that Cu composing the electroless Cu plated film with sodium phosphinate used as a reduction agent existed as a mixture with Ni as an impurity (including a small amount of phosphor).

4. Conclusions

As the use of formaldehyde which is harmful to human body and difficult to purify environmentally is regulated and restricted, the use of the formaldehyde employed mainly as a reduction agent in electroless Cu plating solution employed to form electroless Cu plated film is also being restricted. As a result of such environmental regulations, characteristics of electroless Cu plating film were investigated and analyzed in the present study by using sodium phosphinate as a reduction agent.

As a reduction agent in the neutral condition of pH 7, sodium phosphinate was used for electroless Cu plating instead of formaldehyde. Through measurement of deposition rates, surface morphology, crystallinity, etc of Cu plating films formed as a function of the added amounts of sodium phosphinate, possibility of eco-friendly electroless plating processes substituting for formaldehyde was ascertained. Although deposition rates of Cu plating films were increased with an increase in the added amounts of sodium phosphinate as a reducing agent in the neutral condition, surface roughness was also increased. In terms of the compositional ratios of materials constituting films, the contents of impurities such as Ni or phosphor were increased as the added amounts of sodium phosphinate were increased. Through these results, conclusion was reached that minimization of the added amounts of sodium phosphinate was desirable to obtain high-purity Cu plating films. Also, in electroless Cu plated film formed in the neutral condition, Cu did not from compounds with other impurities such as Ni or phosphor and existed in the FCC structure as a mixture.

Through the present study, electroless Cu plated film composed of about 94 at.% of Cu could be formed as a result of changes in the added amounts through eco-friendly electroless Cu plating process in the neutral condition by using sodium phosphinate as a reducing agent instead of an environmentally regulated substance of formaldehyde. And Ni contents in the plating films could also be controlled as a result of controlling the added amounts of sodium phosphinate in the neutral condition. Such neutral process not only minimized damages to substrates but also had an advantage that neutralization treatment was not required in waste water processing which occurred in the plating process. Therefore, simplification in waste water processing which always causes problems in plating process is expected to be possible also.

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