One-step fabrication of highly conductive and durable copper paste and its flexible dipole tag-antenna application

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COMMUNICATION

One-step fabrication of highly conductive and durable copper paste and its flexible dipole tag-antenna application

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Highly conductive and durable copper (Cu) paste was successfully fabricated via acid treatment and mechanical blending with corrosion inhibitors. Screen-printed Cu pattern was evaluated as dipole tag-antenna with long term and thermal stability, and structural flexibility.

Line patterning techniques using conductive metal pastes have recently attracted a great deal of interest in flexible display devices because of their high resolution, conductivity and flexibility.[1] Among the various line pattering methods, screen printing has been shown as an effective method for defined deposition of conducting materials.[2] As a representative metal ink for screen printing, silver (Ag)-based paste has received a lot of focus and attention in the past decade from display manufacturing industries.[3] Despite the outstanding conductivity, it is limited by high price (700 USD/kg) and low dispersion stability originated from the particle aggregation, which can prevent consecutive patterning process.[4] In these regards, copper (Cu)-based paste is able to be good candidate for screen printing metal ink due to its high conductivity, good mechanical workability and low cost (7 USD/kg).[5] However, Cu has suffered from the readily oxidized species at relatively low temperature, which caused the electrical conductivity to drop.

Therefore, a large effort using corrosion inhibitor has been devoted to prepare Cu-based conductive paste with high stability against oxidation. As oxidation inhibitors, heterocyclic organic compounds consisting of a π–system and their derivatives such as azoles, amines and amino acids have been widely utilized.[6] The presence of heteroatoms in the organic compound molecule can improve the resistance to Cu oxidation. Because vacant d orbitals in Cu atom can form coordinative bonds with electron-donating heteroatom via physisorption or chemisorption, which resulted in reduction of Cu corrosion rate. However, with regard to high efficiency of Cu oxidation protection, these technologies still have the difficulty in the long term and thermal stability.[7] Furthermore, the high temperature curing process using thermoset resins such as acryl, epoxy and ester should be required to hold the conductive filler together and to make the filler stick to the substrate.[8]

Herein, we report a simple route for the fabrication of highly conductive and durable Cu paste as screen printing metal ink. To the best of our knowledge, this is the first experimental evidence for Cu paste with outstanding resistance to oxidation using phosphoric acid treatment and mechanical blending with poly(vinylimidazole-*co*-vinyltrimethoxysilane) poly(VI-*co*-VTS) and poly(4-styrene- sulfonate) (PSS). Importantly, as a compatibilizer, PSS binder increased the dispersibility and interfacial interaction between the Cu flakes, and caused the enhanced adhesion of Cu-based film to a flexible substrate without further hardening process. Our results demonstrated that Cu-based thin film fabricated by screen printing had a long-term and thermal stability with low oxidation rate. In addition, we applied it for a practical dipole tag-antenna electrode.

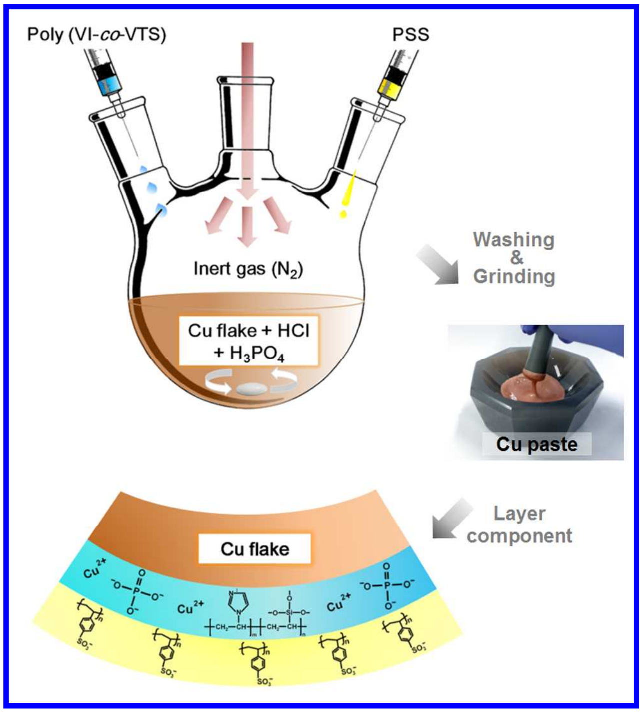

Fig. 1 One step fabrication of highly conductive and durable Cu paste using acid treatment and mechanical blending with poly(VI-*co*-VTS) corrosion inhibitor and PSS binder. The procedure was performed under nitrogen atmosphere. For improving the dispersibility of Cu paste, grinding process using an agate mortar was included.

The one step method to synthesize highly conductive and durable Cu paste via acid treatment and mechanical blending with poly(VI-*co*-VTS) and PSS is illustrated in Fig. 1. The hydrochloric acid (HCl) and phosphoric acid (H_3PO_4) have been used for chemical etching and polishing agents to make clean, oxide-free Cu flake surface. As a result of H_3PO_4 treatment,

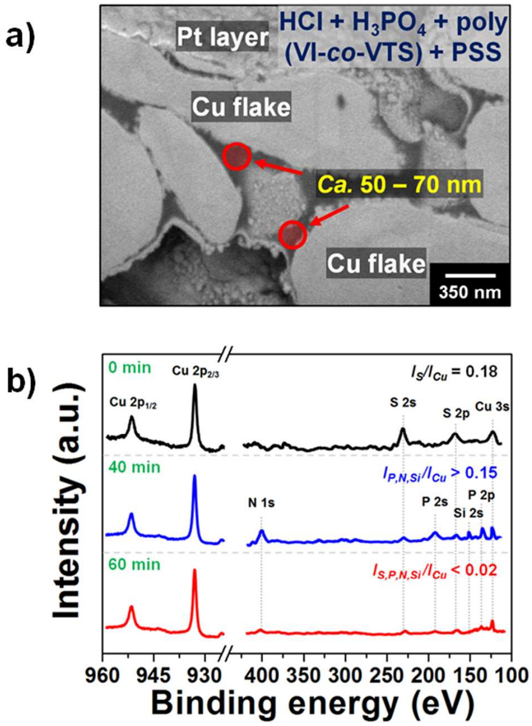

Fig. 2 (a) SEM cross section image and (b) XPS depth profile of HCl/H$_3$PO$_4$/poly(VI-*co*-VTS)/PSS-treated Cu thin film. For cutting the Cu-based surface, FIB using Ga element was used, and Pt nanoparticles were deposited on the surface by sputtering to distinguish between Cu surface and oxidation protection layer.

insoluble solid species of Cu$_3$(PO$_4$)$_2$ could be formed on etched Cu surface.[9] As a corrosion inhibitor, poly(VI-*co*-VTS) and PSS were synthesized by free radical polymerization using an azobisisobutyronitrile (AIBN) initiator, and they adhered to Cu surface via chemical bonding and physical interaction, respectively. Namely, the Si-OH group in the silane unit contributes to the adhesion onto the Cu surface through chemical bond formation (Cu-O-Si), and the nitrogen atom in the imidazole ring, through the complex bond formation. Furthermore, high molecular weight (> 1,000,000) and viscosity (> 50,000 Pa.s) of PSS made it possibile to be used as compatibilizer and binder to increase the dispersibility and interfacial interaction between the Cu flakes. Cu paste could have been easily prepared by grinding Cu precipitate after centrifugation. In our experiment, Cu flake has been selected for synthesizing Cu paste owing to its good conductivity in comparison with bead and dendrite types (ESI†).

FTIR spectra indicate that the as-prepared Cu paste consisted of three corrosion inhibitors (ESI†). The peaks at 1160, 938 and 640 cm^{-1} are attributed to P=O, O−P−O and P−O bonds of the phosphate group, respectively.[10] The peak at 3111 cm^{-1} originates from the C=C−H/N=C−H stretching, and the peak at 1498 cm^{-1} is due to the C=C/C=N stretching in the imidazole ring. The characteristic peaks of VTS unit are observed at 2947 cm^{-1} and 2842 cm^{-1}, which indicated of CH$_3$ asymmetric and symmetric stretching from Si−O−CH$_3$, respectively. The presense of PSS was demonstrated by the peak at 1185 cm^{-1} and 1045 cm^{-1}, ascribed to the asymmetric and symmetric stretching of the SO$_3^-$ group.[11]

In order to investigate the formation of four different Cu pastes, FIB analysis was performed. It revealed that each distinct coating layer was presented via phosphoric acid treatment and addition of poly(VI-*co*-VTS) (ESI†). Furthermore, the layer thickness of HCl/H$_3$PO$_4$/poly(VI-*co*-VTS)/PSS-treated Cu thin film was estimated to be *ca.* 50 – 70 nm as shown in Fig. 2a. There results suggest that oxidation protection layer such as cupric phosphate, poly(VI-*co*-VTS) and PSS can be successfully formed on Cu flake surface. Moreover, vacant sites of Cu flake were able to be filled with PSS binder, which indicated of enhanced the dispersibility and interfacial interaction between Cu flakes.

To gain some insight into the oxidation protection layer on Cu flake surface, XPS depth profile was analyzed (Fig. 2b). The initial surface of Cu-based thin film mainly consisted of Cu (2p$_{1/2}$ at 952 eV, 2p$_{2/3}$ at 933 eV, and 3s at 123 eV) and S elements (2s at 230 eV and 2p at 169 eV), and the I_S/I_{Cu} ratio was *ca.* 0.18. Notably, as a result of surface milling for 40 min, the ratio value gradually has decreased, whereas the N (1s at 400 eV), P (2s at 190 eV and 2p at 135 eV) and Si elements (2s at 152 eV) has appeared ($I_{P,N,Si}/I_{Cu} > 0.05$). Moreover, the S, N, P, and Si elements have almost disappeared as milling time of 1 h ($I_{S,P,N,Si}/I_{Cu} < 0.02$), which meant that the thickness of oxidation protection layers assumed to be *ca.* 60 nm. Considering these results, it can be inferred that copper complex and poly(VI-*co*-VTS) layers with thickness of *ca.* 20 nm are firstly deposited on Cu flake surface via chemical bonding, and the surface has been entirely covered with PSS layer by physical interaction (*ca.* 30 – 50 nm thickness). In order to confirm the protection from oxidation on Cu flake surface, Cu 2p$_{2/3}$ and O 1s XPS analysis of

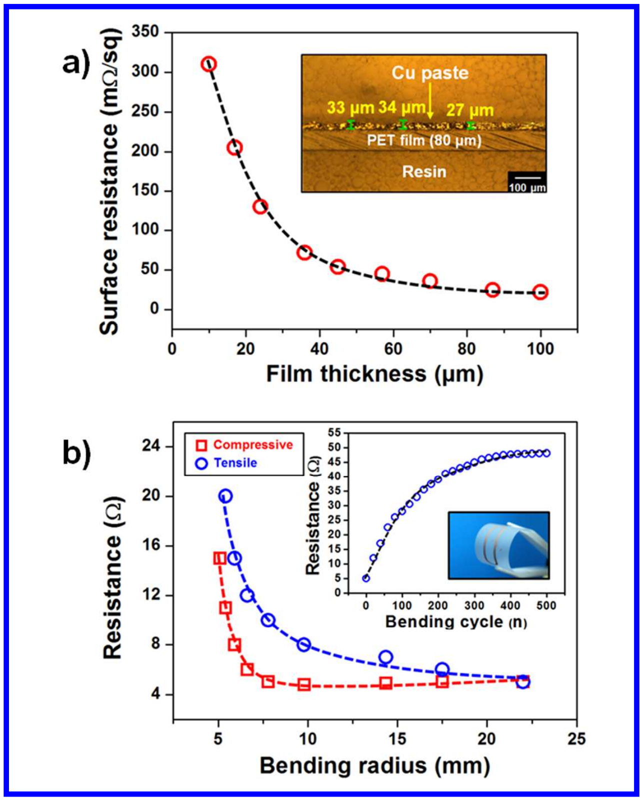

Fig. 3 (a) Surface resistance of the Cu-based thin film as a function of film thickness. The inset shows a homogeneous film thickness of 30 μm. (b) Line resistance of a patterned Cu-based thin film according to the bending radius under compressive and tensile strain (inset: the data represented by line resistance versus bending cycle).

Cu-based thin film was conducted (ESI†). From the data, the ratio of I_{Cu_2O}/I_{Cu} has highly reduced (0.11). As a result, the relative atomic ratio of O to Cu element has also decreased from 1.72 to 0.42 by addition of corrosion inhibitors, leading to an outstanding resistance to oxidation.

Synthesized Cu paste could be used as screen printing ink, allowing its application for dipole tag-antenna electrode. The optical images of patterned Cu-based thin film on a flexible substrate demonstrate well-defined pattern (ESI†), which could be attributed to the surface energy matching between the substrate and Cu paste.[12] Namely, the surface tension of Cu paste was measured to be *ca.* 61.07 mN m^{-1} by the Owens-Wendt equation, which was similar to that of PET film (65.12 mN m^{-1}), resulting in an excellent compatibility. Therefore, sharp Cu-based pattern could have been obatained without line-edge waves.

Fine-tuning of the surface sheet resistance can be accomplished by controlling the mesh interval of screen printings as shown in Fig. 3a. The Cu-based thin film thickness has increased up to *ca.* 100 µm with a gradual decrease in surface resistance. However, peeling off the film from the substrate limited the film thickness to 30 µm with 105 mΩsq^{-1} of surface resistance, which was applicable to be used as a substitute for commercial Ag paste (71 mΩsq^{-1}) (ESI†). The cross-sectional optical image in the inset represented that the screen-printed Cu thin film was uniform in thickness.

To achieve an in-depth insight into the flexibility of patterned Cu-based thin film, the bending test was performed. End to end line resistance (*R*) has decreased gradually in inverse proportion to the bending radius (*r*) (Fig. 3b). Especially, bending the film (*r* = 9.79 mm) under compressive strain led to *ca.* 4% decrease in *R* compared to flat condition (5 Ω) due to high overlapping Cu flake stacking, which caused extensive charge delocalization. This phenomenon has disappeared with increasing compressive strain (5 mm < *r* < 9.79 mm), and mechanical deformation of stacked Cu-based thin film has occured, leading to reduced charge-carrier mobility. In the case of tensile strain to patterned Cu thin film (5 mm < bending radius < 22 mm), the considerable extent of decrease in electrical conductivity arises since extended defects can be introduced into the Cu lattice. Furthermore, when the samples were released from bending after 500 cycles, *R* value has increased by *ca.* 43 Ω. It indicated that patterned Cu-based thin film exhibited an extremely outstanding structural stability without further curing process, which originated from the good adhesion of the film to flexible substrate by PSS binder.

Long term and thermal stability testings of patterned Cu-based thin films were conducted (Fig. 4a and b). As a result, poly (VI-*co*-VTS) made it possible to have outstanding corrosion protection capability owing to the strong adhesion at the copper/copolymer interface whereas electric conductivty of H_3PO_4-treated Cu film has been lost under heat treatment due to short circuit effect, which caused the activation of oxidation (ESI†). Most of all, H_3PO_4/poly (VI-*co*-VTS)/PSS-treated Cu-based thin film has a low oxidation rate with only 12% increase in surface resistance under hot pressing for 10s, which is required

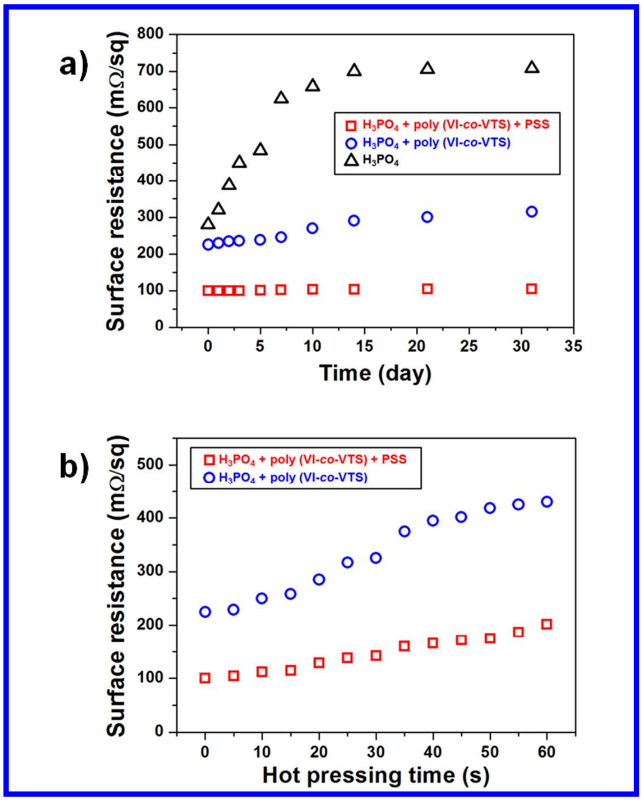

Fig. 4 (a) Long term and b) thermal stability testing of patterned Cu-based thin film. The long term reliability was tested through checking the variation of surface resistance for 1 month at room temperature. For thermal stability testing, hot pressing process using hot bar was conducted, and the applied temperature and pressure of hot plate were ca. 160 °C and 700 psi, respectively.

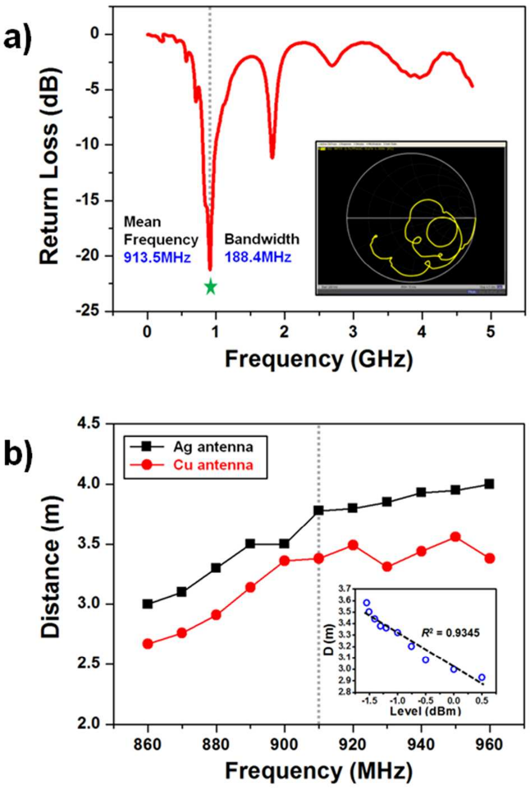

Fig. 5 (a) The return loss curve of the Cu-based dipole tag-antenna (inset: Smith chart impedance diagram of the designed dipole tag-antenna). (b) Recognition distances of the Ag- and Cu-based dipole tag antennas as a function of frequency. The relationship between sensitivity level and recognition distance is also presented in (b).

for tag-antena chip bonding. Taking these facts into account, it was apparent that highly conductive and durable Cu paste was succesfully fabricated via one step process.

On the basis of the above analysis, patterned Cu-based thin film is able to be applied for the electrode of dipole tag-antenna. Generally, two key parameters such as bandwidth and voltage standing wave ratio (*VSWR*) or return loss (*RL*) of the antenna have to be considered to evaluate the performance of the designed antenna.[13] As a result, the Cu-based dipole tag antenna had a 913.5 MHz center frequency and 188.4 MHz bandwidth as shown in Fig. 5a. Furthermore, the *VSWR* of 1.19 and *RL* value of 21.2 dB at the mean frequency proved a high transmitted power efficiency of 99.2% (ESI†). The inset Smith chart indicated of small *RL* value. In particular, the Cu-based dipole tag antenna could be detected within 3.3 m at 910 MHz, which was similar value of commercial Ag-based dipole tag antenna (Fig. 5b). In addition, the sensitivity level of Cu-based dipole tag antenna has decreased in inverse proportion to the recognition distance.

In conclusion, a highly conductive and durable Cu paste was successfully fabricated via acid treatment and mechanical blending with corrosion inhibitors. Most of all, Cu-based dipole tag antenna would be suitable for use as a commercial signal-receiving apparatus that could detect nearby objects.

Notes and references

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† Electronic Supplementary Information (ESI) available: [a detailed experimental procedure, FTIR, SEM, XPS analysis of Cu paste, optic image, electrical property of patterned Cu thin film, and Cu-based dipole tag-antenna efficiency]. See DOI: 10.1039/b000000x/

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