A study on the interfacial composition of the electroless-copper-plated BPDA-PDA polyimide sheet

W.-X. Yu, L. Hong, B.-H. Chen and T.-M. Ko

Department of Chemical and Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260. E-mail: chehongl@nus.edu.sg; Fax: +65 – 6779–1936; Tel: + 65 – 6874–5029

Department of Chemical Engineering, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan

IBM Microelectronics, 2070 Route 52, Mail Stop - E40, Hopewell Junction, NY 12533, USA

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This work studies the chemical composition at the interface generated through the electroless deposition of a copper layer onto a polyimide (PI) slice. Upilex-S®-50 [poly(biphenyl dianhydride-p-phenylenediamine)] (BPDA-PDA) polyimide film was selected as the substrate, on which wet chemistry modifications were carried out before plating. The modifications comprise the alkali catalyzed imide ring-opening reaction and the subsequent acidification, through which polyamic acid segments are generated at the surface. A copper thin film was then developed on this surface using the electroless plating technique. Changes in composition of the surface/interface caused by the modification as well as by the plating were examined using XPS and XPS depth profiling techniques. It reveals that the copper deposited initially contains both Cu2+ and Cu+ species in addition to Cu0; among them Cu+ and Cu0 are much more abundant. Furthermore, XPS depth profiling analysis suggests that there is a layer consisting of copper species spreading in the PI matrix underneath the copper film. The etching on the PI slice is believed to assist with the filtering of the copper species. On the other hand, topographic changes in the course of copper plating were traced by the AFM. The results suggest that the copper film grew by following a “mountain–valley” template.

1. Introduction

Polyimides have been increasingly used in the microelectronic packaging industry. In several of these applications, deposition of a metal layer on PI substrates is a necessary step to creating an electrically conducting via or interconnections. Therefore, understanding the interfacial structure between metal and polyimide is an important topic to advance the technology. There are numerous methods for performing metallization on
the PI substrates. In addition to the PVD approaches, electroless plating, a water-borne process, has found a niche for itself in this industry mainly because it can deposit thicker metal film onto geometrically miniature surfaces. For performing electroless plating on a PI surface, creating a pertinent surface roughness is a basic measure to enhance adhesion strength. Implementation of nucleophilic organic functional groups at the PI surface would further enhance the PI/Cu binding.

Previous investigations into the chemical structure of the interface formed by electrolessly depositing a metallic film (Ni or Cu) on the PI substrate were very scanty because of the difficulties in probing the interaction between the first few layers of metal atoms and the PI surface matrix underneath. Burrell et al. found a way for the characterization of electroless copper/polyetherimide interface, by which the surface of the freestanding copper film was exposed after a major part of the polyetherimide layer was deprived through its dissolution in dichloromethane. However, this method is not applicable to those PIs that are solvent-insoluble, e.g. the commonly used poly(pyromellitic dianhydride-oxydianiline) (PMDA-ODA) and BPDA-PDA.

The present investigation attempts to gain an insight into the composition and the related microstructure at the interface between Cu and BPDA-PDA. The copper layer was deposited electrolessly onto the alkali-etched BPDA-PDA surface. The surfaces of both PI substrate and Cu layer and the interface between them were examined by XPS and AFM after each stage of modification or plating. The results obtained suggest the presence of an interlocking structure formed through the coordination of the organic functional groups of the polymer to the copper species; this interfacial structure is believed to enhance the adhesion strength of the copper film onto the PI substrate.

2. Experimental
2.1. Surface modification
Upilex-S 50 polyimide film was obtained from UBE Industries, Ltd. (Tokyo, Japan) and cut into 1 × 1 inch square pieces. One face of the film was mechanically roughened to introduce micro-scratches before it was subjected to the chemical treatment. The surface modifications include the following steps: the PI slices were cleaned in 2-propanol under ultrasonication for 20 min at room temperature and washed by deionized (DI) water. After being dried in air, the PI slices were soaked in an aqueous solution of KOH (1 M) at 80°C for 20 min. They were then treated in 0.2 M HCl aqueous solution at room temperature for 5 min. The chemistry of the above two steps is illustrated in Fig. 1.

![Image of 3D-AFM images of PI surfaces](image_url)

*Fig. 3* The 3D-AFM images of the PI surfaces: a, after roughening; and b, after the chemical treatment.
2.2. Sensitization and activation for electroless plating

The PI slices were immersed into an aqueous solution of SnCl₂ (10 g L⁻¹) and HCl (~5 M) for 1 min. After rinsing with deionized water, the slices were then immersed in an aqueous solution containing PdCl₂ (0.37 g L⁻¹) and HCl (~1.3 M) for 1 min. The slices taken out were then rinsed with DI water before plating.

2.3. Electroless plating

A home-made electroless copper plating solution with the bath composition given in Table 1 was used in this research. Electroless copper plating was carried out at room temperature for up to 5 min in a sufficiently stirred plating bath. Compared with the plating temperature (~50 °C) normally used in the alkaline copper bath, adopting a relatively lower temperature in this experiment was necessary to reduce the thickness of copper film so the interfacial region could be examined by XPS. The plated PI slices were washed by DI water and dried by nitrogen blowing, and stored under nitrogen atmosphere.

![Figure 4](image)

Fig. 4 The XPS spectra of: a, the tin species, and b, the palladium species at the activated PI surface.

| Table 1 The composition of electroless copper solution |
|-----------------|------------------|
| Constituent                  | Concentration    |
| Copper sulfate (CuSO₄·5H₂O)                  | 10 g L⁻¹         |
| Potassium sodium tartrate          | 50 g L⁻¹         |
| Formaldehyde (HCHO)              | 50 ml L⁻¹       |
| Sodium carbonate (Na₂CO₃)         | 10 g L⁻¹       |
| Sodium hydroxide (NaOH)           | 10 g L⁻¹       |

2.4. Instrumental

XPS spectra were obtained on a Kratos Axis Hsi-165 Ultra instrument (Manchester, UK), using Al Kα (1486.6 eV) as the X-ray source. The electron take-off angle with respect to the surface of study was 90°. A pass-energy of 150 eV was used for the survey spectra and 40 eV for high resolution scans. In the ion sputtering experiment, a 4.5 kV Ar⁺ source was used to supply an ion beam of 2–3 μA for spraying over a 2 mm × 2 mm area. All spectra recorded were calibrated by C 1s at 284.6 eV. A computer program was employed to perform de-convolution with which one experimental peak could be fit precisely by more than one Gaussian curves, and the relative surface concentration of the specific chemical species in question was obtained from the product of the peak area and the corresponding atomic sensitivity factor.

AFM images (tapping mode) of the topographies of the modified PI surface and the Cu-film were taken on a Nanoscope II instrument (Digital Instruments, Santa Barbara, CA, USA). To obtain a better visual effect, some images are converted to the inverted mode. The mean roughness (Rₐ) over a selected area of 10 × 10 μm was determined automatically by the equipment.

3. Results and discussion

3.1. Characterizations of the formation of polyamic acid

As shown in Fig. 1, polyamic acid was derived from the imidization reaction at the surface of the PI (Upilex-S®) slice. XPS survey spectra reflect the changes in chemical composition due to the hydrolysis reactions on the polyimide sheets. For the PI surface in virgin form, only C, O, and N peaks were observed in the survey scan (Fig. 2a). After KOH treatment, two additional K peaks were observed (Fig. 2b), and they disappeared after acidification treatment (Fig. 2c). The 3D-AFM image of the mechanically roughened surface (Fig. 3a) has an average Rₐ of 2.16 nm before chemical modification. The mechanical roughening played a role in increasing the contact area of the PI to the alkaline solution, which was expected to boost the surface concentration of the functional groups generated. The chemical treatment caused a slight decrease in the surface roughness and also some pinholes (Fig. 3b). This phenomenon can be attributed to the removal of some low-molecular-weight polymer segments at those sites where loose PI matrices were present because over-hydrolysis could cut down the PI chains.

3.2. Characterization of the activated PI surface for Cu plating

To plate an electrically insulating surface, sensitization and activation at the surface are essential steps through which metal nuclei (Pd) are implanted in the surface matrix and will function as initial sites whereon a continuous metal deposition will be triggered upon contacting the plating solution. It has been known that Sn⁺ is the reducing reagent and Pd²⁺ the oxidizing reagent. In this study, we found that there were still a small number of Sn²⁺ ions retained on a PI surface matrix after it was treated with PdCl₂·SnCl₂ system. As far as the particle sizes of Pd⁰ nuclei are concerned, a comparison of the inverted AFM images of the PI surface before and after being treated with the PdCl₂ solution shows Pd⁰ nuclei have dimensions of a few hundred nanometers (according to the dark dots on Fig. 5b).
3.3. Electroless Cu deposition

In the 3D-AFM images of the Cu-plated PI surface (Fig. 6), which are differentiated by the plating time of 1, 2 and 3 min, respectively, the mountain-valley topography displayed on these images suggests that the copper layer grew initially on the Pd\textsuperscript{0} nuclei; it agrees quite well with the mapping shown in Fig. 5b. According to this morphology, the increase in the average roughness (\(R_a\)) of the surface, i.e., from 17.9 nm (at 1 min) to 21.2 nm (at 2 min) and to 33.2 nm (at 3 min), can be taken as the approximate thickness of the copper layer.

To study the Cu/PI interface by using XPS technique, a very thin copper layer is necessary since the penetrating depth of the X-ray of Al K\(\alpha\) is less than 50 nm. Fig. 7 demonstrates the effect of blockage by the copper layer to the penetration of X-ray through varying the duration of the PI in the plating bath (\(a \sim 30\) s, \(b \sim 1\) min and \(c \sim 3\) min), can be taken as the approximate thickness of the copper layer.

To study the Cu/PI interface by using XPS technique, a very thin copper layer is necessary since the penetrating depth of the X-ray of Al K\(\alpha\) is less than 50 nm. Fig. 7 demonstrates the effect of blockage by the copper layer to the penetration of X-ray through varying the duration of the PI in the plating bath (\(a \sim 30\) s, \(b \sim 1\) min and \(c \sim 3\) min). Based on the plating bath condition specified in Table 1, a plating time of 30 s could allow us to observe a desired XPS spectrum in which peaks of various elements (C, N, O, Sn, and Pd) can be discerned for the purpose of probing the chemical valences of interfacial species. Both the LMM Auger lines and 2p satellite peaks of the Cu species locating at the PI surface (shown in Fig. 7a) are of interest. With respect to the Auger peaks of Cu in Fig. 7a, two close peaks at 568.0 eV and 569.8 eV that were assigned to Cu\textsuperscript{+} and Cu\textsuperscript{0} ions, respectively, were observed on Fig. 8. Since Cu\textsuperscript{+} was unlikely to be produced from the oxidation of Cu in air, which normally gives rise to CuCO\textsubscript{3} or Cu(OH)\textsubscript{2},\textsuperscript{9,12} it is thus considered to be the product of partial reduction of Cu\textsuperscript{2+} ions. A previous study also observed the presence of Cu\textsuperscript{+} species.\textsuperscript{7}

Furthermore, the range (920–960 eV) in which 2p satellite peaks of Cu appear was expanded to result in Fig. 9, wherein the first three spectra correspond to those compared in Fig. 7. The sample obtained by 30 s of plating time exhibited the 2p\textsubscript{3/2} peak of Cu\textsuperscript{2+} (at 934.0 eV) besides the other peaks; however, this peak does not appear in the other two samples with longer plating time (Fig. 9b and c). It is suggested that the Cu\textsuperscript{2+} ions exist only at the Cu/PI interface; the observation of a 1 s peak of Na\textsuperscript{+} on the same spectrum (Fig. 7a) is the evidence to show that the PI surface has not been covered by copper yet. The Na\textsuperscript{+} peak comes from a fast ion exchange between the carboxylic acid group on the modified PI sheet and the Na\textsuperscript{+} ion in the copper plating solution (with pH \(>7\)) at the very early stage of the plating process.

Another approach employed to verify the composition of the Cu deposit at the PI surface is of Ar\textsuperscript{+} ion etching and in situ XPS analysis. In Fig. 9, spectrum d was obtained after the
sample of spectrum c had been subjected to Ar$^+$ ion etching for 2 min, which removed a number of atom layers and exposed a fresh surface. Only one 2P$_{3/2}$ peak and one 2P$_{1/2}$ peak of Cu were observed at the resulting surface, indicating that both Cu$^0$ and Cu$^+$ were produced during electroless plating because these two Cu 2p peaks are the fingerprint of these two valences.

Fig. 6 The 3D-AFM images of the copper layers developed on the PI surface with the different plating time: a, $t = 1$ min; b, $t = 2$ min; and c, $t = 3$ min.
In the light of the above XPS outcomes, the generation of Cu$^{2+}$ ion is believed to be the result of a diffusion-controlled process:

$$
\text{HCHO(aq)} \xrightarrow{\text{Pd}} \text{CO(g)} + 2\text{H(ad)} \quad (1)
$$

$$
\text{Cu}^{2+} + \text{H(ad)} + \text{OH}^- \rightarrow \text{Cu}^+(s, \text{aq}) + \text{H}_2\text{O} \quad (2)
$$

$$
\text{Cu}^+ + \text{H(ad)} + \text{OH}^- \rightarrow \text{Cu}(s) + \text{H}_2\text{O} \quad (3)
$$

At the early stage of plating that took place at the surface of the PI, the supply of the adsorbed hydrogen atoms might be far from enough to reduce Cu$^{2+}$ ions around to Cu atoms, which brought about a mixed deposition of both Cu$^{+}$ ions and Cu atoms on the PI slice. At the same time, the disproportionation of Cu$^{+}$ might also take place at the Cu/PI interface:

$$
2\text{Cu}^+(s) \rightarrow \text{Cu}^{2+}(s) + \text{Cu}(s) \quad (4)
$$

The extent of this reaction depends upon the concentration of the nucleophiles (e.g. –COO$^-$, –NH$_2$, and –CO–, etc.) available at the PI surface since they help transport the Cu$^{+}$ ions.

The XPS depth profile analysis, performed by the control of the Ar$^+$ etching time and in situ XPS sampling, was conducted using the sample prepared after 3 min of plating. The results are summarized in Fig. 10, on which it can be seen that a higher organic contamination (such as grease) existed at the initial surface (before etching). After 5 min of etching, the Na$^-$ ion was found, indicating that the ion sputtering reached the PI surface. Plausibly, in the next instant it was also observed that the concentration of the carbon species overtook that of copper species. Below this level, the copper species show a decreasing concentration gradient, which supports the presence of a diffusion layer of copper species inside the PI matrix beneath the surface. According to Figs. 8 and 9, Cu$^{+}$ ions as well as Cu atoms were found to be the major copper species existing at the interface region, including the PI matrix right below. If the depth arrived at after 5 min of Ar$^+$ sweeping was taken as the surface of PI, one can see from Fig. 10 that copper species could still be found far deeper than this benchmark. This is an indication of the formation of a rather thick diffusion layer. Referring to Fig. 3b, we are inclined to believe that the porous surface resulting from the chemical etching facilitated the penetration of copper species into the PI matrix. It is very likely that the Cu$^{+}$ ions entering into the PI matrix have formed coordination complexes with the functional groups of PI (C=$\equiv$O or –NH–), which is expected to yield a favorable effect on the adhesion of the Cu layer through the restriction of thermal motions of the polymer segments underneath the copper film. As a result, the chance of introducing air gap into the interface could be minimized.
4. Conclusions

Very thin Cu layers (<40 nm) were fabricated on the alkali-etched polyimide (PI) [poly(biphenyl dianhydride-p-phenylenediamine)] film via managing the plating at ambient temperature and within a short plating time. The interfacial chemical composition was investigated by the XPS method. Besides Cu, Cu\(^+\) ion was identified as a product formed at the early stage of plating. The XPS depth profiling proves the presence of a diffusion layer of Cu\(^+\)/Cu species inside the polyimide matrix. This work also employed AFM to study the topographies of the three representative surfaces, which are (1) the chemically modified PI surface, (2) the pre-plating activated PI surface, and (3) the surface of electrolessly deposited copper film. The chemical modifications caused a porous PI surface, which would surely facilitate the entry of Cu\(^+\)/Cu into PI matrix. Also observed was the “mountain-valley” morphology on the copper film, which is interpreted as a result of the presence of loosely dispersed Pd seeds on the activated PI surface.

References