Silver Metallization of Polyimide Surfaces Using Environmentally Friendly Reducing Agents

Fang-Yu Shen, Shang-En Huang, and Wei-Ping Dow[*,z]

Department of Chemical Engineering, National Chung Hsing University, Taichung 40227, Taiwan

Two environmentally friendly reducing agents, ascorbic acid and glucose, were employed to fabricate Ag-thin-film-coated polyimide (PI) films. Ascorbic acid is an acidic reducing agent, whereas glucose is an alkaline reducing agent. Both of these reducing agents are capable of reducing Ag^+ ions doped in poly(amic acid) (PAA) formed by hydrolysis of a PI surface. Only glucose can produce a continuous and dense Ag thin film on a PAA surface. Granular and discontinuous Ag thin films were obtained when ascorbic acid was employed as a reducing agent. This difference in reactivity is attributed to the pH values of these reducing solutions.

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A printed circuit board (PCB) is employed to assemble numerous electronic components and possesses a certain thickness and hardness. A flexible printed circuit board (FPCB) is thin and bendable and has applications in laptops, smart phones, digital cameras, CD players, photocopy machines, and other electronic devices.[1–3] FPCBs must be capable of withstanding being bent millions of times to satisfy the reliability requirements of flexible electronic products. In recent years, the demand for rigid-flex printed circuit boards (RFPCBs) has increased alongside the demand for FPCBs.[1–3] Both FPCBs and RF-PCBs are constructed from polyimide (PI) because of its excellent physical and chemical properties, which include high thermal stability, good mechanical strength, a low dielectric constant, and superior chemical resistance to acidic environments.[3–12]

Two approaches can be used to metallize a PI surface. One approach is a dry process that involves plasma or electron-beam surface treatments.[13–24] The other approach is a wet process that involves heterogeneous chemical reactions, ion exchange, and the chemical reduction of metallic ions. Using the wet process, researchers have in situ embedded metal nanoparticles, such as Ni,[5,12,25–28] Pt,[26] Cu,[4–6,8,9,11,26,29–31] Ag,[7,10,18,32–35] and Au,[36] in PI. For the fabrication of FPCBs, the PI surface must first be metallized by copper, after which copper patterns are obtained through exposure, development, and etching processes. Copper-foil-clad laminates are the basic materials used for most FPCBs. Typically, a laminate is created by bonding together a sandwich composed of a PI film, an adhesive, and a piece of copper foil.[1,2] However, the adhesive causes problems when a through-hole passes through the laminate. Therefore, an "adhesiveless" construction is considered to be superior to the sandwich construction.

The previously mentioned wet process can produce an adhesiveless copper-coated PI film in which the copper thin film on the PI surface is deposited by electroless plating.[5,8,10,11,31,37] To catalyze electroless copper deposition onto the PI surface, metal nanoparticles (NPs), such as Pd, Ag, Ni and Cu, are embedded on the PI surface and contact the copper electroless plating solution. If these metal NPs are buried in the PI surface, they cannot catalyze copper deposition onto the PI surface.[31] The doping of metallic ions into the sublayer of a PI film is achieved through an ion-exchange approach. Following the ion-exchange step, the use of an appropriate reducing agent is important to reduce the doped metallic ions in the PI sublayer to metal NPs. However, if the reducing agent diffuses into the PI sublayer, metal NPs will be formed in the PI sublayer, where they cannot contact the copper electroless plating solution. Hence, a gaseous reducing agent, such as hydrogen, is not appropriate for this process.[31] Some aqueous reducing agents are also capable of diffusing into the PI layer and reducing the doped metallic ions. This process renders many metal NPs useless for catalyzing the electroless deposition of copper. Herein, we attempt to discover an environmentally friendly reducing agent that can induce the diffusion of doped silver ions in the PI sublayer and

promote their aggregation toward the outermost surface of the PI; i.e., no Ag NPs should remain in the PI sublayer after the reduction step, which can significantly enhance the coverage of the Ag thin film on the PI film.

Experimental

Polyimide films were purchased from DuPont (Kapton HN, 50 μm thick). The details of the process used for the chemical modification of the PI surface is described elsewhere.[31] A cleaned PI film was immersed in a 5 M KOH solution at 50°C for 5 min to hydrolyze the PI surface, which resulted in the formation of a poly(amic acid) (PAA)-coated PI film. This KOH-induced hydrolysis leads to the formation of potassium salts of carboxylic acids via cleavage of their imide rings.[31] The resulting carboxyl groups serve as cation-exchangeable groups. After the hydrolysis reaction, the surface-modified PI film was immersed in a 50 mM $AgNO_3$ solution at 25°C for 5 min to incorporate Ag^+ ions into the PAA layer through an ion-exchange reaction with potassium ions. The Ag^+-doped PI film was then immersed in a 0.17 M reducer solution at 25°C to reduce the doped Ag^+ ions.

The surface morphologies and cross-sections of these Ag-thin-film-coated PI films were observed using field-emission scanning electron microscopy (FESEM, JEOL, JSM-7401F) and transmission electron microscopy (TEM, JEOL JEM-1400 electron microscope), respectively. For cross-sectional TEM observations, samples were sectioned into slices approximately 100 nm thick using a conventional microtome technique and a diamond knife. The structural orientations and grain sizes of the Ag thin films were examined using X-ray diffraction (XRD, Rigaku Rint 2500) with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5405$ Å). The grain sizes of the Ag thin films were calculated using Scherrer's equation. We obtained the mean thickness of the Ag thin films by averaging the measurements taken at ten different positions on the TEM images of the thin films.

Results and Discussion

Figure 1 shows the surface morphologies of the Ag-thin-film-coated PI surfaces after the reduction treatments in two different reducing solutions for different amounts of time. Although both reducing solutions were capable of reducing the doped Ag^+ ions to Ag NPs irrespective of their pH values, ascorbic acid led the reduced Ag atoms to aggregate, thereby forming numerous small Ag nodules on the PAA surfaces. The ascorbic acid also led to PAA surfaces that were not fully covered by the reduced Ag atoms, as shown in Fig. 1b. In contrast with ascorbic acid, glucose uniformly induced the reduction of doped Ag^+ ions on the PAA surface. Inner Ag^+ ions were observed to continuously diffuse toward the PAA surface as the reduction process progressed. Therefore, the surface morphology, shown in Fig. 1f, was still smooth after a reduction time of 6 min. This result is in agreement with a previous study which showed that

*Electrochemical Society Active Member.

zE-mail: dowwp@dragon.nchu.edu.tw
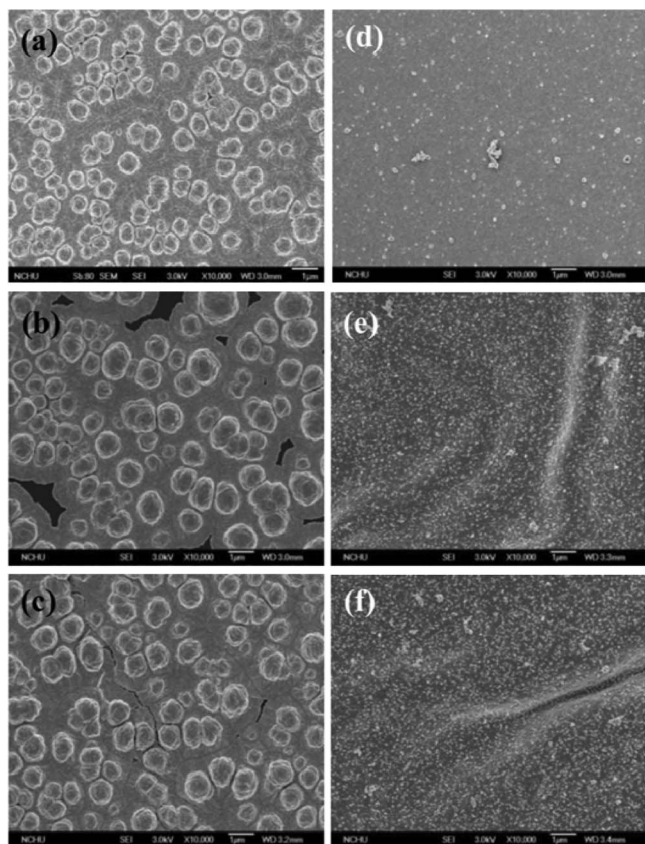
Figure 1. FESEM images of the surface morphologies of the Ag-thin-film-coated PI films. Samples (a, b, c) were in a 0.17 M ascorbic acid solution (pH 2.23) for (a) 2 min, (b) 4 min, and (c) 6 min; samples (d, e, f) were in a 0.17 M glucose solution (pH 12) for (d) 2 min, (e) 4 min, and (f) 6 min.
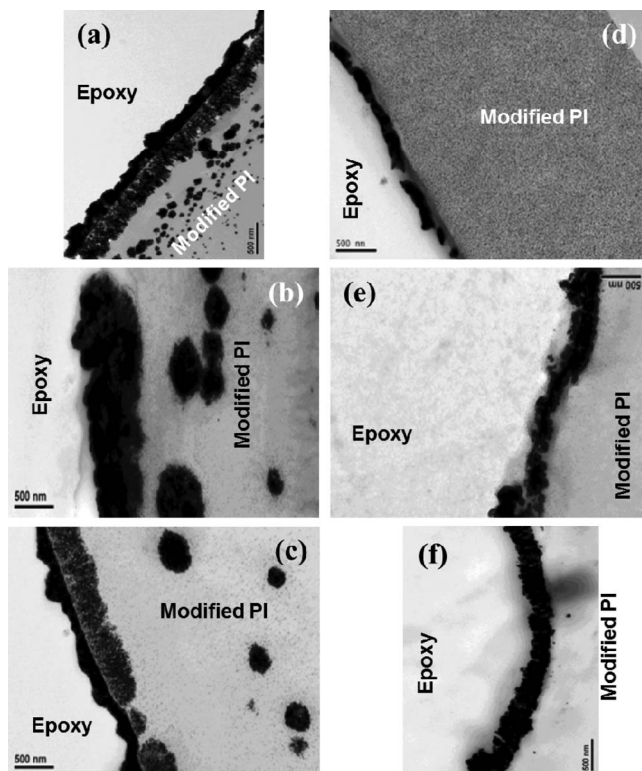

Figure 2. TEM images of the surface morphologies of the Ag-thin-film-coated PI films. Samples (a, b, c) were in a 0.17 M ascorbic acid solution (pH 2.23) for (a) 2 min, (b) 4 min, and (c) 6 min; samples (d, e, f) were in a 0.17 M glucose solution (pH 12) for (d) 2 min, (e) 4 min, and (f) 6 min.

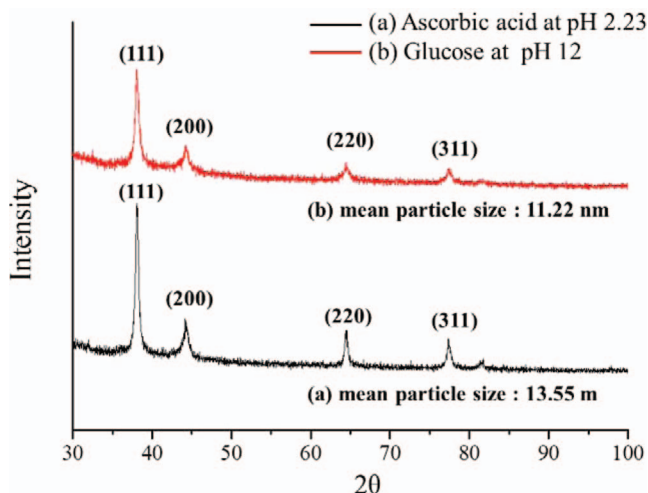glucose can induce the formation of a mirror-like silver layer on a PI surface.[35]

Figure 2 shows the TEM cross-sections of the composite films shown in Fig. 1. Evidently, ascorbic acid was not capable of inducing all of the doped Ag^+ ions to diffuse toward the PAA surface during the reduction process. Consequently, many Ag NPs remained in the PAA sublayer. Moreover, the reduced Ag atoms aggregated on the PAA surface, which led to discontinuous Ag thin films and Ag-unoccupied PAA surfaces. Interestingly, when ascorbic acid was substituted with glucose, the doped Ag^+ ions continuously diffused toward the PAA surface as the reduction process progressed, as confirmed by Figs. 2d–2f. After 2 min. of reduction time, most of the doped Ag^+ ions remained in the PAA sublayer, as shown in Fig. 2d. After 4 and 6 min. of reduction time, all of the doped Ag^+ ions diffused to the outermost PAA surface and were reduced to a continuous Ag thin film, as shown in Figs. 2e and 2f. These TEM images are in agreement with the FESEM images shown in Fig. 1.

Figure 3 shows the XRD patterns of the Ag-thin-film-coated PI films. Because glucose can uniformly induce the reduction of doped Ag^+ on a PAA surface without the local aggregation of silver atoms, the grain size (11.22 nm) of the reduced Ag thin film obtained using a glucose solution is smaller than that obtained using an ascorbic acid solution (13.55 nm). This result is in agreement with the surface morphologies observed by FESEM, shown in Fig. 1, and with the TEM cross-sections shown in Fig. 2. Figure 4 further demonstrates that the thickness of the Ag thin film was nearly constant over time when the silver was reduced in the ascorbic acid solution, whereas the thickness of the Ag thin film increased with increasing reduction time in the glucose solution. This result indicates that doped Ag^+ ions in

the PAA sublayer gradually move toward the outermost PAA surface and are reduced to a dense Ag thin film in the glucose solution. This result is not obtained with the ascorbic acid solution; instead, most of the doped Ag^+ ions barely move and are reduced in place in the PAA sublayer. Consequently, the Ag thin film thickness is independent of the reduction time when the ascorbic acid solution is used as a reducing agent.

Figure 3. XRD patterns of the Ag-thin-film-coated PI films.

Figure 4. The thicknesses of Ag thin films formed on the PI films plotted as a function of the reduction time.

Conclusions

Two environmentally friendly organic reducing agents were used to reduce Ag$^+$-doped PAA to an Ag-thin-film-coated PI. Only glucose could produce a continuous and dense Ag thin film on the PAA surface. Ascorbic acid reduced the doped Ag$^+$ to form a granular Ag thin film on the PAA surface and dispersed Ag NPs in the inner PAA layer. This effect was attributed to the pH levels of these reducing agents. An alkaline reducing agent (glucose) reduced doped Ag$^+$ and maintained the carboxylate form of PAA such that inner Ag$^+$ ions could diffuse toward the PAA surface along a concentration gradient of Ag$^+$ ions formed by the ion-pair attraction between R–COO$^-$ and Ag$^+$. However, the carboxylate group of the PAA was converted into a carboxylic acid group after ascorbic acid reduced the doped Ag$^+$ to Ag NPs, and ascorbic acid, driven by the acid–base neutralization reaction, diffused into the inner PAA layer.

The root cause of this result is explained as follows:

[1]

[2]

[3]

Reaction 1 represents the reduction of PAA–Ag$^+$ to PAA and two silver atoms by ascorbic acid. Reaction 1 is not only a redox reaction but is also an acid–base neutralization reaction. Therefore, the acid–base neutralization reaction drives ascorbic acid to diffuse into the PAA and reduce the PAA–Ag$^+$ in place. In contrast with reaction 1, reaction 2 occurs in an alkaline intermedium such that PAA returns to its original carboxylate state after the doped Ag$^+$ ions are reduced by glucose to Ag atoms. The carboxylate can induce the diffusion of inner Ag$^+$ ions toward the outer PAA surface, as expressed by reaction 3. Therefore, no Ag NPs exist in the inner PAA layer after a reduction that is longer than 4 min, as shown in Fig. 2. The thickness of the Ag thin film on the PAA surface increases with the reduction time, as shown in Fig. 4.

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