Surface Modification and Metallization of Polyimide Using Gold Colloids As a Seed Layer

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ABSTRACT: Herein we report on metallization of Cu on to surface-modified polyimide resin, the method of which relies on potassium hydroxide-induced modification of the polyimide surface to introduce carboxylic acid groups and incorporation of gold colloids as a seed layer through reduction of chloroauric acid. The contact angle of modified polyimide surface with water changed from 70 to 35° due to the hydrolysis of polyimide. Secondary amine group on the surface was detected with attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectrophotometry, suggesting that tertiary amine group has turned into secondary group. In addition, on the basis of hydrophilic behavior, we succeeded in depositing gold colloids on the chemically modified surface. SEM image of copper electroless plated on polyimide surface indicated that copper particles were compact and about ∼ 300 nm in diameter. It showed that gold colloids provide an excellent conductive layer to catalyze the electroless plating of Cu on polyimide surface. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2044–2048, 2009

Key words: polyimide; surface modification; gold colloids; metallization

INTRODUCTION

Polyimide is known to be a high performance organic dielectric material that has been used extensively in multichip module packaging, printed circuit board fabrication, and ultra-large scale integrated circuit technology because of its good thermal stability, chemical resistivity, and excellent mechanical and dielectric properties. In the fields of these electrics device, copper (Cu) have become the most useful metallization candidate because of their high electrical conductivity and electromigration resistance.[1–4] Compared with the existing copper clad laminate, copper-clad polyimide has thinner conductive layer and better flexibility, so it is more suitable to the development requirements of modern electronic technology, and now copper-clad polyimide can be used as components in mobile phones, keyboards of computers, and so on. Many conventional techniques, including photolithography, electron lithography, and focused ion beam lithography, combined with vacuum evaporation, sputtering, electroplating and electroless plating of metals, have been used for metallization of polyimide. However, increasing use of these conventional techniques is limited by the high costs imposed by the metallization procedures, which involves resist coating, etching processes, high-energy consumption, and numerous lithographic steps. Ikeda et al.[5] for the first time presented a method of direct metallization of Cu on to the surface-modified polyimide resin by photochemical reduction of copper ions with the aid of preadsorbed colloidal TiO_2 as photocatalyst, they also demonstrated that silver circuit patterns could be easily fabricated on polyimide surface using a similar technique.[6] Recently, the same group reported on direct patterning of copper on polyimide using ion exchangeable surface templates generated by site-selective surface modification.[7]

In this article, we describe an experimental study involving a new approach for direct formation of a copper layer on polyimide surfaces by electroless plating and electroplating, which depends essentially on surface predeposited gold colloids as a catalyst. We also characterize the chemically modified polyimide surface with FTTR-ATR and contact angle measurement. In addition, site-selective direct Cu metallization on surface-modified polyimide using micromolding in capillaries (MIMIC)[8,9] technique is currently under development in our group.

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EXPERIMENTAL

Materials and reagents

KOH, $HAuCl_4{\cdot}5H_2O$, KBH_4, and $CuSO_4{\cdot}5H_2O$ were pursed from Shanghai Chemical Co. and were used as received. Other chemicals were of reagent grade and used as received. Distilled water was used for all experiments. A Upilex-s type polyimide film (50-μm thick) was provided by China-Japan DAyang technical Co. The polyimide films were rinsed with ethanol under ultrasonification and dried with warm air for 1 min prior to use.

Polyimide metallization

Processing steps presently employed for polyimide metallization are schematically presented in Figure 1. A hydrolysis reaction involving aqueous KOH solution was used to modify the polyimide surface to form carboxylic acid groups and secondary amine groups through cleavage of the imide rings.[10] First, a polyimide film was immersed in an aqueous KOH solution (5 mol/L) for about 5 min at 50°C. Incorporation of gold colloids can be achieved by subsequent reduction of $HAuCl_4$ through immersion of the surface-modified films into aqueous $HAuCl_4$ solution (w/w, 1%) for about 2.5 h at room temperature and then reduction with KBH_4 solution (0.7 mg/mL).Copper was electroless plated onto the gold colloids preadsorbed polyimide surface by placing the polyimide in a copper plating bath containing 5 g/L $CuSO_4$, 25 g/L sodium potassium tartrate, 7 g/L NaOH, and 10 g/L formaldehyde. With gentle shaking, the plating was carried out for about 30 min at 40–45°C. After plating was complete, polyimide with copper layer was rinsed with copious amount of water and dried. Finally, to make the Cu layer thicker, the polyimide was immersed into a electroplating bath containing 60–80 g/L $CuSO_4$, 100 mL/L sulfuric aid, 10 mL/L HT-290A brightener, with a current density of 0.04 A/cm^2. Te electroplating was carried out for about 60 min at room temperature.

Film characterization

The contact angle of pristine and modified polyimide surface with water was measured by a contact angle measuring apparatus (model HARKE-CA). The changes of functional groups on modified polyimide was determined by Fourier transform infrared (FTIR) spectrophotometry with attenuated total reflection (ATR) (model Nicolet0460).Gold colloids deposited on polyimide surface was characterized using UV-vis spectrophotometer, pristine polyimide was used as the background for the experiment. A WAT-2315 optical microscope equipped with a CCD camera was used to investigate the thickness of copper on the films. The surface morphology of the films were observed using a JSM-6360LA scanning electron microscopy (SEM) microscope operating at 20 KV, equipped with an energy-dispersive X-ray (EDX) microanalyser.

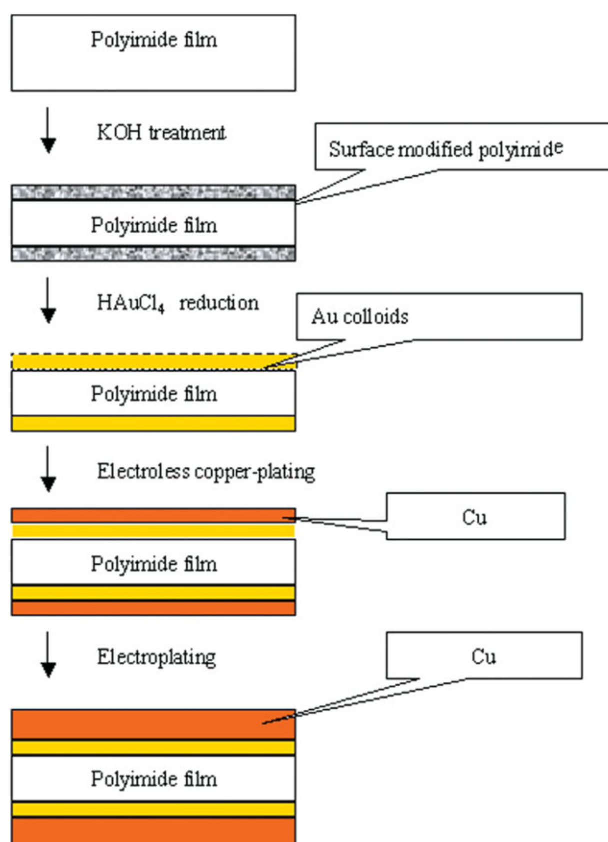


Figure 1 Schematic of the proposed processes for directly forming copper layer on a modified polyimide surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Surface modification of polyimide by base hydrolysis

The KOH treatment leads to cleavage of the imide ring to form amide bonds and carboxyl groups on the polyimide surface, as shown in Figure 2. The kinetics of the hydrolysis has been previously reported[11] and we should noted that base hydrolysis of polyimide is a surface-bound processes. That is, exposure of polyimide to base yields hydrolyzed products on the surface of the polymer rather than in the bulk polymer. One explanation for this phenomenon stems from the fact that the surface-bound products formed during hydrolysis, such as carboxylate moieties, are negatively charged (deprotonated) at the high pH values required for base hydrolysis. Because the hydroxyl ions of the base are also negatively charged, electrostatic repulsion prevents the

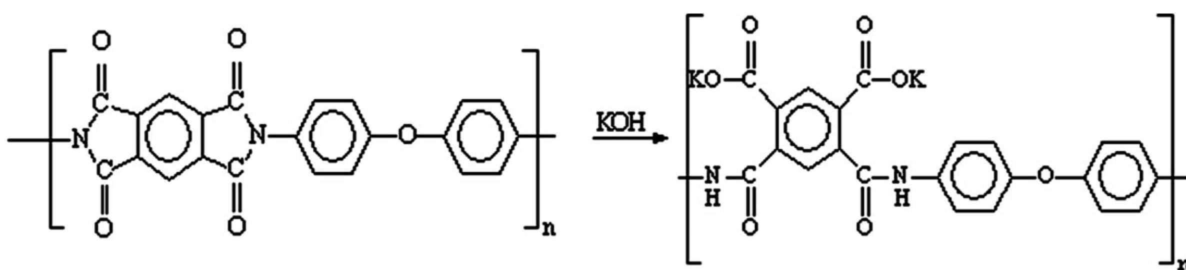
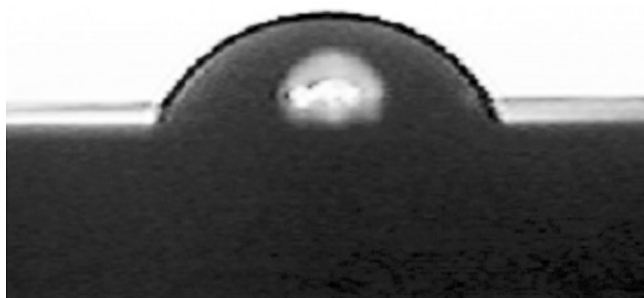


Figure 2 Reaction scheme of the KOH hydrolysis of polyimide surface to yield functional groups such as amine and carboxylic groups.

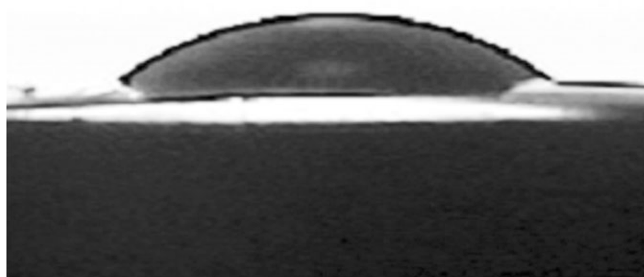
hydroxyl species from further hydrolyzing the bulk polymer. As a result, hydrolysis of polyimide should be a surface selective process.

Sessile drop water contact angle measurements

After a polyimide film was immersed in an aqueous KOH solution and then rinsed with distilled water, a wetting film of water was retained on the polyimide surface. From Figure 3, we can see that contact angle between water and the polyimide surface was reduced from 70° for pristine polyimide to 35° for KOH hydrolyzed polyimide. These observations confirmed the formation of reactive carboxyl groups on the surface-modified polyimide surface.



(a)



(b)

Figure 3 Water droplets (5 μL) on unmodified (a) and KOH-treated (b) polyimide surfaces.

Analysis of pristine and modified polyimide films by FTIR-ATR

A representative FTIR-ATR spectrum of pristine and KOH-treated polyimide film is presented in Figure 4. Strong bands corresponding to carbonyl stretching at 1700 cm^{-1}, aromatic C=C stretching at 1500 cm^{-1}, asymmetric O—C—O stretching at 1228 and 1170 cm^{-1} are present in spectra of pristine polyimide. Upon base modification, there are two significant changes in the spectra. Firstly, a broad peak between 3250 and 3500 cm^{-1} appeared in the spectra of KOH treated polyimide, which is characteristic of the NH-stretch. The result indicated that tertiary amine group has turned into secondary amine group during base hydrolysis. Secondly, a red-shift of 120 cm^{-1} (1700–1580 cm^{-1}) is observed for the carbonyl stretching after surface modification of the polyimide film, which is in agreement with the fact that carbonyl groups has changed into potassium carboxylate during surface modification.

Deposition of gold colloids multilayers on modified polyimide surface

Gold colloids were deposited on amine-terminate polyimide (AT-PI) surfaces by adaptation of a

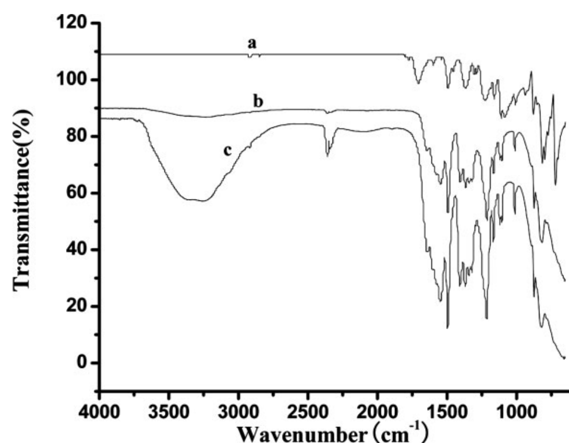


Figure 4 FTIR-ATR of pristine polyimide (a), polyimide treated with KOH for 10 min (b), and polyimide treated with KOH for 20 min (c).

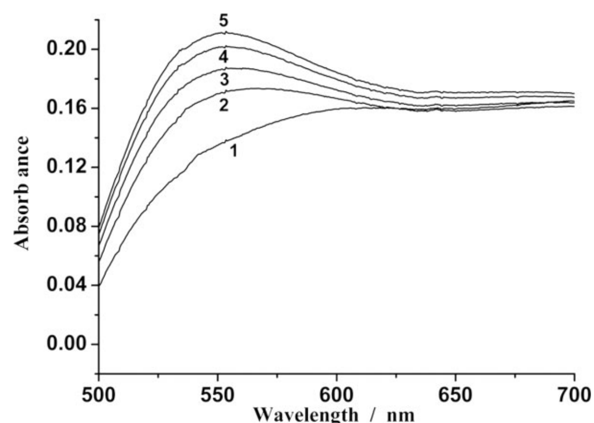


Figure 5 Absorbance spectra of AT-PI films exposed to 1% $HAuCl_4$ for 5 min (1); 30 min (2); 60 min (3); 90 min (4); 120 min (5), and then reduced with KBH_4.

electroless deposition protocol described previously with some modifications.[12] In Ref. 12, for coordination of gold (III) to the amine groups, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride and ethylenediamine were used as coupling agent and ligand respectively,, and then gold (III) is reduced by $NaBH_4$ to form gold nanoparticles that served as the seed to catalyze the final electroless gold plating. However, in our experiments, secondary amine groups are formed during the hydrolysis of polyimide, so no additional ligand and coupling agent were added to the solution of $HAuCl_4$. The incorporated gold (III) was then reduced by KBH_4 to form gold colloids which serves as a seed layer for the subsequent electroless copper plating. Displayed in Figure 5 are optical absorption spectra of electroless-deposited gold on AT-PI films. The feature at $\sim$ 540 nm is evident in the spectra corresponding to immersion times (in the $HAuCl_4$) of 5 min and greater. In addition, the intensity of the band at 540 nm increases with increased time of immersion in the $HAuCl_4$ solution. These data indicate that ionic gold species are being coordinated by the surface amines and then subsequently reduced to form gold colloids structures on the surface of the AT-PI. The band at 520 nm is due to the gold plasmon band[13] associated with nanometer-sized gold particles. When gold nanoparticles aggregate, their surface plasmon resonance shifts to a longer wavelength (in our experiment, 540 nm) and we estimate the size of the gold particles to be in the 2–5 nm range.

Metallization of polyimide surface by electroless deposition

The overall reaction for the electroless deposition can be depicted as

$HCHO + Cu^{2+} \rightarrow Cu + HCOOH$ (with catalytic surface). Catalyst was necessary for the deposition; the only solution for electroless deposition was quite stable under normal conditions without the catalyst.[14] In our experiment, freshly generated gold colloids were used as the catalyst. The process of electroless Cu deposition involves the use of formaldehyde, a chemical reducing agent to plate Cu from solution onto a surface with a catalyst. The most important requirement of an electroless deposition bath of this type is to arrange the chemistry such that the kinetics of homogeneous electron transfer from the reducing agent to the metal ion is slow. Otherwise the metal ion would simply be reduced in the bulk solution. Figure 6 is the SEM image of copper electroless plated on polyimide surface with predeposited gold colloids as a catalyst. We can see that copper particles electroless plated on polyimide surface were compact and about $\sim$ 300 nm in diameter. The result indicated that gold colloids provide an excellent conductive layer to catalyze the electroless plating of Cu on polyimide surface.

Adhesion test

The so called "Scotch tape"[15] qualitative test was also performed to assess the adhesion of Cu electroless deposited on the modified polyimide surface. Clear adhesive tape is applied and smoothed to remove any air bubbles; the tape is then peeled off the polyimide surface. We observe no obvious removal of the Cu layer (less than 5%). The peel test was done by removing the tape both rapidly and slowly with the same results: no gross removal of the Cu layer is observed.

CONCLUSIONS

In this study, we have described a novel fabrication process of copper thin films on polyimide surface

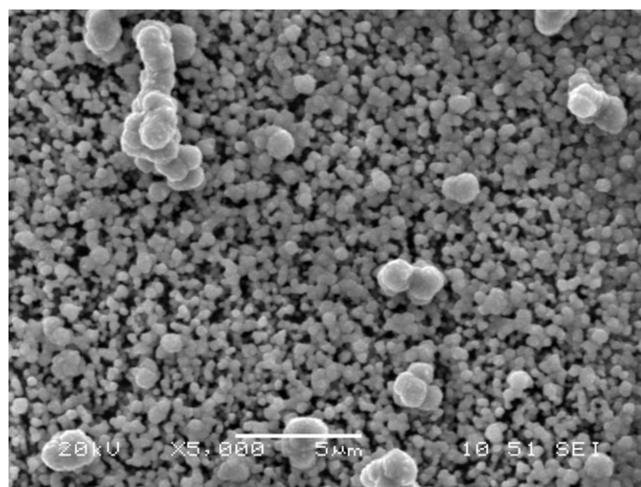


Figure 6 SEM image of copper electroless plated on polyimide surface with predeposited gold colloids as a catalyst.

using gold colloids as a seed layer. Incorporation of Cu on polyimide was successfully achieved through surface modification of the polyimide surface by chemical treatment with KOH to form secondary amine groups which can act as complexing agent to combine gold colloids. The use of gold colloids deposited on the modified polyimide surface was found to be effective in catalyzing reducing Cu ions to metallic Cu. This method is relatively simple and requires no expensive equipment or high energy consumption. In addition, site-selective direct Cu metallization on surface-modified polyimide using MIMIC technique is currently under development in our group. It is thus envisaged that this procedure will be suitable for the practical manufacturing of Cu circuit patterns in the microelectronic industry.

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