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Direct photochemical formation of Cu patterns on surface modified polyimide resin

Shingo Ikeda,[a] Kensuke Akamatsu*[b] and Hidemi Nawafune*[b]

[a] *Graduate School of Science, Konan University, 8-9-1 Okamoto, Higashinada, Kobe 658-8501, Japan*
[b] *Faculty of Science and Engineering, High Technology Research Center, Konan University, 8-9-1 Okamoto, Higashinada, Kobe 658-8501, Japan.*
E-mail: akamatsu@center.konan-u.ac.jp

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A novel method is presented for the direct metallization of Cu on to surface modified polyimide resin by photochemical reduction of copper(II) ions with the aid of pre-adsorbed colloidal TiO_2 as photocatalyst: for the first time copper circuit patterns are successfully fabricated simply by using a quartz-on-glass photomask without the requirement for a photoresist.

Polyimide is known to be a high performance organic dielectric material that has been used extensively in multi-chip module (MCM) packaging, printed circuit board (PCB) fabrication, and ultra-large scale integrated circuit (ULSI) technology because of its good thermal stability, chemical resistivity, and excellent mechanical and dielectric properties. In the fields of these electronics device applications, copper (Cu) films have become the most useful metallization candidate because of their high electrical conductivity and electromigration resistance.[1–4] Incorporation of wiring layers of copper onto dielectric polyimide is therefore a long-term goal for fabricating high-performance microchips in the microelectronic industry,[5] and such copper/polyimide systems have been the subject of intensive research from practical viewpoints.[6–11] In PCB fabrication, patterned formation of metal layers on the substrate is necessary, the majority of which can be achieved so far *via* photolithographic steps for the coated photoresist followed by a subtractive or an additive electroless deposition process,[12–15] or more recently *via* electroless plating combined with simultaneous and/or alternating laser patterning.[16,17] These conventional techniques for the formation of metal patterns require a number of processing steps, *e.g.*, coating of resist, photolithographic step, metal deposition and etching. In order to reduce fabrication costs, a process for area-selective direct metallization of Cu on the substrate is thus desirable, from which Cu thin film patterns with desired structures can be directly formed on the substrate.

In a previous publication, we reported a novel process for surface chemical modification of polyimide resin utilizing alkaline and acid treatment, and demonstrated experimentally that metal ions could be adsorbed onto the modified polyimide surface.[18] We have also reported that copper thin films can be successfully formed on polyimide surfaces by chemical reduction using $NaBH_4$ aqueous solution.[19] Although this novel process allows the polyimide surface to be metallized directly, patterned formation of Cu layers is difficult without using a photoresist.

In this paper, we describe an experimental study involving a new approach for the direct formation of a copper layer on polyimide surfaces by UV-light-induced photoreduction, which depends essentially on surface pre-adsorbed TiO_2 colloids as a photocatalyst. We also demonstrate experimentally the application of such photocatalytic copper film formation in fabrication of copper circuit patterns on polyimide surfaces, simply by the use of a metal-on-quartz photomask without requiring a plating resist, which is usually the case for the conventional copper plating technique.

The processing steps employed in this work for direct metallization are schematically presented in Fig. 1. The procedure involves five steps: (i) surface modification of the polyimide (Kapton 200-H, Toray-DuPont) by alkali treatment (5 mol dm^{-3} KOH aq., 50 °C, 5 min), (ii) adsorption of Cu^{2+} ions on the surface-modified polyimide surface (5 mmol dm^{-3} $CuSO_4$ aq., 1 min), (iii) adsorption of TiO_2 colloids as photocatalyst (Ishihara Techno. Ltd. anatase TiO_2 sol, *ca.* 20 nm diameter particles), (iv) fabrication of Cu patterns by photochemical reduction with UV irradiation using a quartz-on-glass photomask, and (v) removal of TiO_2 colloids and Cu^{2+} ions remaining on non-irradiated regions (with dilute H_2SO_4 aq.). Steps (ii)–(iv) are crucial in this methodology for direct area-selective metallization. The adsorption of Cu^{2+} ions on the

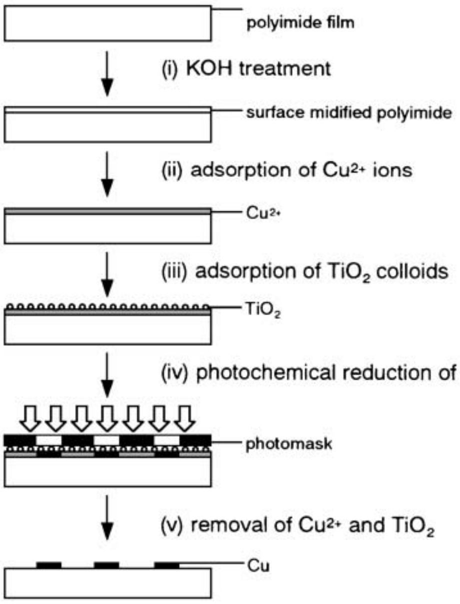

Fig. 1 Schematic diagram of the present direct formation process of Cu patterns utilizing the photocatalytic reaction of pre-adsorbed TiO_2 colloids.

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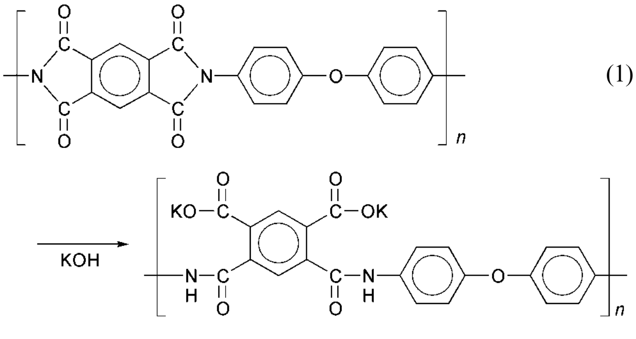
surface-modified polyimide surface was confirmed by inductively-coupled plasma (ICP) atomic emission spectroscopic measurements (SPS7700 plasma spectrometer, Seiko Instruments). The chemical state of Cu in the film and morphology of Cu patterns were studied with X-ray photoelectron spectroscopy (XPS, ESCA850, Shimazu) and scanning electron microscopy (JSM-6340F, JEOL), respectively.

The KOH treatment leads to cleavage of the imide ring to form amide bonds and carboxyl groups on the polyimide surface, as expressed by eqn. (1).[18,19]



(1)

The formed carboxyl groups act as cation exchange groups and can adsorb Cu^{2+} ions on immersing the modified film into $CuSO_4$ aqueous solution. The amount of adsorbed Cu^{2+} ions can be systematically controlled by varying the KOH treatment time and adsorption time of Cu^{2+} ions, and also depends on the pH during subsequent adsorption of TiO_2 colloids.[20] Cu(II) is photocatalytically reduced to Cu(0) by electrons in the conduction band of colloidal TiO_2 produced by UV absorption.[21] A detailed study related to the reduction mechanism is currently under way and the results will be presented elsewhere.

After UV irradiation for 2 h, the polyimide substrate exhibited a metallic luster and moderate reflectance. The chemical state of Cu in the polyimide film was confirmed by XPS measurements. Representative results are presented in Fig. 2. Although there is a slight increase in peak intensity there is no significant shift of the Cu $2p_{3/2}$ core level binding energy upon UV irradiation. An indication of the oxidation state of Cu can be provided from the Cu LMM Auger peak. The peak in kinetic energy of Cu for the as-deposited sample is observed at 916.6 eV, which is very close to the literature value observed for Cu(II) ionic species.[22] As the UV irradiation time is increased, the peak shifts toward higher energy (918.7 eV after 2 h irradiation), which is comparable to kinetic energy of 918.8 eV for bulk metallic Cu,[22] indicating complete reduction of Cu^{2+} ions to metallic Cu. Preliminary X-ray diffraction measurements for the films before and after UV irradiation revealed the formation of a Cu thin film on the polyimide substrate after irradiating the surface for 2 h (not shown) and supported the results shown in Fig. 2.

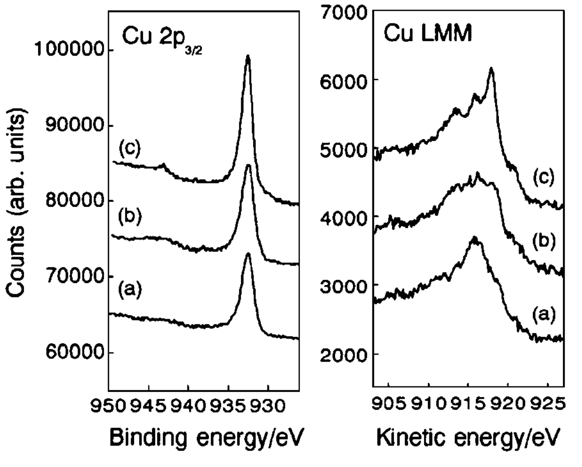


Fig. 2 Cu 2p core level electron and Cu LMM Auger electron spectra of Cu^{2+}-adsorbed polyimide films before (a) and after UV irradiation for 1 h (b) and 2 h (c).

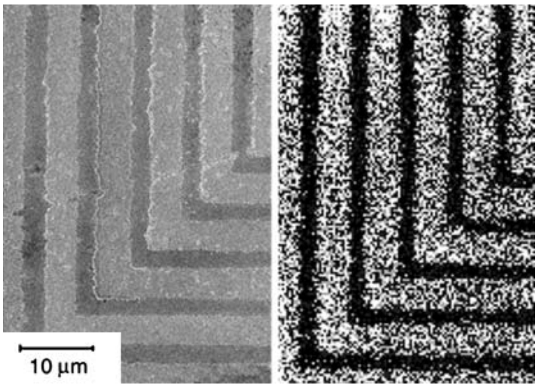


Fig. 3 Scanning electron micrograph (left) and corresponding elemental mapping image (right) of the Cu patterns formed on the polyimide substrate by UV irradiation for 2 h followed by removal of TiO_2 colloids and Cu^{2+} ions in non-irradiated regions. The Cu linewidth is 5 µm. The sample was examined in a JSM-6340F FE-SEM operating at 15 kV (HRC, Konan Univ.).

As shown in Fig. 3(left), scanning electron microscopy of the UV-irradiated sample using a photomask confirms that Cu thin film patterns with a linewidth of *ca.* 5 µm were successfully formed on the polyimide surface. Patterned formation of Cu films was also revealed by EDX elemental mapping analysis. In Fig. 3(right), the elemental mapping image, bright regions obtained from the Cu-Kα line reveal the structure of the Cu patterns formed, indicating the complete removal of Cu ions on non-irradiated parts of the film upon acid treatment after UV irradiation. The deposited Cu thin films exhibited a surface electrical conductivity of 1.12×10^{-5} S, sufficient to initiate a subsequent Cu electroplating reaction.

In conclusion, we have described here a novel fabrication process of copper thin films on polyimide surfaces, using TiO_2 colloids as a photosensitive layer. Incorporation of large loadings of copper ions on polyimide was successfully achieved through surface modification of the polyimide surface by chemical treatment with KOH to form carboxyl groups which can act as ion exchange groups. The use of TiO_2 colloids adsorbed on the ion-exchanged polyimide surface was found to be effective in reducing copper ions to metallic copper upon UV-light irradiation and is the most important aspect of this fabrication procedure. The present TiO_2 colloid-promoted photochemical reduction provided a direct fabrication of copper circuit patterns on polyimide surfaces simply using a photomask. This method, which can be described as a fully additive-based direct metallization process, is relatively simple and requires no expensive equipment or high energy consumption. It is thus envisaged that this procedure will be suitable for the practical manufacture of Cu circuit patterns in the microelectronic industry.

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20 The amount of adsorbed Cu^{2+} ions in the polyimide film was *ca.* 8.0×10^{-7} mol cm^{-2} after immersion of the Cu^{2+}/polyimide film in to the colloidal TiO_2 solution which was carefully adjusted to pH 4.0.

21 In this process, sodium formate was used as a hole scavenger in order to shorten the irradiation time, and was coated on the substrates before irradiation by pipetting a few drops of sodium formate on to the substrate before irradiation.

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