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Formation of embedded fine copper patterns in various resins by the transfer of plated metal patterns

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A combination of two techniques was used to form metal patterns embedded in flexible resin films. First, metal patterns were formed on sacrificial glass substrates using a photodefinable metal complex solution to form a latent catalyst image. Then, copper was selectively deposited on the catalyst image by electroless plating. In the first step, copper mesh patterns with ca. 90%T visible light transmittance and sheet resistance less than 1 Ω/□ were formed on glass substrates. In the next step, copper patterns were transferred by forming flexible thin resin films on sacrificial glass surfaces with the copper patterns, then curing the resin and delaminating the resin films from the glass. Height differences on the nanometre scale between the film surface and embedded copper pattern showed that complete embedding of the copper structures was attained. After the transfer, change in the optical and electrical properties of the mesh pattern was not detected.

Introduction

Recently, device miniaturisation and performance enhancement have been achieved by developments in packaging technology. In the manufacturing process of electronic devices, electroless plating has been used to impart electrical conductivity to insulating materials. In this case, surface modification during the pre-treatment has been vital for improving the adhesion of the metal at the deposit–insulative material interface. Conventionally, strong oxidising agents, such as permanganate or chromic acid, have been applied for general resin surface roughening.[1,2] Environmentally friendly pre-treatment alternatives, such as vacuum ultraviolet irradiation, air ultraviolet irradiation, plasma treatment, ozone water treatment and fine bubble low ozone water treatment methods, have also been studied.[3–10] The formation by these processes of a roughened surface layer rich in hydrophilic moieties, such as carboxyl groups and hydroxyl groups, formed by oxidising the surface of the resin has been shown to contribute to the adhesion strength improvement. However, sometimes, the original characteristics of the resin, such as embrittlement, increase in

hygroscopic character and optical properties, such as haze, can also change by modifying the resin surface.

In this paper, without relying on a modification process, embedding and transfer of metal patterns during the curing step for film formation using various liquid resins was investigated. As outlined in Fig. 1, the metal patterns were formed on a glass surface by selective plating on catalyst patterns using a photolithography method.[11–13] Embedding conductive layer patterns in the resin circumvented the above issues associated with surface modification methods. Furthermore, metal pattern adhesion may be obtained by embedding into the resin surface. Transferred metal mesh patterns for application as transparent electrodes were studied using the following resins: cycloolefinpolymer (COP: excellent optical transparency and electrical properties), polymethyl methacrylate (PMMA: lightweight alternative to glass), polyimide (PI: high temperature resistance and good physical properties) and polydimethylsiloxane (PDMS: high biocompatibility).

Experimental

As outlined in Fig. 1, latent catalyst patterns on glass substrate were formed using an experimental photosensitive coating solution that contains Ti^{4+} and Cu^{2+} complexes, GLADOTYTE-P (experimental chemical available from JCU Co. Ltd.) for selective electroless plating on glass substrates. First, 0.4 mL GLADOTYTE-P solution was spin-coated (Mikasa Co., Ltd., Opticoat MS-A100) onto the sacrificial glass substrate at 1000 rpm held for 20 s then at 4000 rpm for 5 s. Next, the coated glass was

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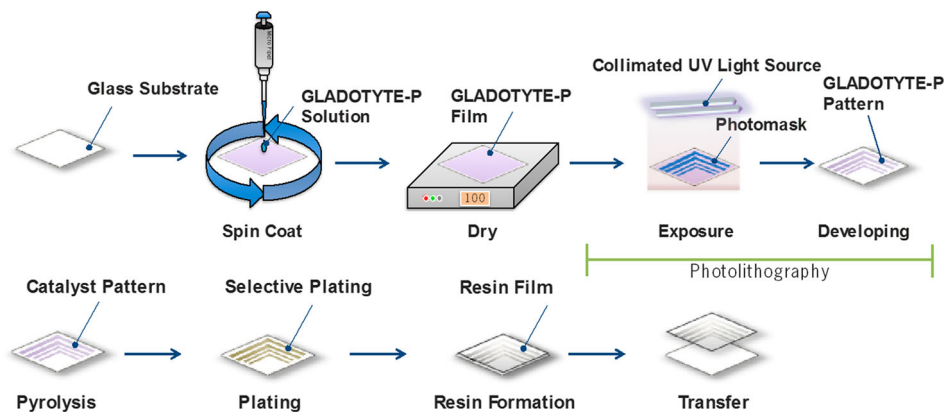
1 Copper pattern formation procedure on the sacrificial glass and transfer to the resin

dried at 100°C for 10 min on a hotplate before photopatterning the GLADOTYTE-P film. The GLADOTYTE-P film was patterned by exposure to collimated UV light (170 mJ cm^{-2} at $\lambda = 365$ nm) from a super high pressure Hg-Xe lamp (USHIO Inc., USH-250BY/D-z1) through a quartz photomask (line width 5 μm chrome grid lines, space 100 μm, %T = ca. 90%). The selectively irradiated GLADOTYTE-P film was developed in 0.25% tetramethylammonium hydroxide solution at 25°C for 30 s to selectively dissolve the irradiated film material and obtain the GLADOTYTE-P pattern. The GLADOTYTE-P pattern was transformed into the titanium–copper oxide pattern by calcination at 500°C at a heating rate of ca. 5°C min^{-1} in an electric furnace. After calcination, the titanium–copper oxide pattern was reduced in a 2 g L^{-1} sodium borohydride solution at 50°C for 2 min. Then, the reduced pattern was immersed in a 0.3 g L^{-1} palladium chloride solution at 50°C for 2 min. The remaining ionic palladium in the catalyst layer was then reduced by immersion in a 30 g L^{-1} monosodium hypophosphite monohydrate solution at 50°C for 2 min to give the catalyst pattern on the sacrificial glass substrate. Copper was selectively deposited on

the catalyst pattern by electroless plating (thickness: 0.2–0.3 μm) with a Rochelle salt-type bath (PB-506, JCU Co., Ltd.). When thicker films were desired, copper mesh patterns were electroplated (JCU Co., Ltd., Cu Brite 21) to a thickness of 2 μm.

In the next step, liquid resins were spin-coated onto copper patterns on the glass at 1000 rpm for 20 s, and then cured to form the respective film on a glass substrate under the following conditions: COP (JSR Co., Ltd., LUCERA) was cured at 100°C. PI was formed from a precursor poly(pyromellitic dianhydride-co-4,4′-oxydianiline) solution (Sigma-Aldrich Co., Ltd.) by curing at 100°C and imidising at 250°C. PMMA (Mitsubishi Rayon Co., Ltd., Acrylite L) was dissolved in acetone and ethyl lactate (1:1 vol.) and cured at 150°C. PDMS (Shin-Etsu Chemical Co., Ltd., SIM 240) was cured at 150°C. All resins were cured and cooled under atmospheric condition. Once the resin solidified into a film, the embedded copper pattern was peeled off the glass substrate with the cured resin. Prepared patterns were observed using a laser microscope (Olympus Co., Ltd., LEXT OLS4000). Light transmittance of copper patterns was calculated from the difference in substrate
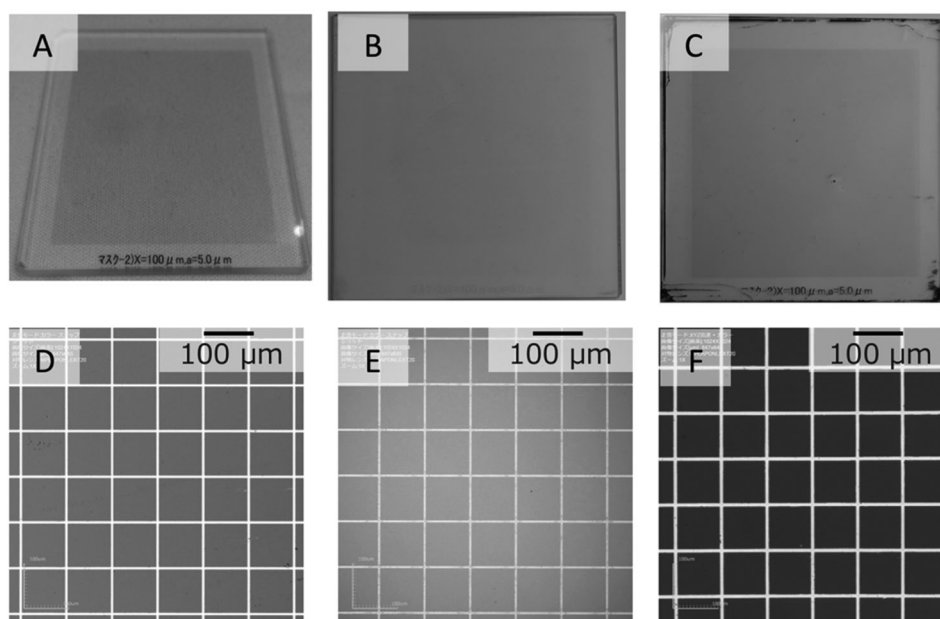
2 Images of the photomask (*a* entire and *d* micrograph), GLADOTYTE-P (*b* entire and *e* micrograph), and electroless copper (*c* entire and *f* micrograph) mesh patterns. These patterns appeared as light lines on a dark background
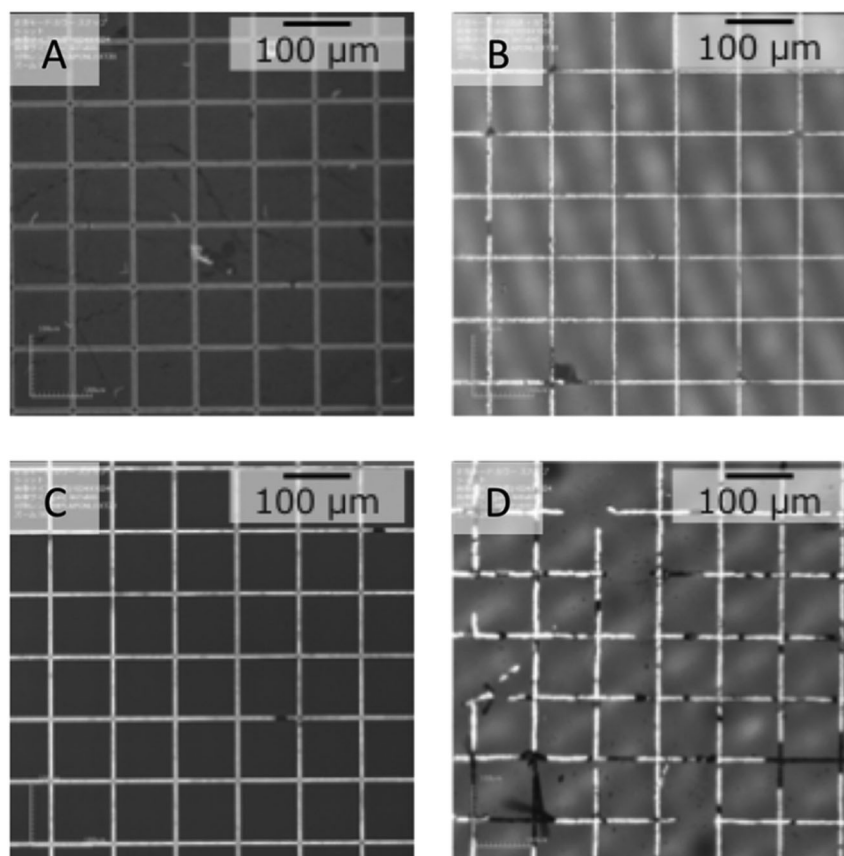
3   Optical microscope images of embedded copper mesh patterns in COP *a*, PMMA *b*, PI *c* and PDMS *d*

with the copper pattern and bare substrate using a turbidity meter (Nippon Denshoku Industries Co., Ltd., NDH-5000W). Sheet resistance was measured by a 4-point probe on a resistivity measuring instrument (NPS Inc., Sigma-5). Elemental analysis of the delaminated glass and resin surfaces was performed using an electron probe micro analyser (EPMA, Shimadzu Co., EPMA-1610) and by an X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., AXIS Ultra DLD). The copper pattern-embedded resin surface was analysed by atomic force microscopy (AFM, Hitachi High-Tech Science Co., Ltd., SPI4000 E-seep).

Results and discussion

The GLADOTYTE-P film is a positive-type photosensitive composition, in which carboxylic acid moieties are generated by a UV light-induced photochemical reaction in the exposed areas. By becoming acidic, the irradiated area becomes soluble in the alkaline developer compared to unexposed area. The remaining titanium–copper complex film on glass substrate was transformed to titanium–copper oxide by the pyrolysis treatment. Copper oxide in the patterned film was reduced to metallic state and then displaced by palladium to enhance initiation of the electroless plating reaction.

In this way, the autocatalytic deposition reaction on the latent catalyst image was initiated and copper patterns were formed by electroless plating. Figure 2 shows images of the photomask, GLADOTYTE-P and electroless copper mesh patterns. The pattern dimensions were accurately preserved at each stage of the procedure. Visible light transmittance of the metal patterns formed on the

glass substrate was ca. 90%T, similar to that of the photomask. The sheet resistance was ca. $0.5 \, \Omega/\square$ when the copper thickness was ca. 0.3 µm. Typical ITO films used in touch panels are 30–100 $\Omega/\square$ at 90%T; therefore, in application as a transparent electrode material, the optical and electrical properties were more than sufficient.[14–16] With electrolytic copper plating, even lower sheet resistance was attained; however, overgrowth resulted in decrease in light transmittance. When the copper thickness was ca. 2 µm, the sheet resistance was $0.17 \, \Omega/\square$ and the light transmittance was 72%T.

Liquid resins were spin-coated onto the entire glass substrate to give resin films several tens of micrometres thick after the curing step. Images of the metal patterns after transfer to the various resins from the glass substrate are shown in Fig. 3. In resins other than PDMS, the metal patterns were perfectly transferred to the resin from the sacrificial glass substrate without defects and cracks. Resin films were easily peeled off without release agent,

Table 1   Properties of copper mesh patterns on the glass substrate and embedded resins

Substrate	Copper mesh properties		
	Line width [µm]	Light transmittance [%]	Sheet resistance[$\Omega/\square$]
Glass	5.36	89.8	0.54
COP	5.34	88.6	0.58
PMMA	5.42	87.5	0.76
PI	5.64	88.4	0.65
PDMS	5.57	…	…
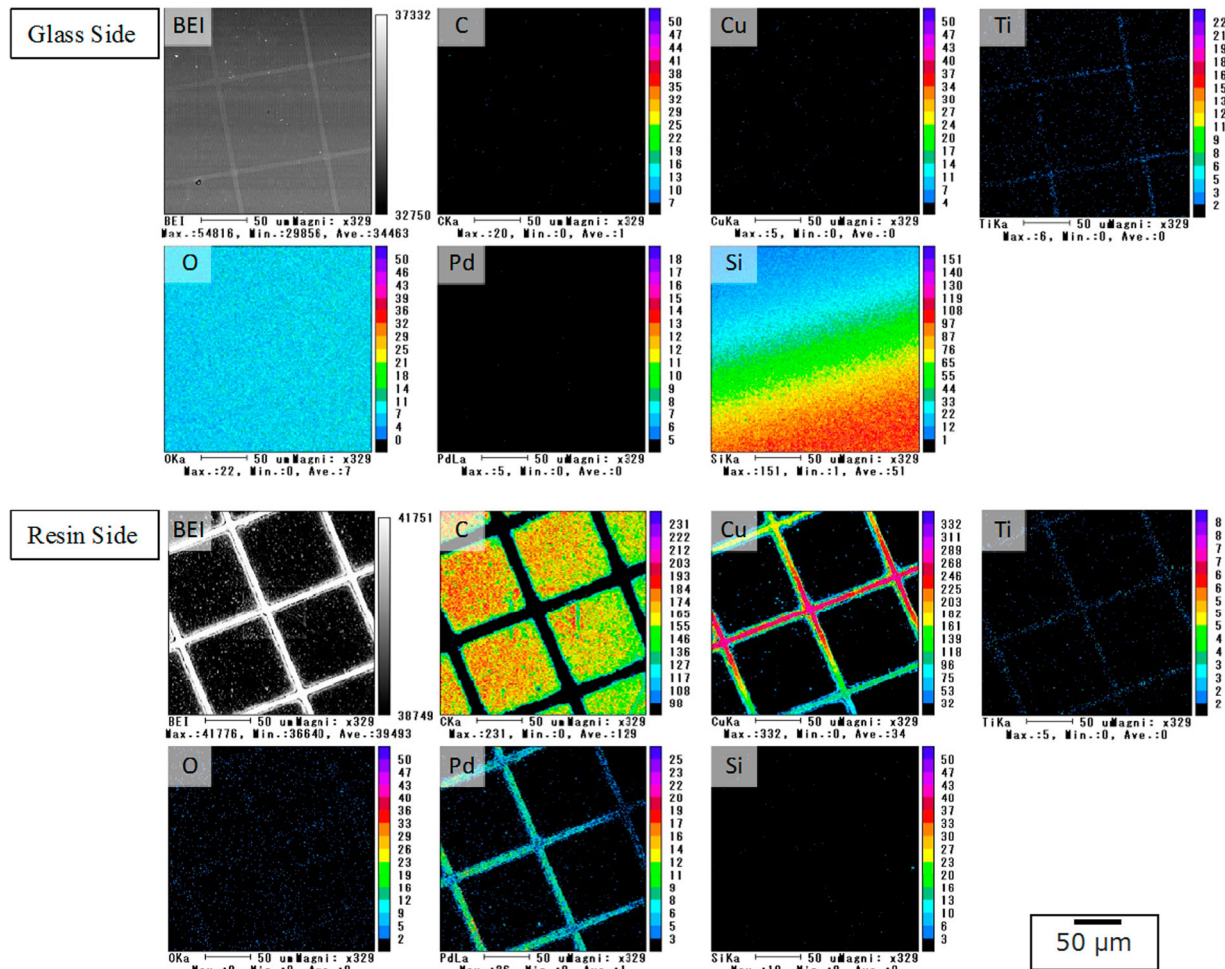
4 EPMA mapping images of the delaminated glass (gold coated) and resin surfaces

suggesting that the interface bonding strength between the glass and the resin was poor. Transfer to PDMS resulted in distorted and broken patterns. PDMS is a silicon-based organic polymer characterised by high elasticity and resilience, hence, Si–O bonding of glass and PDMS was formed in a strong chemical bonding. Therefore, during the peeling step, high adhesion and extensive stretching force ruined the copper pattern. Line width, light transmittance and sheet resistance of copper mesh on glass and resins are shown in Table 1. The difference in the line width in resins was caused by the difference in the delicate condition in the plating process on the glass substrate. Light transmittance and sheet resistance of the metal pattern embedded in the resins were retained with the exception of PDMS. These results indicate that mesh patterns were transferred without having to degrade the characteristics of the resin material.

The delaminated interfaces were determined by elemental analysis. EPMA mapping images of delaminated surfaces of glass and resin are shown in Fig. 4. To prevent charge up, the glass surface was sputtered with a thin gold layer. A residual titanium mesh pattern remained on the glass surface and carbon derived from the resin was not detected. On the resin side, palladium and titanium were detected on the copper mesh pattern; however, silicon originating from the glass substrate was not detected by EPMA. This means that copper plating–glass delamination occurred by titanium–copper oxide layer destruction. The electrical resistance

measured by 4-point probe was not affected by the thin titanium–copper oxide layer on the copper pattern. Further elemental analysis was conducted using XPS from which the results are listed in Table 2. The pattern layers of titanium–copper oxide and palladium catalyst were detected on both sides. These results clearly indicated that the catalytic oxide layer was destroyed and separated between the glass and resin sides in the transfer process.

AFM analysis of the copper pattern-embedded COP surface showed that the embedded copper mesh and COP film surface was continuous and smooth, as can be observed in Fig. 5. The height difference between the COP surface and copper surface was 23 nm; therefore, the copper pattern was almost perfectly embedded in the COP film. Full embedding of the copper mesh pattern in the resin was conducive to high adhesion strength.

In applying the metal transfer method, the embedded copper mesh patterns for transparent conductive film

Table 2 Elemental components of delaminated glass and PI surfaces by XPS analysis

Delaminated surface	Elemental components [at.-%]			
	Cu2p	Ti2p	Pd3d	Si2p
Glass	7.3	3.1	0.1	89.5
PI	58.4	11.0	0.2	30.4
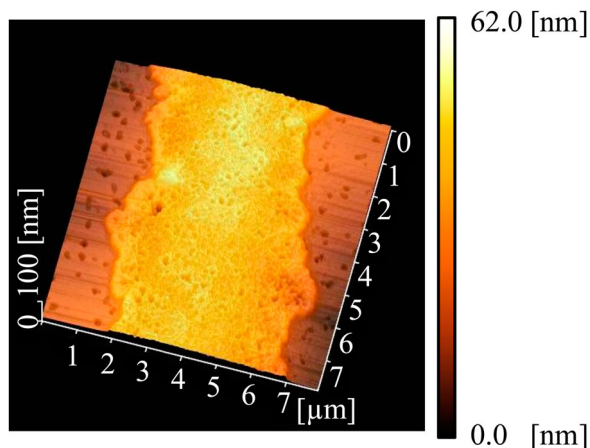
5 AFM image of the copper pattern embedded in the COP film surface

were obtained with a flat surface. Application of this transfer method to fabrication of components, such as contact lens-embedded sensors, pressure sensors and strain gauges in flexible film, could be possible.[17–22]

Conclusions

Copper mesh patterns (line width 5 μm/pitch 100 μm) on the glass substrate were formed by photopatterning titanium–copper complex film from which a latent catalyst image was formed that was selectively metallised by electroless copper plating. Copper mesh patterns with ca. 90%T visible light transmittance and sheet resistance less than 1 Ω/□ were formed on glass substrates. Copper mesh patterns were cast in COP, PMMA, PI and PDMS resins and then transferred to the formed films. The embedded mesh patterns retained the original sheet resistance and transparency except when the resin was PDMS. The copper pattern protrusion from the resin film surface was of the nanometres order demonstrating almost perfect embedding. This method of forming embedded micrometre scale metal patterns in resin films without a modification process is expected to be applicable in the fabrication of a wide range of electronic devices without using a modification process that can be detrimental to the resin properties.

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