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Selective electroless copper plating micro-coil assisted by 248 nm excimer laser

C.T. Pan *

Department of Mechanical and Electro-Mechanical Engineering, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaoshiung 804, Taiwan

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Abstract

In the study, template of micro-coil patterns created by the excimer laser and activated by reactants for electroless copper plating is described. The generated micro-coil patterns are transformed into copper patterns on the substrate and formed copper microstructures. This method simplifies the manufacturing process of making circuits on boards comparing with the conventional lithography process of forming copper patterns on the substrate. Micro-patterns generated by the excimer laser result in the change of surface electric properties and activation selectively. A chemical reaction through the selective activated area may deposit metal, such as copper. The krypton–fluoride excimer laser (KrF, 248 nm in wavelength) not only provides simple and fast machining patterns, but also uses its high energy density to drill holes and circuits directly. Palladium ions are added as mediators in the electroless plating solution to enable a continuous electroless copper deposition. According to the experiment of excimer laser assisted electroless copper plating, the procedures of pretreatment and post cleaning are key factors resulted in excellent selective plating. The samples were pretreated by sodium dodecyl sulfate (SDS) and post cleaned by acetone and diluted nitric acid resulting in distinct micro-patterns. The deposition area is confined in the excimer laser ablated portion resulting in well selective plating.

Keywords: Excimer laser; Palladium; Micro-coil; Electroless; Copper; Selective

1. Introduction

The electronic industry has fast progressed including IC industry, information transportation, personal computers, and their accessories. The printed circuit board (PCB) industry provides a fundamental role to compose these related products. Although the manufacturing technology of PCB is mature and skillful, its sophisticated process consists of a metal film formed onto the insulative polymer substrate, drilling and plating of buried or blind microvias, lithography process (resist coating, UV exposure, development, and resist stripping) as well as etching. Direct writing of patterns eliminates the need for employing photolithographic process [1]. A simplified process

* Tel.: +886-7-5252000x4239; fax: +886-7-5254299.
E-mail address: panct@mail.nsysu.edu.tw (C.T. Pan).

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to produce micro-patterns precisely and formation of metal selectively on polymer substrates is interesting.

Copper has been proposed as an interconnect metal for submicron integrated circuit technology. A simple reason is that copper is a better conductor than aluminum, copper will reduce the interconnect RC delay time [2]. Electroless plating has a low capital investment and operating costs and the relatively high throughput associated with it. It seems appropriate to explore the feasibility of using the process for forming conductors and filling via holes in microelectronic structures [3]. The essential advantages of electroless plating include low tool cost and low processing temperature as well as high quality deposits and good via-trench filling capability [4].

The electroless deposition of copper is one of the major process steps involved in the manufacture of electronic packages for the computer industry. The fabrication of high-performance multilayer boards via plated through-hole interconnections is based on electroless copper plating. Cu(EDTA)/formaldehyde-based systems have been used [5]. The activation or seeding of substrate is necessary to initiate copper deposition in the electroless process. Laser-assisted electroless deposition and laser-induced prenucleation have been used to create selective seeds [6]. The interface may exhibit little or no adhesion unless the polymer is pretreated prior to metal deposition [7]. The conventional methods for polymer pretreatment rely on plasma, wet-chemical or mechanical methods to produce either chemical or morphological changes in the surface, which strengthen the metal/polymer interfacial bond. The ablated surface of polyimide (PI) films can be modified by imagewise metallization [8,9] by excimer laser.

Surface potential of polyimide films was positively changed after XeCl laser irradiation. Coulombic attraction between ablated films and the changed colloid was essential for the surface activation process. The selective-area plating on a polymer film by laser ablation could become a fascinating process, because the electroless plating on polymer films is an indispensable process for high-density multichip interconnect substrates of copper conductors in particular use. Since PI and other high-performance polymer films are known to have hydrophobic surfaces with the result of poor wettability and poor polymer/polymer and polymer/substrate adhesion, surface modification of Kapton and other PI films is made by UV light and excimer laser exposure [10]. Post-treatment of the removal debris was washed away or partially dissolved in water, indicating that this debris was of fairly hydrophilic nature [11]. Under UV irradiation of polymers in air, the polymer surfaces undergo a chemical modification such as photo-oxidation, photo-induced hydrolysis, photo-degrading, and photo-induced cross-linking. In Kapton, poly phenyl quinoxaline (PPQ) and poly phthalazinone ether sulfone (PPES), either photo-induced hydrolysis or oxidation predominates in UV-exposure in air, resulting in reduced contact angle in both modes and great enhancement of the hydrophilicity of the polymer surfaces.

Hirsch et al. [1] used a scanned, focused argon ion laser to locally heat a thin polymer/palladium film applied to a PI-coated substrate, thereby reducing chemically bound palladium to palladium metal. Laser heating modifies the film making the irradiated film resistant to an etchant which strips unirradiated film. Thus, the laser-patterned catalytic film has been utilized to define electrolessly plated copper links between copper conductors on a PI substrate. The photo-induced deposition and patterning of a thin activator on a substrate surface followed the electroless metal deposition on the activated surface [12,13]. Laser-drilled holes were first subjected to a cleaning step, followed by copper flash metallization. The cleaning steps removed laser residue from the hole walls to ensure proper coverage and good adhesion of the metallization [14].

Excimer laser irradiation induces the organometallic compound photo-decomposition due to the weak bond between the metal ion and the organic radicals of the compound. Simultaneously, the UV-laser light may induce the cross-linking of the polymer. The metal clusters formed in the polymer matrix act as catalysts for subsequent electroless metal deposition [15]. Using excimer lamps to selectively decompose activation precursors generally involve the deposition of metal salt or organometallic coating [8,16]. The bath consists of a mixture of a copper ionic solution and a reducing agent, formaldehyde (HCHO). Deposition rate and resistivity of electroless Cu deposits increased slightly with increasing concentration of cupric sulfate and formaldehyde. Ethylene diaminetetra-acetic acid tetra sodium salt (EDTA) concentration does not significantly influence the deposition rate and resistivity. Temperature has the strongest effect on the deposition rate and resistivity. Deposition rate increases and resistivity decreases with increasing the deposition solution temperature [4]. The decomposition of palladium acetate films at low UV intensities of the Xe_2 excimer laser source was achieved by Esrom et al. [17,18]. The exposed substrate temperature lower than 20 °C, they concluded that the decomposition mechanism is mainly photolytical. The light acts directly on the molecules to decomposition of palladium acetate.

In this paper, the excimer laser to create lines/patterns in the substrate surface and then activate them with complex reactants is described. Patterns generated by the excimer laser result in the change of surface electric properties and activation selectively. The KrF excimer laser not only provides simple and fast machining patterns, but also uses its high energy density to drill holes and circuits directly. These advantages are beneficial for its applications to the electronic industry.

2. Experimental methods

The excimer laser (Lambda Physik COMPex–110 industrial type) with wavelength 248 nm, maximum pulse energy 400 mJ, maximum repetition rate 100 Hz, and pulse duration 25 ns was used to ablate specimens. The excimer laser machine mainly consists of mask stage with two axial freedom (x and y direction) and workpiece stage with four axial freedom (x, y, z and θ direction). The schematic drawing is illustrated in Fig. 1. Mask projection method to transfer patterns onto workpieces was applied in the study. The magnification from mask to workpiece is four times. Therefore, after excimer laser micromachining, pattern of one fourth in dimension can be made on substrate.

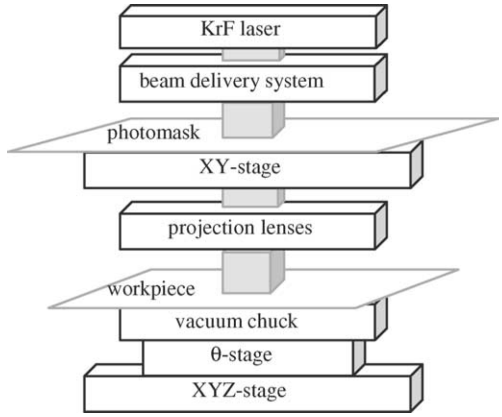

Fig. 1. Schematic drawing of the excimer laser machine.

All test patterns were designed on the quartz photomask. PI substrate with 100 μm in thickness was used as the substrate. PI substrates were ablated with the projection method using the excimer laser workstation. The designed patterns on mask were transferred on PI substrate.

Since PI film is an insulator, this experiment attempts to investigate the feasibility of conductive metal selectively onto PI substrate. These patterns can be used for further metallic formation via the procedures of the electroless copper plating. Various test patterns were designed and practiced in this experiment. Fig. 2 illustrates schematically the experimental procedures of electroless copper forming microstructures assisted by the excimer laser.

After PI samples were ablated by excimer laser, they were then immersed in distilled water or surfactant (SDS, 2 mM) for pretreatment. The samples were immersed in an activator for 1 min and cleaned with distilled water, nitric acid (3% in volume) and acetone. Finally, the samples were immersed in an electroless copper plating solution for 10 min at 25 °C, the pH value was 12 and the samples were cleaned with distilled water.

The electroless copper bath includes PTH-502A, 10% with H_2O and PTH-501B, 10% with H_2O purchased from Chaang Yuan Company in Taiwan. The main composition of electroless copper bath is as listed in Table 1. If the experiment is successful, copper will deposit on the ablated patterns.

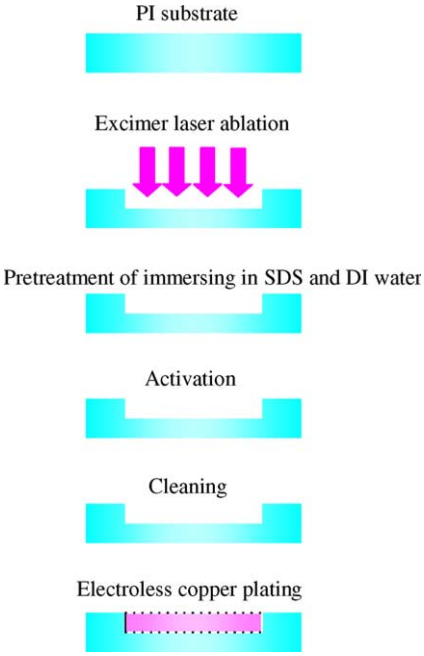

Fig. 2. Schematic process of excimer laser-induced electroless copper plating experiment.

Table 1
Main composition of electroless copper bath

Contents	
Copper sulfate	0.03 M
EDTA	0.06 M
Formaldehyde	0.045 M
Pyridine	5 ppm

Selective electroless plated copper on PI substrate were analyzed by optical microscope (OM) and with scanning electron microscope (SEM). Also, the resistance of copper lines was measured.

3. Results and discussion

3.1. Experiments of micro-coil patterns

PI specimens with 2.5×2.5 cm^2 in square area were ablated by 248 nm KrF excimer laser. Parameters of excimer laser ablation including laser fluence, shot number, and repetition rate were tested. Fig. 3(a) shows the ablation rate (depth per pulse, μm/pulse) versus fluence and Fig. 3(b) reveals that the ablation depth versus laser shot number. It makes sense that higher laser energy absorbed by PI material will result in higher ablation rate and ablation depth at a constant level of repetition rate. Fig. 3(c) shows the effect of laser repetition rate. It is worth noticing that when higher repetition rate is applied, constant ablation rate is achieved. It is due to laser induced plasma interrupting the incident laser beam onto the material surface.

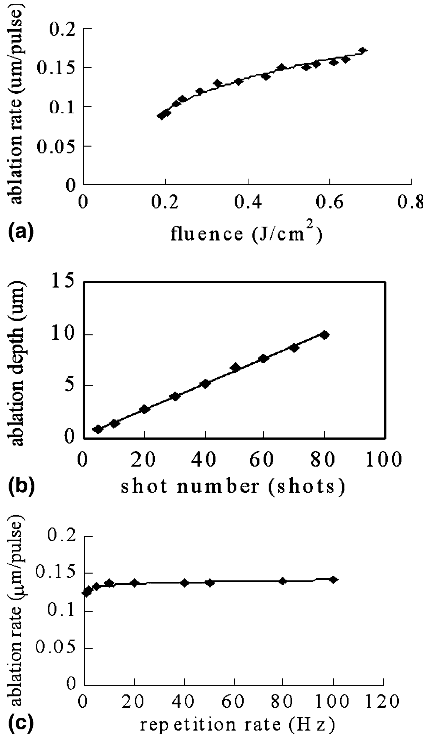

Fig. 3. Experimental result of excimer laser ablating PI substrate. (a) Fluence versus ablation rate (40 Hz, 50 shots). (b) Shot number versus ablation depth (40 Hz, 0.445 J/cm^2). (c) Repetition rate versus ablation rate (0.445 J/cm^2, 50 shots).

On the other hand, higher fluence will destroy Cr film on the conventional quartz mask during excimer laser projection ablation. Furthermore, higher fluence, shot number and repetition rate cause cumulative heat on PI substrate and degrade the quality of adjacent PI significantly. The experimental result is shown in Fig. 4(a)–(c). It reveals that when higher fluence, shot number, and

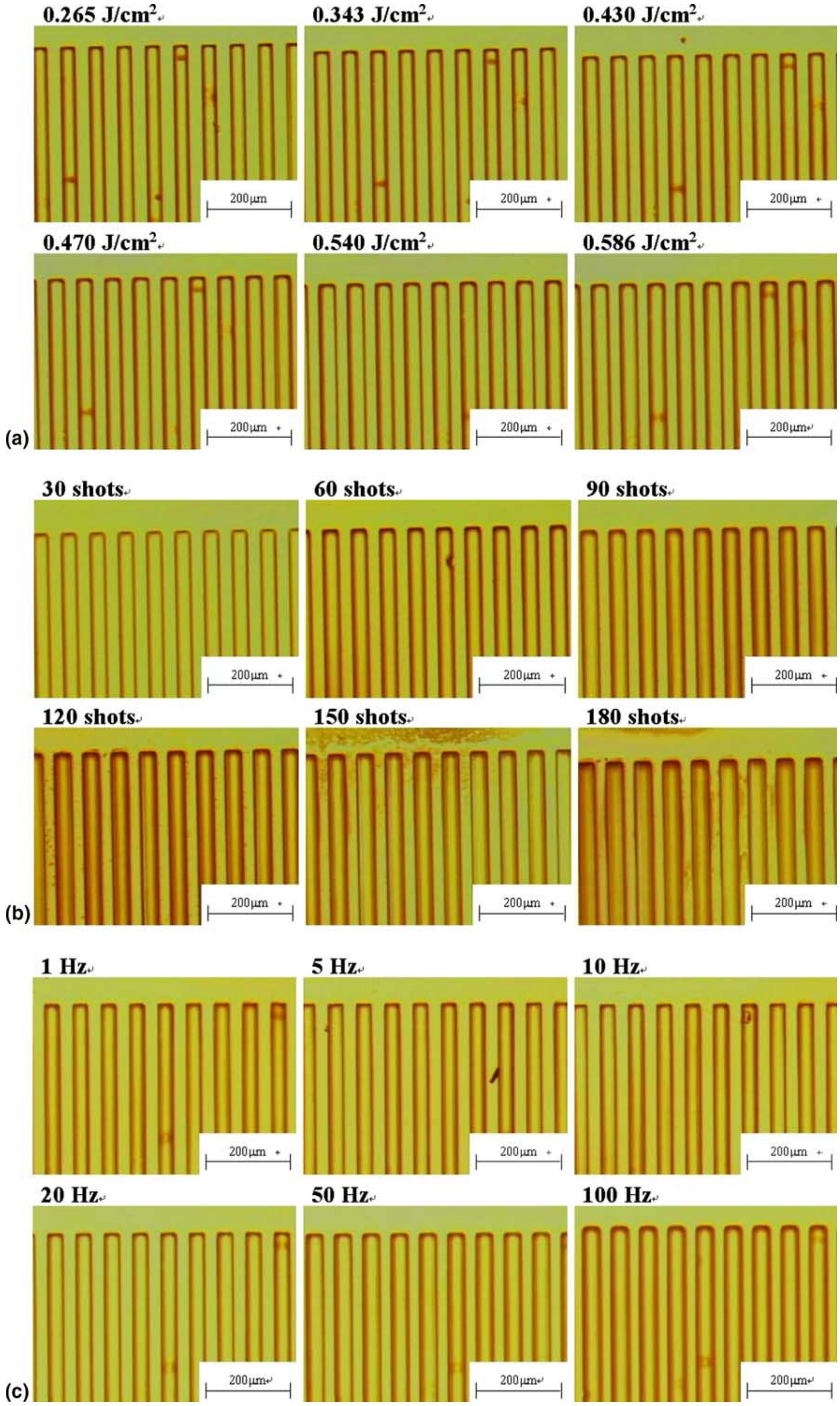

Fig. 4. Effect of excimer laser ablation parameters on PI substrate. (a) Repetition rate 40 Hz, 100 shots. (b) Fluence 0.54 J/cm^2, repetition rate 40 Hz. (c) Fluence 0.265 J/cm^2, 100 shots.

repetition rate were applied, heat affected zone around the ablated area will become more obvious. Besides, the laser scanning speed is proportional to the repetition rate. The tape angle of the PI is related to fluence and repetition rate. Therefore, based on the experimental results, a proper working parameter of the fluence, shot number and the repetition rate are selected; fluence 150 mJ/cm^2, shot number 150 shots and pulse repetition rate 40 Hz, respectively. An experimental result of ablated micro-coil pattern is shown in Fig. 5.

Various immersing time of activation were applied and cleaned by DI water, there was no distinctly selective electroless copper deposited after immersed in the electroless copper bath for 10 min. It could be attributed to strong attraction of colloidal SnPd on the substrate; the selected area could not completely be cleaned. Later, it was improved by using nitric acid (3% in volume) or acetone to clean it. But the non-ablated area still has deposited copper which means that the sample was cleaned incompletely. The correcting strategy then focused on the pretreatment of the sample before the excimer laser ablation. Since PI surface becomes positively charged after laser ablation, immersing workpiece in aqueous solution with negative charges turn them into neutral and non-ablated area with negative charges. The particles of colloidal SnPd are difficult to attach on workpiece surface with negative charges. The experimental results are listed in Table 2. The successful samples were marked “Yes” in the column of selective plating. Those samples marked “Partial” are incomplete selective plating. It can be found that the workpiece using SDS to pretreatment has a better result of selective electroless copper formation. Fig. 6 shows the better result of the large size workpiece for selective electroless copper

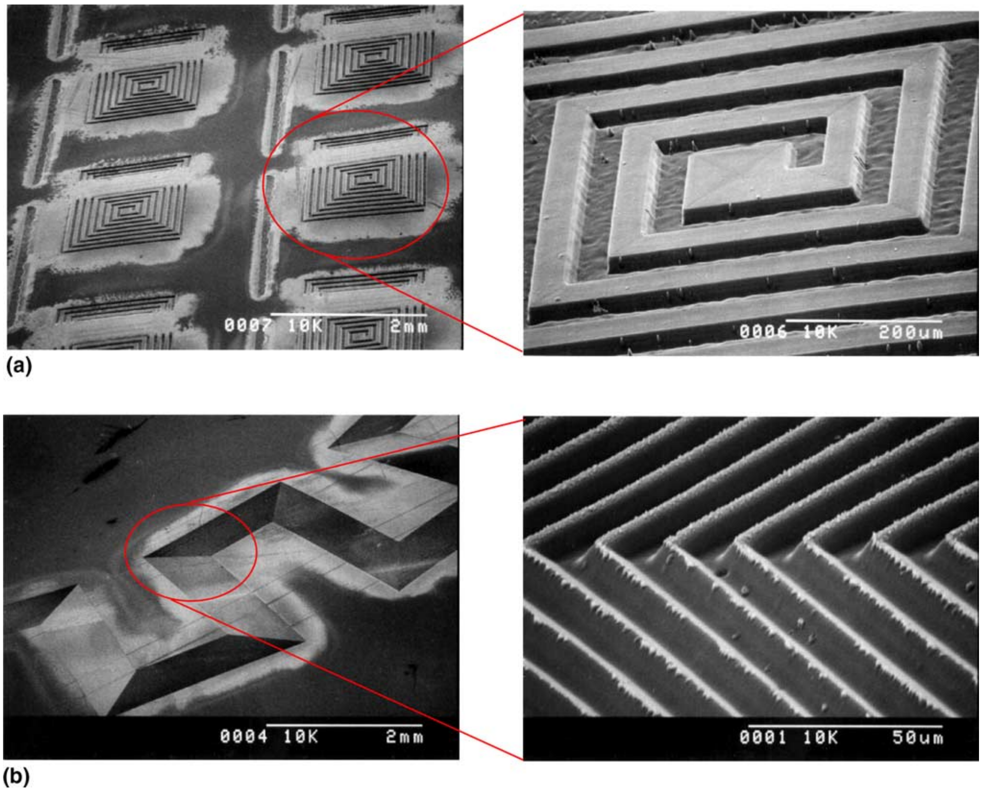

Fig. 5. Experimental result of micro-coil pattern ablated by excimer laser (150 mJ/cm^2, shot number 150 shots, pulse repetition rate 40 Hz). (a) Micro-coil patterns with 2.5×2.5 cm^2 in area. (b) Micro-coil patterns with 6×6 mm^2 in area.

Table 2
The experimental results of 2.5×2.5 cm^2 in square patterns used for selectively copper deposition

No.	Pretreatment	Activation	After activation	Selective plating	Reproducible
1	No treatment	1 min	No treatment	No	–*
2	No treatment	1 min	DI-stir for 5 min	No	–*
3	No treatment	1 min	HNO_3 (3%)-stir for 5 min	Partial	Low
4	No treatment	1 min	Acetone-cleaning	No	–*
5	DI-stir for 5 min	1 min	No treatment	No	–*
6	DI-stir for 5 min	1 min	DI-stir for 5 min	Partial	Low
7	DI-stir for 5 min	1 min	HNO3 (3%)-stir for 5 min	Partial	Low
8	DI-stir for 5 min	1 min	Acetone-cleaning	Partial	Low
9	SDS (2 mM)-stir for 5 min	1 min	No treatment	No	–*
10	SDS (2 mM)-stir for 5 min	1 min	DI-stir for 5 min	Partial	Low
11	SDS (2 mM)-stir for 5 min	1 min	HNO_3 (3%)-stir for 5 min	Yes	High
12	SDS (2 mM)-stir for 5 min	1 min	Acetone-cleaning	Yes	High

*: No repeated experimental result.

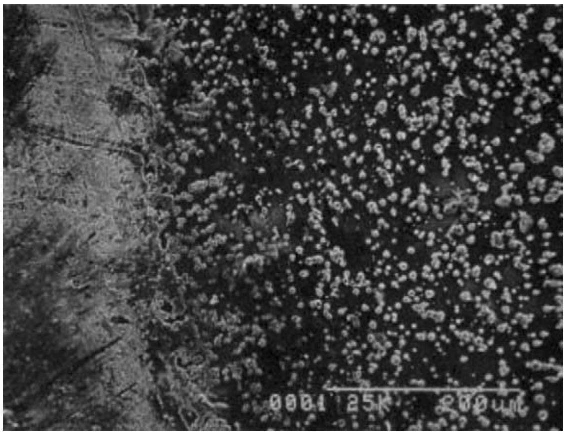

Fig. 6. The surface morphology of the large workpiece for selective electroless copper.

pattern. Left side of the figure is the ablated area and right side is the joint portion of ablated area. Since the laser diffraction resulted in low energy density deposited on non-ablated area, there is scattered copper deposited. However, pretreatment by SDS has proved the good result of selectively electroless copper formation in this experiment.

After completing the experiment with large workpieces for selective electroless plating copper, the experimental objective is towards the formation of copper micro-coil patterns. The ablation parameters of the excimer laser were same as those mentioned above; fluence 150 mJ/cm^2, shot number 150 shots and pulse repetition rate 40 Hz. Pretreatment by SDS, same as in previous experiment was applied; the experimental results are listed in Table 3. It is proved that the pretreatment by SDS showed better results. The pretreatment by DI water rinse showed ambiguous edges as shown in Fig. 7. But the samples rinsed by SDS before activation and cleaned by acetone and nitride acid (3% in volume) post-activation showed excellent

Table 3
The experimental results of micro-scale patterns for electroless copper plating

No.	Pretreatment	Activation	After activation	Selective plating	Reproducible
13	No treatment	1 min	DI-cleaning	No	–*
14	DI-stir for 5 min	1 min	DI-cleaning	No	–*
15	SDS (2 mM)-stir for 5 min	1 min	HNO_3(3%)-stir for 5 min	Yes	High
16	SDS (2 mM)-stir for 5 min	1 min	Acetone-cleaning	Yes	High

*: No repeated experimental result.

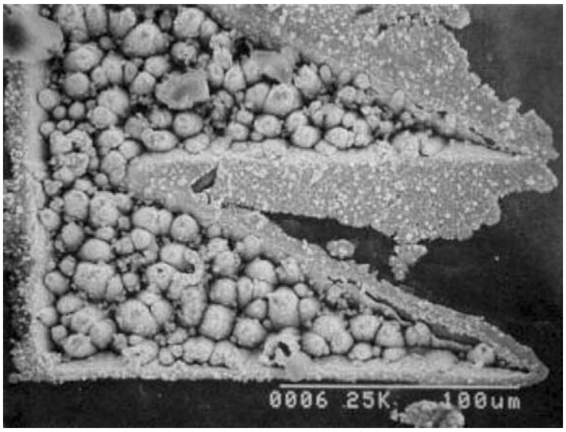

Fig. 7. An illustrated electroless copper pattern that is rinsed by DI water showing incomplete cleaning edges, the dark portion is the PI substrate.

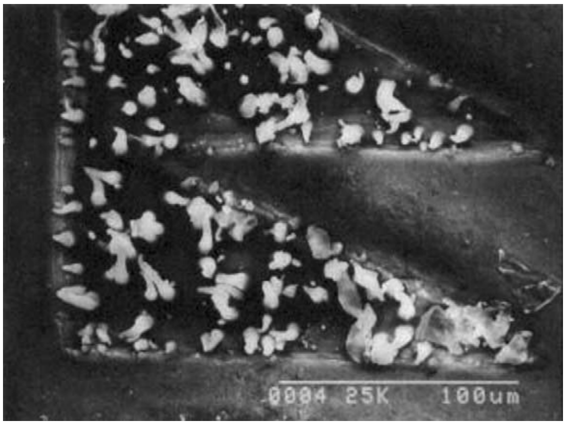

Fig. 8. The electroless copper nucleation grown in pattern that wetting by SDS before activation and acetone-cleaning after activation.

results. As shown in Fig. 8, the tiny nucleation of copper is grown in the ablated area. The sample has distinct copper patterns; copper only deposited on the ablated area as shown in Fig. 9.

3.2. Resistivity of the plated micro-coil

A Hewlett 4155A semiconductor parameter analyzer and probe station were used to measure the resistance of the micro-coil. The measurement result is shown in Fig. 10. Various input voltages were used to obtain output current. The resistance of the plated micro-coil is $5.0 \pm 0.5\ \Omega$. The formation of copper micro-coils assisted by excimer laser ablation and electroless copper plating has been done in this study, as shown in Fig. 11.

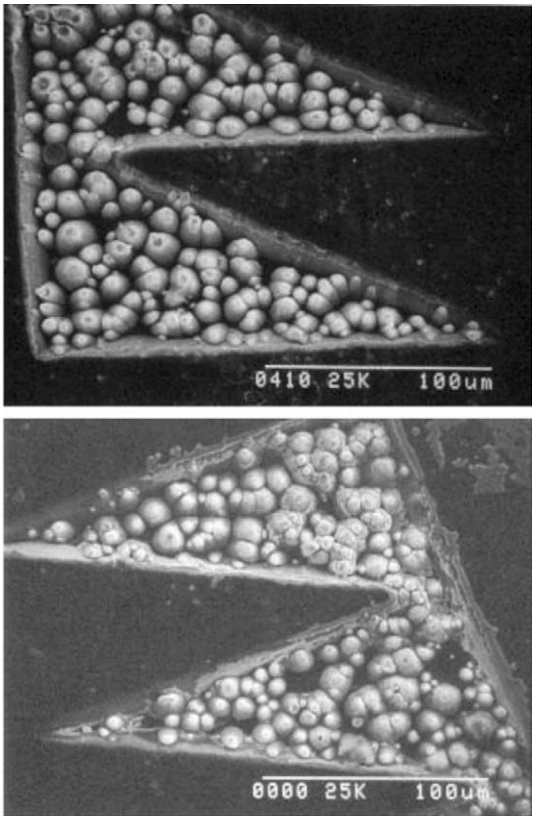

Fig. 9. The electroless copper pattern that wetting by SDS before activation and acetone-cleaning after activation.

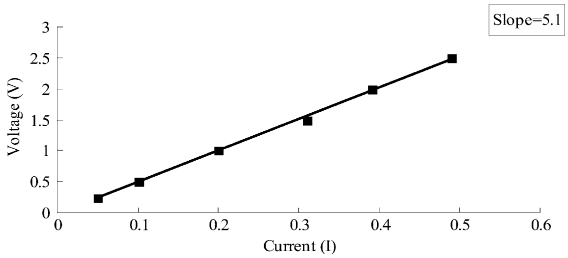

Fig. 10. Measurement of electric property for micro-coil by electroless copper plating.

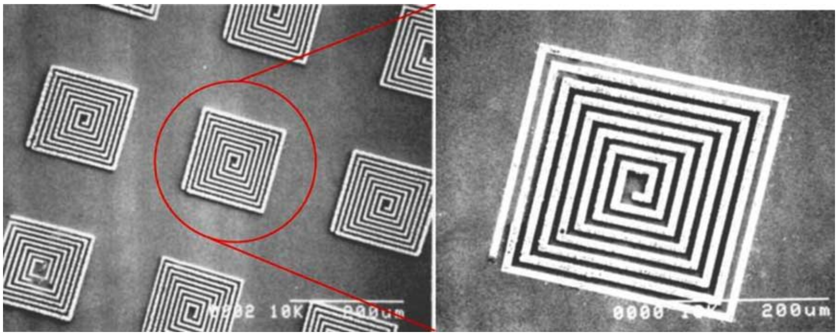

Fig. 11. A successful case of the micro-coil (linewidth 25 μm) on PI substrate.

4. Conclusions

As found in the experiments of selectively copper electroless plating in the PI substrate, the cleaning steps before activation and cleaning post-activation play an important role to establish good results. Such using SDS rinsing before activation and acetone-cleaning as well as diluted nitric acid post-activation generated good micro-patterns are proved by this study. DI water can change electric charges on PI surface before activation; two solutions selected here can enhance the surface clearness and result in excellent selective copper plating. Using SDS before activation can not only modify surface electric charges, but also improve the wettability of PI surface.

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