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# Higher-resolution selective metallization on alumina substrate by laser direct writing and electroless plating

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ABSTRACT

How to fabricate conductive patterns on ceramic boards with higher resolution is a challenge in the past years. The fabrication of copper patterns on alumina substrate by laser direct writing and electroless copper plating is a low cost and high efficiency method. Nevertheless, the lower resolution limits its further industrial applications in many fields. In this report, the mechanisms of laser direct writing and electroless copper plating were studied. The results indicated that as the decomposed products of precursor $PdCl_2$ have different chemical states respectively in laser-irradiated zone (LIZ) and laser-affected zone (LAZ). This phenomenon was utilized and a special chemical cleaning method with aqua regia solution was taken to selectively remove the metallic Pd in LAZ, while kept the PdO in LIZ as the only active seeds. As a result, the resolution of subsequent copper patterns was improved significantly. This technique has a great significance to develop the microelectronics devices.

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## 1. Introduction

Rapid fabrication of fine conductive patterns on insulators is of paramount importance for the increasing requirements of miniaturization and high integration of many microelectronic devices [1,2]. The potential applications include light-emitting diodes (LED), radio-frequency identification (RFID), labs on chips (LOC structures), semiconductors (contacts in solar cells) and so on [3–5].

Alumina ($Al_2O_3$) ceramic is a well-developed and commercialized ceramic material for electronic packaging due to its excellent thermal, electrical, and mechanical properties [6]. Copper is an attractive interconnect material because of its low electrical resistivity, high electromigration resistance, excellent weldability and high melting point. Higher electrical current densities can be imposed on Cu line with smaller cross-sectional area, and resistance-capacitance (RC) delay of the devices can also be reduced [7]. On the surface of ceramic substrates, Cu metallization can be achieved using many methods, for example, physical vapor deposition (PVD) processes including magnetron sputtering, ion plating, and vacuum evaporation [8,9]. The main shortcomings of these techniques include high equipment cost and low deposition rate. In addition, complex lithographic processes are needed for subsequent circuit micro-patterning [10].

In comparison, electroless Cu plating (ECP) is a cost-efficient production method for the metallization of ceramic substrates due to its low cost and fast deposition rate at low operation temperature [11]. It is well known that alumina ceramic cannot initiate ECP process itself because of lacking catalytically active centers (i.e., active seeds). Precious metals such as silver (Ag), palladium (Pd) and gold (Au) are usually used as the active seeds, while Pd is the optimal due to its excellent catalytic activity [12]. However, the conventional Pd-based catalyst is also unable to achieve selective activation [13]. Therefore, it is significant to develop an efficient method for rapid fabrication of fine Cu patterns on alumina ceramic.

Laser-assisted selective activation of insulators (LASAI) for consecutive ECP has received extensive concerns in the past years since it is a simple, flexible, and efficient process [14,15]. Up to now, many researches demonstrated the capacity of laser directly activating ceramics without using additional precursors, but the activation was only possible by using limited lasers that match the substrate materials [16,17]. In contrast, there is no special requirement for the materials with pre-coating precursors such as metallic compounds. The laser beam is used to locally decompose precursor films and embed the decomposed products into the substrates as the active seeds to catalyze the ECP. Much effort has been put to achieving fine Cu patterns. Chang et al. [18] developed an approach for patterning a thin palladium film by decomposing palladium acetate/acetone layer with a 532 nm Nd:YAG laser. The morphology of Cu lines near the edge was obviously looser than that in the center due to the fact that the precursors around the focal spot were

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incomplete decomposition. Chen et al. [19] reported the laser irradiation of silver nitrate films using a 266 nm Nd:YAG laser with a pulse repetition frequency of 10 Hz and a pulse width of 5 ns. The deposited Cu line width was ~35 μm, which was much wider than the focal spot diameter (20 μm). In order to eliminate the influence of heat diffusion, Liao et al. [20] proposed the decomposition of silver nitrate thin films using a 800 nm Ti:sapphire laser with a pulse repetition frequency of 1 kHz and a pulse width of 40 fs. Although femtosecond laser has the potential to decrease the influence of heat diffusion, obvious lateral growth of Cu on both sides of the ablated groove was still observed, which led to the increase of line-width.

In general, rapid fabrication of Cu patterns could be achieved by current LASAI techniques. However, there are still numerous issues to settle, (1) the widths of the plated Cu lines are obviously wider than the focal spot diameter, and (2) the densities of the Cu lines at the edges are lower than that at the central parts. In order to improve the line/space resolution further, different methods have been taken, such as shorter-wavelength laser [19], ultrashort-pulse laser [15], or the optimization of optical systems parameters [21]. However, attentions are rarely turned to the mechanisms of laser direct writing and the following electroless plating.

In this paper, laser direct writing was combined with ECP to realize selective Cu deposition on alumina ceramic substrate. Detailed surface analyses were carried out to investigate the decomposition mechanism of precursor palladium chloride ($PdCl_2$) in different zones. Then, an effective method was proposed to decrease the widths of Cu lines and improve the densities at the edges of the lines, which significantly improve the resolution of circuit patterns.

## 2. Experimental details

### 2.1. Formation of PdCl2 precursor films

At room temperature, commercial 96 wt.% alumina ceramic boards (10 mm × 10 mm × 1 mm) were ultrasonically rinsed in alcohol for 10 min and in deionized water for 5 min, respectively, and then immersed in a 1.0 g/L $PdCl_2$ aqueous solution for 5 min. Next, the boards were taken out and dried. Thus, thin films of $PdCl_2$ were evenly distributed on their surface.

### 2.2. Generation of active seeds

The generation of active seeds was carried on using a home-made laser direct writing system. The system include, (1) a 355 nm DPSS-type Q-switched laser with a pulse width of ~40 ns, a pulse repetition frequency of 100 kHz, and an average power of 3.2 W, (2) a 2D galvanometer scanner, and (3) a micrometer-precision computer-controlled stage. During laser irradiation, the samples were fixed on the stage, and the process was carried out in air and at room temperature.

### 2.3. Ultrasonic rinse

After laser irradiation, some of the samples were ultrasonically rinsed in deionized water to remove un-irradiated $PdCl_2$ films. For comparison, a unique chemical cleaning in aqua regia solution was used for other samples.

### 2.4. Electroless Cu plating

Next, the samples were immersed into a commercial electroless Cu plating bath with a deposition temperature of 313 K. After that, they were rinsed in deionized water. Thus, the selective metallization of the alumina ceramic was achieved.

### 2.5. Measurements and characterization

A Quanta 200 scanning electron microscope (SEM) was used for microstructures observation. The chemical states of active seeds were analyzed by X-ray photoelectron spectroscopy (XPS, VG Multilab2000X).

## 3. Results and discussion

### 3.1. $PdCl_2$ precursor films on the surfaces

Fig. 1(a) and (b) shows the SEM images of the original ceramic surface. After coating with $PdCl_2$ film, a large quantity of nanometer-scale particles appeared on the surface and in the boundary of original ceramic grains, as shown in Fig. 1(c) and 1(d). Whereas, their adsorption to the surface was weak, and they could be easily removed by ultrasonic rinse in deionized water.

### 3.2. Activation of ceramic surface

When the samples were irradiated by laser beam with the fluence of 19.3 J/cm$^2$ and the scanning speed of 50 mm/s, a groove of ~15 μm in width and ~14 μm in depth was formed, as shown in Fig. 2(a). The laser irradiated zone could be classified into two zones, i.e. laser-irradiated zone (LIZ) and laser-affected zone (LAZ). Then the sample was ultrasonically rinsed in deionized water, and the high magnification morphologies of LIZ and LAZ are shown in Fig. 2(b) and (c), respectively, in which no obvious particles are observed within the groove (i.e. LIZ). However, there are still a lot of small residuals on both sides of the groove (i.e., LAZ) after the conventional cleaning process. The small residuals are suggested to be the main reason that broadens the active zone for ECP.

Fig. 3 shows the schematic diagram of the laser direct writing process, from which it could be seen that precursor-coated ceramic was affected by two effects under laser irradiation. First, the interaction effect of high energy density laser and substrate materials, which led to the ablation and evaporation of the majority of the precursor. The residuals were mixed and immersed in the LIZ as the active seeds. At the same time, the precursor in the LAZ was also decomposed because of heat diffusion and light scattering. Thus, both zones would have the catalytic activity for electroless plating, which caused the width of Cu line wider than focal spot diameter.

### 3.3. Analysis of laser-induced decomposition of $PdCl_2$

It is significant to characterize the element composition and chemical state of the active seeds in LIZ and LAZ by XPS. The minimum analysis width by XPS is larger than that of a single ablated groove in this experiment. Thus, several parallel laser scanning lines overlapped exactly with the line interval of 15 μm were especially fabricated to obtain the pure LIZ, while the mixture area of LIZ and LAZ was acquired with the scanning line interval of 30 μm.

Fig. 4 showed the Pd3d and Cl2p XPS spectra of the precursor-coated ceramic surface before (a) and after (b and c) laser irradiation. The spectra were fitted with a Shirley background and d type peaks within XPSPEAK 41. From Fig. 4(a), it could be seen that the Pd3d spectrum presented a doublet corresponding to $Pd3d_{5/2}$ (337.4 eV) and $Pd3d_{3/2}$ (342.7 eV) with a binding energy difference of about 5.3 eV [22,23]. Here, the chemical state of the element Pd was attributed to $Pd^{2+}$ in $PdCl_2$ compound [24]. Fig. 4(b) showed the Pd3d spectrum of the mixture area of the LIZ and LAZ. The Pd3d peaks shifted toward lower binding energies and two obvious asymmetric peaks appeared. The peaks could be fitted with two spin-orbit doublets with the first peak located at 334.9 eV and the second peak located at 336.9 eV. This suggested that the element

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