Laser Sintering of Metal Nanoparticle Film  
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Laser sintering of Au nanoparticles on a Cu substrate was studied toward an alternative to gold plating. The laser sintering by laser direct writing method required much higher laser power density in comparison with that on a glass substrate. The laser-induced heat accumulation method is proposed as a new laser sintering method which can be applied to a metal substrate with a high thermal diffusion coefficient such as a Cu substrate. In the sintering process, the dissipation through the Cu with a high thermal diffusion coefficient was reduced by using a thermally isolated Cu substrate, where the heat accumulation in the Cu micropattern was caused sintering of whole area by laser pulse irradiation at a small spot without laser beam scanning. The SIMS profile showed that the diffusion of the Cu atom through the gold layer was reduced remarkably by the laser sintering compared to the conventional heat treatment. The reduction of Cu diffusion into gold layer is due to the extremely short sintering time of the laser-induced heat accumulation method.

Keyword: laser sintering, laser direct writing, gold plating, metal nanoparticle ink, copper substrate, copper diffusion, alternative to gold plating.

1. Introduction

Recently an alternative to plating is required to reduce the environmental impact. Traditional precious metal plating such as gold plating has not been considered a polluter to the environment, but now even this area has also come under scrutiny. More environmentally friendly systems where the developments in eliminating potentially hazardous chemicals from both the plating bath the deposition process are desired [1, 2]. Ink jet printing technique using metal nanoparticle ink is one of the candidates for the traditional plating technique. The additional advantage of such a printing process is to save the precious metal resource due to the spatially selective deposition. In the fields of the electrical connectors and printed circuit boards, gold plating is widely used to provide a corrosion-resistant electrically conductive layer on copper. However, the gold coating on copper surface by inkjet printing has a difficult problem to solve. The copper atom easily diffuses to the surface through the gold layer and to form an oxide layer at the surface during the thermal sintering of gold nanoparticles.

The diffusion of Cu atom in Au layer is common problem in the direct gold on copper plating [3, 4]. The nickel plating on the copper substrate as a barrier metal is usually employed in traditional precious metal plating. However, it increases the number of processing steps, cost, and environmental impact. In the case of the gold coating using Au nanoparticle ink, the nickel barrier is often not enough because of a long sintering time. The surface of the Au nanoparticle is modified by organic groups and stabilized in an organic solution. The thermal decomposition of the organic moiety in air and the fusion of Au nanoparticle are necessary to form a continu-
ous Au layer, which also enhances the Cu atom diffusion from the Cu substrate to Au layer and the oxidation of the Cu atom at the surface of the Au layer during the heat treatment in air. The sintering temperature of Au nanoparticle ink is generally around 250 °C and the sintering time is longer than 30 min when the heat treatment was carried out using a conventional electric furnace. To reduce the diffusion of Cu atom through Au layer, a rapid sintering process is necessary. In previous papers, we have reported the laser sintering of metal nanoparticle dispersed film and the laser direct writing using the metal nanoparticle ink [5-10]. In the laser processing, plasmon resonance band of metal nanoparticle is excited by laser beam, which induces the fast and efficient conversion of the light energy to the thermal energy in a metal nanoparticle. The laser irradiated metal nanoparticle acts as a nano-heater and then the thermal decomposition of organic moiety and the fusion of metal nanoparticle are induced with high efficiency [6]. In this paper, the laser sintering of Au nanoparticles on a Cu substrate toward an alternative to the gold plating is reported.

2. Experimental

2.1. Materials

The Au nanoparticle ink (NPG-J) was purchased from HARIMA CHEMICALS. The 56.7 wt% solution of the NPG-J was spin coated on a Cu plating polyimide substrate at 1500 rpm for 30 sec. The sintering conditions recommended by HARIMA CHEMICALS are at 250 °C for 1 hr in the case of the heat treatment using an electric furnace.

2.2. Laser sintering

The laser beam from a CW DPSS laser (CNI, 532 nm, 1 W) was focused through an objective lens on the metal nanoparticle coated Cu substrate. In the laser direct writing experiments, the laser beam was scanned by a computer-controlled controlled xyz-stage [5, 6]. In the laser-induced heat accumulation experiments, the duration of the CW laser beam (532 nm, 1 W) was controlled by an electromagnetic shutter and the controller (Suruga Seiki, F77). The pulsed laser beam was irradiated on a Au nanoparticle coated Cu micropattern under various conditions changing the duration and laser shot number.

2.3. Measurements

The depth profile analysis of Au nanoparticle coated Cu substrate after sintering was carried out by SIMS (secondary ion mass spectrometry) using PHI-6600 with quadrupole-type mass spectrometer. An incident beam of 5.0 keV Cs+ ions was irradiated to the sample surface, and positive secondary ions were detected.

3. Results and Discussion

3.1 Laser sintering by laser direct writing method

In the previous papers, we have reported the formation of submicron micro-writing by laser direct writing using Ag nanoparticle ink [5, 6]. The laser sintering process by laser direct writing method is schematically illustrated in Figure 1. A Au-particle ink was spin coated on a Cu substrate and then laser beam was focused and scanned on the Au-nanoparticle dispersed precursor film. The Au pattern on the Cu substrate was obtained by removing the unirradiated area using toluene as a solubilizer. This method needs many times scan of laser beam when a rather large-area sintering is required.

![Figure 1. Laser sintering of Au-nanoparticle film on a Cu substrate by laser direct writing method.](image)

Figure 2 shows the Au micropattern by laser direct writing using Au nanoparticle-coated Cu plating polyimide substrate, where the 532 nm laser beam from CW DPSS laser (1W) was focused on the substrate through objective lens 20x and scanned by PC-controlled xyz stage with 5 µm interval. A
continuous gold micropattern can be prepared by laser direct writing as shown Figure 2.

Figure 2. Au micropattern by laser direct writing for an Au nanoparticle-coated Cu plating polyimide substrate. Laser beam: 532 nm of CW DPSS laser 1 W, objective: 20x, scanning area: 320 x 320 μm, interval: 5 μm, scan rate: 5000 μm/s; developer after laser irradiation: toluene.

The Cross-sectional TEM images of the laser-sintered Au layer on a Cu plating polyimide substrate are shown in Figure 3. The TEM image of the Au layer shows that Au nanoparticles and aggregates are completely disappeared and a Au crystalline phase is formed by laser sintering. The cross section of Au/Cu interface shows the spherical crystal-line phase and the growth of the larger crystalline phase toward the surface. At the Au surface, grains with the size of several nanometers were observed.

In the case of a glass substrate, the thermal energy induced by laser irradiation to metal nanoparticle is almost confined in the metal nanoparticle and then efficient sintering is caused as reported in previous papers [5, 6]. However, the laser sintering of Au nanoparticles on a metal substrate has the heat-loss through the substrate with a high thermal diffusion coefficient. The laser sintering of the Au nanoparticle on a Cu substrate needed the laser power density more than 10 MW/cm², whereas the laser sintering of the Ag nanoparticle on a glass substrate is caused by the laser power density lower than 10 kW/cm². The power density for the laser sintering on a Cu substrate is 1000 times larger than that on a glass substrate. Because the laser beam size on the irradiated film is smaller than several micrometers, the heat-loss by the thermal diffusion through a Cu substrate seriously reduces the efficiency of sintering.

3.2 Laser sintering by laser induced heat accumulation method

The formation of micropatterns of Au on the metal substrate with a high thermal diffusion coefficient such as a Cu substrate needs a new concept which enables to improve the sintering efficiency of Au nanoparticles with making good use of the thermal diffusion. The sintering by laser-induced heat accumulation method as shown in Figure 4 is proposed in this study.

Figure 4. Laser sintering of Au-nanoparticle film on a Cu substrate by laser direct writing method.

In the sintering process, the dissipation through the Cu with a high thermal diffusion coefficient was reduced by using a thermally isolated Cu micropattern substrate. A Au-particle ink was spin coated on the mi-
cropatterned Cu plating polyimide substrate and then laser pulse was irradiated on the Cu micropattern without scanning, where the heat accumulation in the Cu micropattern enhanced the laser sintering. Such laser-induced heat accumulation method has an additional advantage due to the thermal diffusion in a Cu micropattern, which causes the laser sintering of the whole area of the Cu micropattern by one spot irradiation.

Figure 5. Confocal microscope images of Cu micropattern (a) and the Au nanoparticle-coated Cu micropattern (b).

In laser-induced heat accumulation method, a Cu micropattern as shown in Figure 5a was used, where a circular Cu micropattern with a diameter of 130 µm is isolated by etching on Cu plating polyimide substrate. A Cu plating polyimide substrate for printed wiring board (PWB) is consisting of a thin Cu layer on a polyimide film. In the actual use for electronic devices, the Cu plating layer of PWB is micropatterned by etching. There is a possibility that the heat accumulation in a Cu micropattern can be applicable to enhance the laser sintering. The Cu micropattern also isolated even after spin-coating of an Au nanoparticle ink as shown in Figure 5b. The thickness of the Au nanoparticle dispersed film on the Cu substrate was 3.25 µm after post baking at 110 °C for 2 min.

The laser sintering of the thermally isolated Cu micropattern was remarkably influenced by the duration of laser beam. Figure 6 shows the influences of the laser duration on the morphological changes of the Au nanoparticle ink-coated Cu micropattern. The laser duration of a CW DPSS laser (532 nm, 600 mW) was controlled by an electromagnetic shutter. When the laser energy is excess with the longer duration, the damage of a Cu micropattern was observed as shown in Figures 6a, 6b, 6c, and 6d, where Cu micropattern was sintered by a one-shot laser-pulse irradiation under the durations of 500, 250, 125, and 33 ms, respectively. The laser beam with a spot size of ca. 2 µm was irradiated at the center of the Cu micropattern with a diameter of 130 µm. Although the spot size of the laser beam is much smaller than the diameter of Cu micropattern, the damage is caused in the whole area. With decreasing the duration, the damage of the Cu micropattern is reduced as shown in Figure 6e and 6f, where the durations are 17 and 8 ms, respectively.

Figure 6. Influences of the laser duration on the morphological changes of the Au nanoparticle ink-coated Cu micropattern by a one-shot laser pulse irradiation. (a) 500 ms, (b) 250 ms, (c) 125 ms, (d) 33 ms, (e) 17 ms, (f) 8 ms, objective lens; 20x, Cu micropattern size; 130 µm, laser spot size on a Cu micropattern; ca. 2 µm.

Figure 7 shows the influences of the laser shot number on the morphological changes of the Au nanoparticle ink-coated Cu micropattern. With increasing the laser shot number, the damage of the Cu micropattern became remarkable. The laser sintering behavior depends on the specific heat of the Au nanoparticle coated Cu micropattern and the
fluence of the laser beam.

![Image](image-url)

Figure 7. Influence of the laser shot number on the morphological changes of the Au nanoparticle ink-coated Cu micropattern. Cu micropattern size: 130 μm, laser shot number: (a) 1, (b) 3, (c) 4, and (d) 5 under the laser pulse duration of 8 ms.

3.3 Depth profile analysis of laser sintered film by laser induced heat accumulation method

The diffusion phenomena of Cu atom into Au layer was compared between the conventional sintering and laser sintering by using SIMS (secondary ion mass spectrometry) depth profile analysis.

Figure 8 shows SIMS depth profiles of Au nanoparticle-coated Cu micropattern after heat treatment by an electric furnace (250 °C, 1 hr in air). The SIMS depth profile analysis gives the element profile in thickness direction of a film by monitoring the secondary ion count rate of selected elements as a function of sputter time. In Figure 8, the element profile at sputter time zero, that is, at the film surface shows that the ratio of Au to Cu is extremely low, which means the remarkable Cu diffusion from the Cu substrate to the surface of Au nanoparticle-coated film. Judging from the high intensity of oxygen, the Cu exists as copper oxide at the surface. The depth profile of Cu shows the remarkable increase around sputter time 2000 s, which suggests that the sputtering reaches the surface of the Cu substrate. Therefore, the region from sputtering time 0 to 2000 s is assigned to the Au nanoparticle-coated layer. The count rate of Au becomes higher around sputter time 1000 s, that is, at the middle depth of the Au nanoparticle coated layer. In the case of the sintering of Au nanoparticle ink-coated Cu substrate by a conventional electric furnace, the diffusion of Cu atom from the Cu substrate to gold layer is serious and the surface of sintered film is covered by Cu and the oxide.

![Image](image-url)

Figure 8. SIMS depth profiles of Au nanoparticle-coated Cu micropattern after heat treatment by an electric furnace (250 °C, 1 hr in air.)

The optical micrograph of the Au nanoparticle-coated Cu micropattern after laser sintering by laser-induced heat accumulation method under a one of optimized conditions and the SIMS depth profiles are shown in Figure 9, where the duration and irradiation time are 1000 ms and 2, respectively. The SIMS profile suggests that the diffusion of the Cu atom through the gold layer can be reduced remarkably by the laser sintering compared to the conventional heat treatment. The element profiles at sputter time zero, that is, at the film surface show the secondary ion count rate of Au is much higher than other elements, and the count of Cu is negligible at the surface. The count of Cu increases around 1000 s and then becomes constant at longer sputtering times, which means that the region of sputtering time from 0 to 1000 s corresponds to the gold layer and the region of sputtering time longer than 1000 s is assigned to Cu substrate. The count of Au also decreased around 1000 s because the sputtering reaches to the surface of Cu substrate.

With decreasing the duration of laser pulse, the secondary ion count rate of oxygen was
lowered as shown in Figure 10, where the duration and irradiation time were 125 ms and 5, respectively. These results suggest the possibility of the laser sintering method using Au nanoparticle ink as an alternative to gold plating. Such reduction of Cu diffusion into gold layer during the sintering is caused by the extremely shorter time of laser sintering process compared to the conventional sintering using an electric furnace.

4. Conclusion
Laser sintering of Au nanoparticles on a Cu substrate was studied toward an alternative to gold plating. Two kinds of laser sintering methods were studied. One is the sintering by laser direct writing, where an Au nanoparticle ink was spin coated on a Cu substrate and then laser beam was focused and scanned on the Au-nanoparticle dispersed precursor film. The laser sintering of the Au nanoparticle on a Cu substrate with a high thermal diffusion coefficient required much higher laser power density in comparison with that on a glass substrate. The formation of a gold micropatterns on the metal substrate with a high thermal diffusion coefficient such as a Cu substrate requires a new concept which enables to improve the sintering efficiency of Au nanoparticles with making good use of the thermal diffusion. In this study, the sintering by laser-induced heat accumulation method was proposed as a new laser sintering method. In the sintering process, the dissipation through the Cu with a high thermal diffusion coefficient is reduced by using a thermally isolated micropatterned Cu substrate, where heat accumulation in the Cu micropattern is caused the sintering of whole area by laser pulse irradiation at a small spot without laser beam scanning. The SIMS profile showed that the diffusion of the Cu atom through the gold layer was reduced remarkably by the laser sintering compared to the conventional heat treatment. The reduction of Cu diffusion into gold layer during the sintering is due to the extremely short sintering time of laser sintering method.

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