Microelectrode fabrication by laser direct curing of tiny nanoparticle self-generated from organometallic ink

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Abstract: In this paper, we present a new laser direct patterning method that selectively cures nanoparticles self-generated from organometallic ink by proper thermal decomposition. This approach has several advantages in the curing rate, resolution and pattern quality compared with the conventional nanoparticle ink based direct laser curing method. It was found that a laser wavelength which is more weakly absorbed by the nanoparticles could produce a more stable and homogeneous curing condition. Finally, arbitrary shaped silver electrodes with narrow width and uniform profile could be achieved on a polymer substrate at a high curing rate of 25 mm/s. This process can be applied for flexible electronics fabrications on heat sensitive polymer substrates.

OCIS codes: (140.3390) Laser material processing; (160.4236) Nanomaterials; (160.4890) Organic materials; (310.3840) Materials and process characteristics; (310.1860) Deposition and fabrication.

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1. Introduction

As an alternative to the conventional microfabrication approach, various laser direct curing (LDC) processes of metal nanoparticles (NPs) ink have been studied to fabricate microelectrodes [1–8]. LDC methods have fascinating advantages over the conventional photolithograph and vacuum deposition based microfabrication approaches. The advantages include broad class of substrate material choice including heat sensitive polymer material, flexibility in design change due to maskless nature of the process, environmentally friendly process without using any corrosive etchant, simple and fast process without using any vacuum deposition step, and high degree of flexibility to control the resolution and size of the micro patterns [9,10]. Previous LDC researches use only chemically synthesized metal NPs ink for laser process. However, metal NPs ink poses several limitations to the LDC process because NPs ink demands a complex synthesis processes to avoid oxidation and to obtain a uniform and narrow NP size distribution. In the process aspect, NPs ink based LDC process has limited curing rate (1 mm/s) because it need a relatively high energy and longer process time to agglomerate conventional NPs ink [1,2]. Moreover, the cured patterns are wider than the laser spot size due to the large heat diffusion caused by the high thermal conductivity of the metal NPs and the high incident laser energy [1,3]. Additionally, a crater-like non-uniform profile that may cause shorting between multilayer commonly arises due to the marangoni flow caused by the surface tension gradient during LDC [2,4–6,8]. Also, the poor surface roughness (~30 nm) cannot produce high quality conductor compared with vacuum deposited layers [5,6].

In this paper, we present a new LDC that is based on organometallic ink to improve the previous NPs ink based LDC approaches. The laser direct curing of tiny NPs of 2~3 nm self-generated from an organometallic ink could improve the curing rate, resolution and pattern quality compared with the conventional methods using metal NPs inks.

2. Self-generation of tiny nanoparticles

An organometallic silver (Ag) ink (Inktec Co., TEC-CO-010, 10% weight) was utilized as a precursor to generate tiny NPs during the processing. Silver/organic complexes, organometallic compounds, are produced by chemical reaction of silver oxide (Ag_2O) and ammonium carbamates ($H_2NCO_2NH_4$). The ammonium carbamates, chemical derivatives, are prepared by reacting dry carbon dioxide with aliphatic amines. The silver/organic complexes dissolve in isopropyl alcohol (C_3H_8O) used as solvent in the weight ratio of 4:6. The silver/organic complexes ink undergoes evaporation of the solvents by heating. And the Ag ions thermally decomposed from the residue silver/organic complexes are reduced to form Ag NPs. Finally, the Ag NPs are thermally grown and aggregated by continuous heating [11]. These conversion processes occur almost concurrently. The organometallic ink is basically transparent and cannot be directly applied to LDC process development due to the absence of solid particles to directly absorb laser energy. However, a short thermal pre-baking below the sintering temperature, Ag NPs start to nucleate uniformly without agglomeration. Once the NPs are formed, a focused laser was irradiated to melt and transform the NPs into the continuous metal. Only the NPs where the laser was scanned will be molten and form

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continuous metal and other NPs will be simply washed away by organic solvent to leave metal patterns, as shown in Fig. 1(a), (b).

The thickness and the optical absorption of the organometallic ink are important parameters for the process optimization. The transient change of those values of the organometallic ink was measured at various pre-baking time after spin-coating at 1000 rpm on a soda-lime glass (Fig. 1(c)). A baking temperature of 100 °C was carefully determined to acquire a uniform thickness and to avoid the agglomeration of NPs in preliminary experiments since the excessive increase of the baking temperature causes the spatial gradient of the pre-baked ink thickness. As shown in Fig. 1(c), the thickness converged to approximately 0.33 μm after 60 sec pre-baking while the optical absorption increased linearly with the pre-baking time. The optical absorption increase signifies the generation of nanoparticles from the organometallic ink. The statistical analysis on the NP size distribution after pre-baking for 90 sec was conducted by a transmission electron microscope (TEM) images as shown in Fig. 1(d). 88% of Ag NPs have a diameter below 3 nm and the average particle size is 2.54 nm with the standard deviation of 0.67 nm. It is clear that the uniform Ag NPs of 2~3 nm were self-generated inside the residual silver/organic complexes. As expected, it can be estimated that such tiny NPs were generated by the mild decomposition of the complexes and mild growth of the Ag NPs.

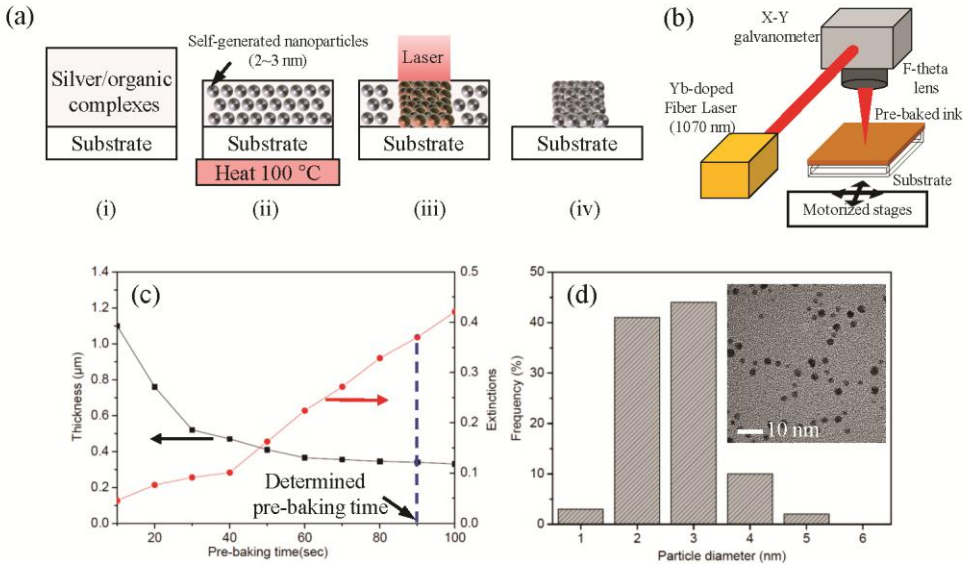

Fig. 1. (a) Schematics of the process steps: (i) spincoating of the organometallic ink at 1000 rpm on a soda-lime glass, (ii) pre-baking on a hotplate at 100 °C for 90 sec to create NPs, (iii) laser irradiation to induce local agglomeration and fusion of NPs into continuous metal microstructure, (iv) washing out the unexposed leftover ink. (b) Experiment setup (c) Variations of the thickness and absorbance (at 532 nm) of coated organometallic ink with the pre-baking time. (d) Statistical analysis of self-generated Ag NP size distribution and the corresponding TEM image after pre-baking for 90 sec.

When a laser is irradiated locally on the self-generated NPs from the pre-baking, as shown in Fig. 1(a), the generation and growth rate of these NPs will be accelerated dramatically to produce larger NPs due to the enhanced absorption by the NPs compared with organometallic complex. Furthermore, the laser irradiation will induce the agglomeration and fusion of the NPs into continuous metal patterns. This process happens at low temperature (~150 °C for 2~3 nm NPs) due to the thermodynamic size effect [12] and happens only at the parts where the laser was scanned. The parts where the laser was not scanned can be easily washed away to leave laser treated metal microstructures. Therefore, it is implied that current

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organometallic ink based LDC method can obtain similar effects with the previous tiny metal NP based LDC approaches [7].

3. Interaction of laser and self generated nanoparticles

The relationship between the pre-baking time and the curing rate can be described using the following equation based on the previous NP based LDC approach [13]:

$$V = \alpha(t)\frac{P}{EWT(t)} \tag{1}$$

where E is the absorbed laser energy, P is the input power density, V is the curing rate, W is the pattern width, $\alpha(t)$ is the absorption coefficient, $T(t)$ is the thickness, and t is the pre-baking time. Figure 1(c) and Eq. (1) show the curing rate can be increased with the longer pre-baking time due to the thickness reduction and the optical absorption increase. However, too long pre-baking cannot be applied because the organometallic ink after 100 sec pre-baking was not able to be removed by washing. 90 sec pre-baking time was found to be optimum for current process.

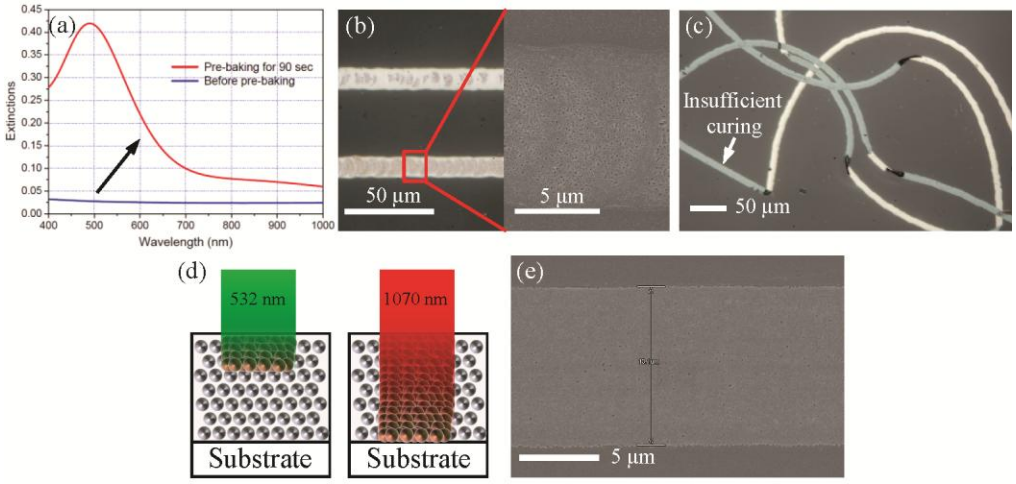

Fig. 2. (a) Absorption spectrum of the organometallic ink before and after pre-baking (90 sec). (b) Optical microscope and scanning electron microscope image of the cured pattern by a 532 nm wavelength laser at 35 mW (upper line)/40 mW (lower line) at 10 mm/s scan rate. (c) Optical microscope image of the peeled off patterns at a laser power at 30 mW (λ = 532 nm) and at 10 mm/s scan rate. (d) Schematics of laser curing condition at two different laser wavelengths (e) Scanning electron microscope image of the cured pattern by a 1070 nm wavelength laser at 40 mW (λ = 1070 nm) and at 10 mm/s scan rate.

Applied laser wavelength for the pre-baked organometallic Ag ink is one of the most important parameter for successful LDC process development. The organometallic Ag ink pre-baked for 90 sec shows an absorption peak around the 480 nm wavelength due to the surface plasmon oscillation modes of self-generated 2-3 nm sized Ag NPs [14], as shown in Fig. 2(a) (red line). To study the laser wavelength dependency, two different wavelength lasers (highly absorbing wavelength: 532 nm, mildly absorbing wavelength: 1070 nm) were used for comparison. A continuous wave laser with 532 nm wavelength (Spectra-physics Millennia) with 10 μm ($1/e^2$) beam diameter was employed to enhance the optical absorption of the NPs.

The experiments were carried out as follows. The organometallic ink spincoated at 1000 rpm for 15 sec on a soda-lime glass substrate, was pre-baked on a hot plate 100 °C for 90 sec. After selective laser curing, the unexposed leftover ink was removed by n-hexane, isopropyl alcohol and acetone sequentially. The cured patterns were then dried on the hot plate at 150 °C for 2 min to remove the residual solvents. As a result, many voids was observed on the

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surface of the patterns cured at laser power of 35 mW and 40 mW and a scan rate of 10 mm/s, as shown in Fig. 2(b). They might have caused by the explosive evaporation of the trapped gas and the un-decomposed silver/organic complexes by the intensive light absorption of the pre-generated Ag NPs on the surface. Although such voids on the surface could be reduced by applying lower laser power, the cured patterns were easily stripped from the substrate during the washing of the unexposed leftover ink, as shown in Fig. 2(c). This signifies that the NPs at the bottom surface were not sufficiently cured by laser because the 532 nm wavelength laser light is absorbed mainly on the surface but cannot penetrated down to the bottom of the NP film, as shown in Fig. 2(d). For such reasons, the thickness that the ink could be cured without the voids formation and the pattern stripping, was limited to approximately 100 nm.

To relieve the explosive evaporation and the pattern delamination problem, more mildly absorbed wavelength (1070 nm) continuous wave ytterbium fiber laser (IPG Photonics YLM-10W) than 532 nm wavelength was applied. With 1070 nm wavelength laser, a uniform line pattern with approximately 10 μm width and above 100 nm thickness could be successfully fabricated on glass substrates under the same curing condition without the voids formation and pattern delamination problem, as shown in Fig. 2(e). From these observations, it was concluded that the 1070 nm wavelength laser makes more favorable curing condition of the ink compared with the use of 532 nm. In other words, the laser wavelength with relatively low absorbance is preferable to the LDC of the pre-baked organometallic ink.

4. Results and discussions

Based on above observations, an x-y galvano-mirror and an f-theta lens with a spot size of 25 μm were employed to fabricate arbitrary patterns, as shown in Fig. 1(b). Here, the specimens were prepared in the same method with above experiment. Figure 3(a) shows the pattern width dependence on the laser power and the curing rate. It should be noted that the current organometallic ink based LDC approach could yield the patterns even at a curing rate of 25 mm/s which is several orders of magnitude higher speed than the previous study using NPs ink based LDC approach (0.2 mm/s) [1,3]. Besides the patterning speed, the resolution could be easily controlled and a wide range of structure size (20~100 μm) was achieved by varying the laser power with a fixed spot size (25 μm), as shown in Fig. 3(a). The patterns which are smaller than the applied laser beam size could be achieved due to the reduced and uniform thermal diffusion by the relatively lower absorption. Conventionally, the pattern width is larger than beam size due to the thermal diffusion by high thermal conductivity of metal NPs for the previous NP based LDC approach [1,3]. The thermal diffusion effect could be relived for the organometallic ink due to the high thermal sensitivity of the pre-baked ink and relatively low thermal conductance of silver/organic complexes. In this study, it was possible to improve the resolution down to 10 μm using laser beam of 10 μm, as shown in Fig. 2(e). However, the pattern resolution could be further improved by decreasing the beam size with a tighter focusing optic system. Practically, it is expected to be possible to achieve 2~5 μm minimum resolution considering the wavelength (1070 nm) and the thermal diffusion.

A profile of the pattern in Fig. 3(b) shows that the rim-type elevations at the edge of the pattern are less pronounced than those usually observed in the conventional NPs ink based LDC [2,4–6,8]. This is because the relative increase of the ink's viscosity caused by the pre-baking procedure and the decrease of the surface tension gradient by using the relative low absorption wavelength depresses the marangoni flow which usually induces the high rim structures. These contentions are supported by the following relationship of the marangoni number [15]:

$$Ma = \frac{\Delta\sigma d}{\mu D} \tag{2}$$

where $\Delta\sigma$ is the surface tension gradient, d is the characteristic length, D is the characteristic dimension and μ is the dynamic viscosity. The absence of the high rim structure and the smooth surface is very important for multilayered electronic fabrication to remove short

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problems. Atomic force microscope (AFM) measurements in Fig. 3(c) revealed that the root-mean-square (RMS) surface roughness (R_a) of the cured metal pattern was approximately 6.0 nm which is much smaller roughness than the previous NP based LDC methods [5,6]. This smooth surface resulted from the uniform distribution of tiny NPs and the homogeneous curing in the thickness direction by removing the explosive evaporation using low absorption laser light source. The optically high reflectivity of the prepared pattern can be easily expected from the theoretical relationship of surface roughness and specular reflectance [17], since the surface roughness value is much smaller than the visible wavelength and only two times larger than that of the E-beam evaporated Ag film (R_a~2.9 nm), as shown in Fig. 3(c), (d). The silver surface prepared by current LDC approach showed high quality reflective surface (reflectivity: 94%) as good as the one prepared by the E-beam evaporation (reflectivity: 96%).

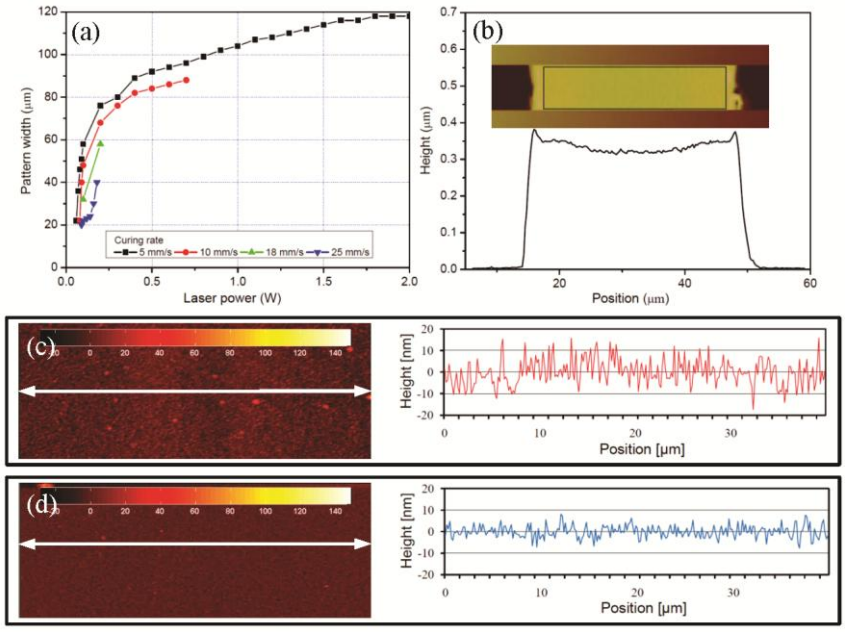

Fig. 3. (a) Pattern width dependence on the laser power (λ = 1070 nm) and the scan rate (spin coated at 1000 rpm and a pre-baking time of 90 sec). (b) AFM profile and image of a laser cured silver line pattern (spincoated at 1000 rpm, 200 mW laser power, 25 mm/s scan rate). (c) 2D AFM surface roughness images and corresponding profile of laser cured pattern and (d) E-beam evaporated pattern.

Figure 4(a) shows the demonstration of the arbitrary letter patterning on a glass substrate at a laser power of 200 mW and a curing rate of 25 mm/s. Due to the low temperature process nature such as the melting temperature drop for small NPs and the low thermal diffusion, our proposed process can produce a electrode on a heat sensitive polymer substrate, as shown in Fig. 4(b) [17]. The reliability of the electrodes is an important evaluation index for the current technique to be applied in the real electronics fabrication industry. To investigate the adhesion property of the laser processed pattern, a peeling test which is so called “scotch tape” method was conducted by using a conventional adhesive tape (3M). The strong adhesion of the laser processed pattern on the polymer substrate was proved after for 100 times scotch tape test, as shown in Fig. 4(c).

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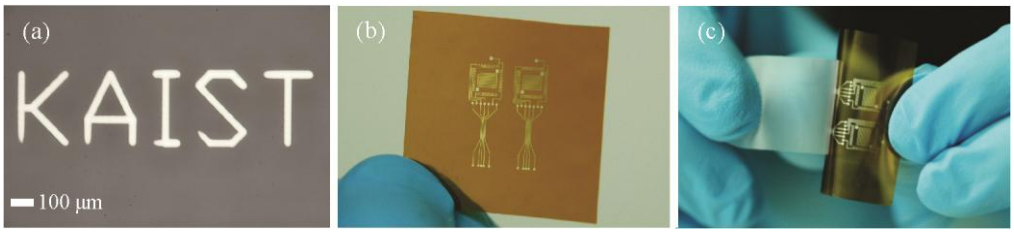

Fig. 4. (a) Optical microscope image of cured patterns on glass at a laser power of 200 mW (λ = 1070 nm) and a scan rate of 25 mm/s (b) Photograph of cured patterns on polyimide (PI) film at a laser power of 200 mW (λ = 1070 nm) and a scan rate of 25 mm/s on glass (c) Adhesion property test.

To check the electrical property characterization, resistivity of the patterns was measured to be 5.7 μΩ·cm. Although this value is about 3.5 times higher than that of bulk Ag (1.6 μΩ·cm), it was regarded as an enough good quality conductor to be used for high performance electronics. The resistance could be further improved by increasing Ag content in the organometallic ink.

5. Conclusion

We demonstrated that laser direct curing using the self-generation of tiny nanopartices (2~3 nm) from organometallic silver ink can improve the curing rate, resolution, cross-sectional profile, and surface roughness of the pattern compared with conventional methods using metal NPs dispersed inks. A longer wavelength with relatively low absorption was suitable to cure the pre-baked ink compared with a shorter wavelength near the surface plasmon mode peak. The determination of the optimized wavelength will be discussed in follow up research. The diverse substrate material choice including flexible polymer and the high quality metal patterning with low resistivity and strong adhesion on the substrate make our approach as a strong potential approach for flexible electronics fabrication on a heat sensitive polymer substrate. Therefore, this method is expected to contribute to continuing advance of fabrication of the flexible electronic devices, such as flexible display [18], flexible solar cell [19], and wearable PC [20].

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