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Laser Direct Synthesis and Patterning of Silver Nano/Microstructures on a Polymer Substrate

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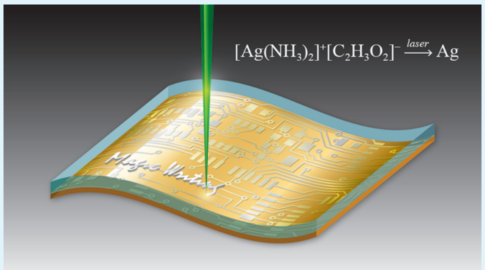

ABSTRACT: This study presents a novel approach for the rapid fabrication of conductive nano/microscale metal structures on flexible polymer substrate (polyimide). Silver film is simultaneously synthesized and patterned on the polyimide substrate using an advanced continuous wave (CW) laser direct writing technology and a transparent, particle-free reactive silver ion ink. The location and shape of the resulting silver patterns are written by a laser beam from a digitally controlled micromirror array device. The silver patterns fabricated by this laser direct synthesis and patterning (LDSP) process exhibit the remarkably low electrical resistivity of 2.1 $\mu\Omega$ cm, which is compatible to the electrical resistivity of bulk silver. This novel LDSP process requires no vacuum chamber or photomasks, and the steps needed for preparation of the modified reactive silver ink are simple and straightforward. There is none of the complexity and instability associated with the synthesis of the nanoparticles that are encountered for the conventional laser direct writing technology which involves nanoparticle sintering process. This LDSP technology is an advanced method of nano/microscale selective metal patterning on flexible substrates that is fast and environmentally benign and shows potential as a feasible process for the roll-to-roll manufacturing of large area flexible electronic devices.

KEYWORDS: *metal patterning, laser direct write, flexible electronics*

1. INTRODUCTION

Flexible, stretchable, and wearable electronics have gained significant attention worldwide and will be among the next generation of consumer electronics with a big market.[1] Applications of flexible electronics include flexible sensors, flexible energy devices, wearable communications devices, flexible computers, displays, and imagers.[2−4] Rapid and cost-effective methods for fabricating electronics on flexible substrates such as polymers are essential to the realization of commercially available flexible electronics. Most polymers are unsuitable substrates for conventional photolithography based fabrication processes for microelectronic devices because of poor chemical and thermal resistance,[5,6] as well as the mismatch on the thermal and mechanical properties of the polymers and the metals or semiconductors which leads to poor adhesion between the functional materials and the substrate.[7] Conductive polymers and mixtures of conductive nanomaterials and polymer resins can reduce the mismatch of material properties between layers.[8,9] However, the electrical conductivity and the flexibility of the process are limited with using these composites. Furthermore, for a flexible substrate such as a polymer, a roll-to-roll manufacturing configuration would be a great advantage. However, it is very difficult to accommodate such a configuration in conventional photolithographic or vacuum based microfabrication systems. There is a clear need for a simple and fast method of fabricating metal patterns on flexible polymer substrates that does not involve photomasking, vacuum deposition, harsh chemical processes, or high temperatures.

In recent years, several types of different fabrication technologies for flexible electronics have been developed. These include inkject printing,[6,10−12] nanoimprinting,[13,14] deposition and mild temperature processes using solution based nanomaterial,[15,16] laser-induced transfer of material,[17,18] laser ablation of predeposited material,[19] and the laser sintering of nanomaterial.[20−25] Laser assisted direct digital sintering and patterning (DDSP) is one of these advanced methods. Metal or semiconductor material can be applied to a flexible substrate from a solution of particulate nanomaterial followed by selective laser sintering, which allows a rapid maskless, high resolution, large area fabrication in a benign environment.[5,26] It is difficult to deposit films on some polymer substrates that have extremely low surface energy such as polydimethylsiloxane (PDMS) by this method. For such substrates, a modified DDSP process such as capillarity assisted laser direct writing (CALDW) technology[7] can be successfully used. However, all such laser assisted sintering and patterning processes require the synthesis of metal nanomaterial and this can be a very complex and costly procedure. The handling (coating, washing, and recycling) of nanomaterial on a polymer substrate is also a challenge due to the highly sensitive nature of nanomaterial to the variation of the environment. This is especially so for thermal impact since most metal nanomaterials are easily

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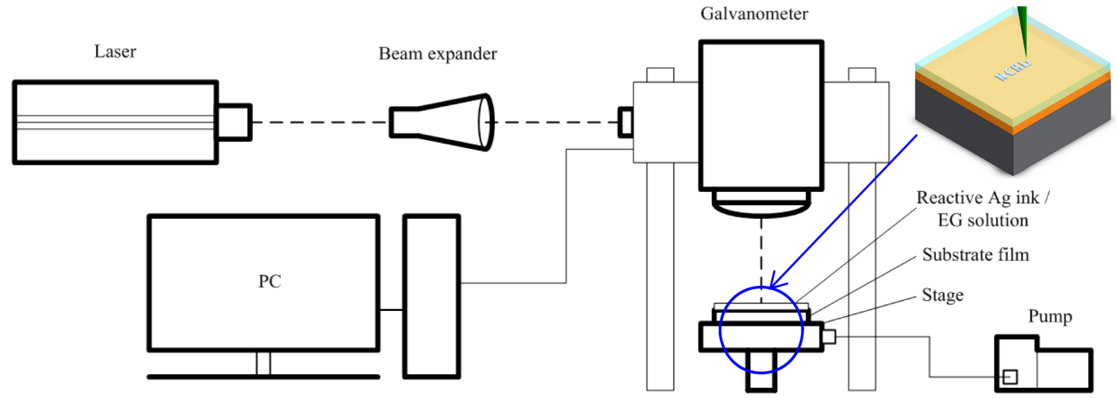


Figure 1. Schematic of the experimental setup for LDSP.

Table 1. List of Process Parameters for Fabricating the Silver Matrix Patterns As Shown in Figure 2a

number of scans	group I—120 mW (16985 W/cm^2)			group II—200 mW (28308 W/cm^2)			group III—280 mW (39631 W/cm^2)		
5	P (Figure 2b)	P	P	P	P	P	B (Figure 2d)	P	P
10	P	P	P	B	G (Figure 2c)	P	B	B	P
15	G	P	P	B	G	G	B	B	G
scanning speed (cm/s)	2	3	4	2	3	4	2	3	4

sintered at moderate temperature because of the melting point depression effect.[27]

In this paper we experimentally demonstrate a novel approach of laser direct synthesis and pattering (LDSP) of silver metal electrodes on a polymer substrate. In contrast to DDSP that utilizes a presynthesized metal nanomaterial solution to deposit the material followed by laser sintering, LDSP uses a modified particle-free metal ion precursor as the processing material. The LDSP approach is relatively fast and simple compared with conventional laser direct writing (sintering) of metal nanoparticles, and shows potential as a feasible process for the roll-to-roll manufacturing of large area flexible electronic devices.

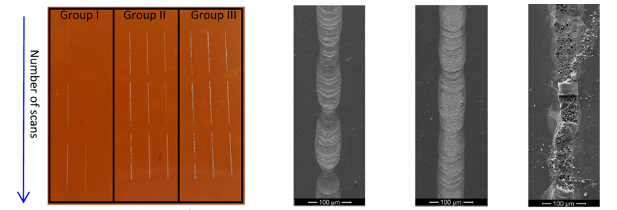
2. EXPERIMENTAL SECTION

2.1. Silver Ink Preparation. The particle-free silver ink is prepared by following a procedure reported by Walker et al.[28] In a typical synthesis process, 1 g of silver acetate (anhydrous 99%, Alfa Aesar) is vortex mixed into 2.5 mL of aqueous ammonium hydroxide (28−30%, ACS Reagent, J T Baker) at room temperature for 10 s. The color of the solution will be pale yellow-gray. Formic acid (88%, ACS Reagent, JT Baker) of 0.2 mL is then added to the solution drop by drop with vigorous stirring. The titration procedure is completed in about 1 min. The formation of fine silver particles, reduced from silver acetate, quickly turn the solution into gray. The solution is then left undisturbed for 12 h to allow the silver particles to precipitate. The supernatant is then filtered through a 220 nm PVDF filter. The resulting clear and particle-free solution which contains 22% of silver[28] is then mixed with ethylene glycol (EG, 99%, Alfa Aesar) (at various ratios) to be utilized as the reactive EG-silver ink.

2.2. Laser Direct Synthesis and Patterning (LDSP) Process. Figure 1 illustrates the setup of the experimental apparatus used in the LDSP process. The 100 μm thick polyimide film with an area of 5 cm × 5 cm used for this experiment was cleaned by rinsing with acetone, ethanol, isopropanol and methanol, consecutively. The film was then treated with oxygen plasma (Atmospheric Pressure Plasma Cleaner, APPC103C, Solar Energy Tech. Inc., Taiwan. Output voltage: 10 000−50 000 V. Output frequency: 4−5 MHz) for 10 s to improve adhesion of the silver to the polymer surface. A vacuum suction sample holder was designed and fabricated to fix and hold the polyimide sheet flat as shown in Figure 1. A small amount of the EG-silver ink (silver ink/EG volumetric ratio 1:1) was prepared and carefully dispensed using a pipet to form a liquid film that covered the surface of the polyimide sheet. Typically, a 2−3 mm thick liquid film is sufficient to prevent the ink from drying out during the experiment. It is noted that the optimal LDSP process parameter could be sensitive to liquid film thickness. If the liquid film is too thin (<1 mm), there could be strong convective heat and mass transport near the laser focal spot on the substrate induced by the laser heating, which leads to poor quality of the resulted silver pattern. For thick liquid film, on the other hand, the heat transfer in the liquid film can be simulated as in a semi-infinite material. In consequence, the heat and the thermal-induced mass transfer are less sensitive to the liquid film thickness. The laser beam from a continuous wave (CW) diode laser (λ = 532 nm) was directed by a programmable galvanometer scanner system (SCANLAB hurryScan II-7). A beam expander was used to assist in focusing the laser beam to 30 μm diameter on the surface of the polyimide sheet. A beam profile analyzer (BeamGage Beam Profiler SP620U, Ophir Optronics) was used to align and focus the laser beam by professional technicians. In the experiment the focused laser beam, directed by the programmable scanner system, selectively scans the pattern through the transparent EG-silver reactive ink and the energy is absorbed by the polyimide. It is emphasized that the silver ink used as the metal precursor in the present study is a clear, particle-free solution. Therefore, there is no significant interaction (absorption or scattering) of the laser light and the ink. The EG-silver ink near the path of the beam on the polyimide surface is heated and reacts to yield elemental silver which simultaneously forms the pattern on the polyimide substrate. After the scanning process is completed, the polyimide surface is washed carefully with deionized water and acetone to remove the excess EG-silver ink.

3. RESULTS AND DISCUSSION

To investigate the effects of the process parameters of LDSP, silver patterns were fabricated at different combinations of laser power, scanning speed and number of scans. The process parameters are listed in Table 1, and the resulted silver pattern matrix is shown in Figure 2. The processed patterns were examined by optical microscopy and SEM. Optical micrographs and SEM images of selected examples of processed patterns are shown in Figure 2. The quality of the silver pattern falls into three categories: (G) a good and continuous line; (P) a partial and incomplete pattern; (B) a burned and highly porous surface.



(a) (b) “Partial” (c) “Good” (d) “Burned”

Figure 2. Characterization for feasible process parameters of LDSP. (a) Silver patterns fabricated with different combinations of laser power, scanning speed, and number of repeating scans corresponding to the process parameters listed in Table 1. (b−d) SEM images of selective silver patterns from the sample in part a with (b) partially patterned, (c) good quality, and (d) burned structures, respectively.

Walker et al.[28] proposed the decomposition reactions of the reactive silver ink subjected to heating:

$$2Ag(NH_3)_2CH_3CO_2 + NH_4CO_2 \rightarrow 2Ag + 5NH_3 + 2CH_3CO_2H + CO_2 + H_2O$$

$$2Ag(NH_3)_2CH_3CO_2 + NH_4CO_2 \rightarrow Ag + AgCH_3CO_2 + 5NH_3 + CH_3CO_2H + CO_2 + H_2O$$

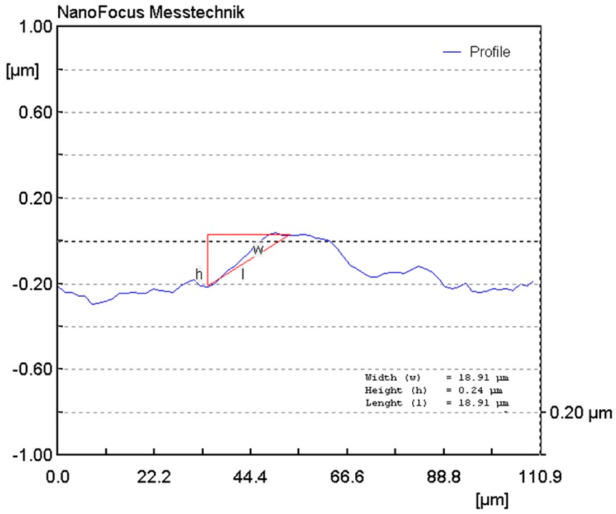
The reaction temperature utilized by Walker et al. was 90 °C. It is noted that elemental silver is formed during this reaction. The electrical conductivity of the resulting silver pattern was reported to be similar to that of bulk silver.[28] It was also noted that low boiling point byproducts, such as carbon dioxide, were produced during the reactions. Therefore, in the current LDSP configuration, minute carbon dioxide gas bubbles may be noticed on the surface near the scanned sites. In addition, the ammonium hydroxide and EG mixture is potentially subject to vaporization if the temperature of the liquid near the laser focus exceeds the boiling point. Such gas bubbles from vaporization of the silver ink components drastically decrease the quality of the fabricated silver film because they interfere with adhesion of the silver to the polyimide substrate. The gas and vapor bubbles also result in local high temperatures because they also interfere with heat transfer. This can lead to burning of the substrate, as well as the formation of minute voids which make the patterned silver being porous structure and discontinuous. As can be seen in Figure 2, significantly burned silver lines were more likely to result from high laser power and low scanning speed.

Gas bubble formation is much less likely to occur if laser power is kept low and the scanning speed is raised. However, decreasing the temperature at the laser focus, while it mitigates bubble nucleation and reduces the number of large bubbles, has a negative effect in that the silver ink reaction rate also decreases. Consequently, the silver lines fabricated with low laser power are less pronounced and in some cases not useable. To ensure good quality silver lines, the laser scanning speed should be decreased and the number of scans increased. This unfortunately increases processing time and is not a preferable solution for an industrial application. It is plausible that good silver lines can be obtained with high power and high scanning speed without damage to the substrate. However, the laser scanner slows down near the ends of each scanned line and the formation of large bubbles and thermal damage to the substrate was seen to happen during the experiments. To reduce the likelihood of large bubble formation, intermediate power (200 mW) and a scanning speed of 3 cm/s were chosen to fabricate the conductive patterns discussed in the following sections.

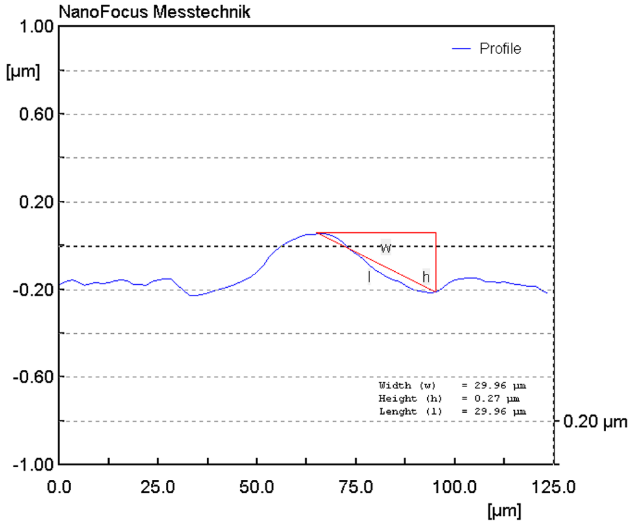
A confocal microscopic surface metrology measurement system (Nanofocus μsurf) was used to measure the profile of the lines resulting from different numbers of scans, and the results are shown in Figure 3. In the conventional laser direct writing process (ex., DDSP process), metal nanoparticles are sintered to form conductive patterns with a nearly rectangular cross-sectional profile. The triangular shape of the cross-section of the silver line in our process is due to the nature of the process is performed in liquid and the fact that the temperature of the substrate and ink is highest at the center of laser focus. Also, the thermal resistance of the liquid silver ink is higher than that of aggregated nanoparticle films (in the DDSP process) and the chemical reaction and silver formation occurs in a “hot region” that is nearly hemispherical on the substrate surface. From Figure 3a−c, the height of the triangle can be seen to range between 250 and 350 nm for 5 to 15 repeated (back and forth) scans and the height of the silver pattern does not seem to increase significantly after ten scans have been completed. It is speculated that the silver pattern formed from ten scans is sufficiently thick to reflect the laser irradiation and thus preventing further heating of the substrate by the laser beam. During the experiment, it was also noticed that the laser beam was strongly reflected by the silver patter after few repeated scans. Thus, it can be expected that soon there was no further heating and the reaction stopped.

The effects of silver ink concentration in ethylene glycol (EG) were investigated with silver ink to EG volumetric ratios of 1:9, 1:1, and 9:1. All the silver lines in this test were fabricated using 200 mW of laser power, a scanning speed of 3 cm/s, and 10 repeated scans. As can be seen in Figure 4a, the silver line with a higher silver ink ratio is thicker but less defined, i.e. the edges of the lines are not very straight and have a hairy structure. This is possibly due to a lower boiling point and viscosity which allows the solution with less EG to vaporize easily and flow readily near the laser focus point. Increasing the ratio of EG raises the boiling point and decreases the flow. In consequence, the silver lines made using solutions with higher EG concentration are straighter and more well-defined as can be seen in Figure 4b and c. Figure 4d and e shows two adjacent silver lines with a line space (center to center) set to 75 and 50 μm, respectively. It can be seen that a 15 μm clear gap between two adjacent lines between silver lines when the line space is set to 75 μm. Considering the hairy structure at the edges is negligible for electrical conductors, the effective gap is approximately 25 μm. Thus, silver line pattern with line space set to 50 μm yields no noticeable gap between lines as shown in Figure 4e. The thickness of these silver lines is less than that from the solution with lower EG concentration, i.e. the thickness of the silver pattern increases with a higher silver concentration. This may be because there are fewer silver ions available at the laser focal point. A thinner silver film also has lower conductivity and more time would be required for fabrication of a useable film. Thus, a solution of silver ink to EG ratio of 1:1 was used in the following sections.

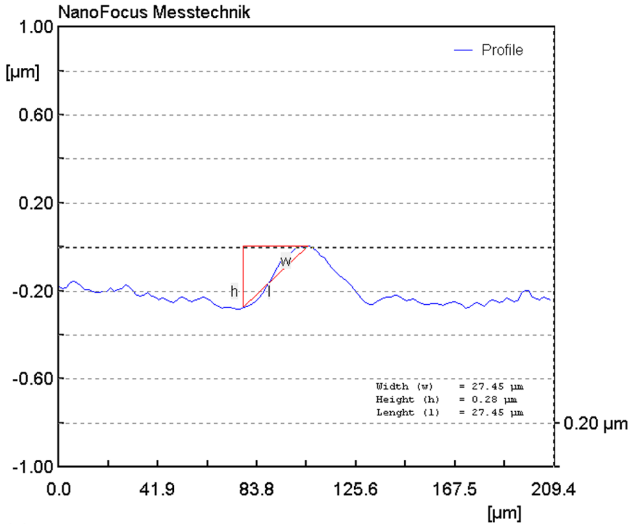
Silver patterns of 1 mm wide and 10 mm long were fabricated by moving the laser beam in the lateral and longitudinal directions on the substrate using the programmable galvanometer system. From Figures 2 and 3, it can be seen that the silver line as fabricated with the aforementioned parameter is approximately 50 μm in width with a nearly



(a) 5× scans

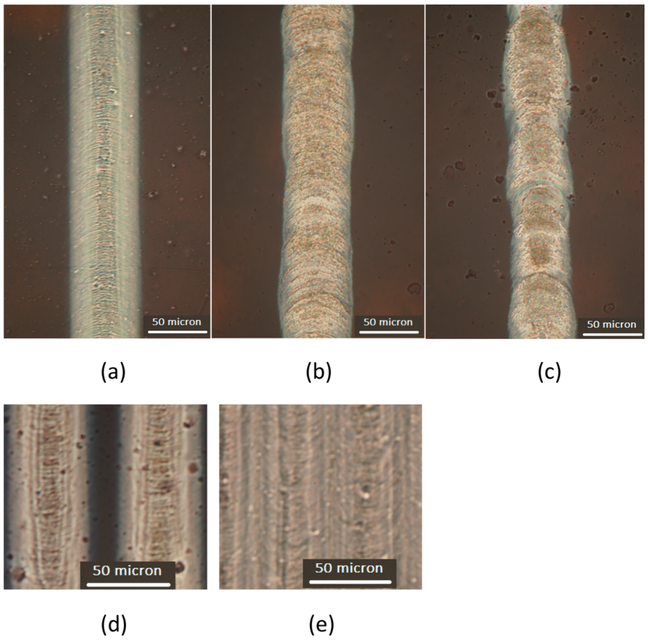


(b) 10× scans



(c) 15× scans

Figure 3. Cross-sectional profiles of LDSP processed silver patterns with various numbers of laser scans: (a) 5, (b) 10, and (c)15 scans.



(a) (b) (c)

(d) (e)

Figure 4. Optical microscopic images of silver lines fabricated by LDSP with silver ink to ethylene glycol ratios of (a) 1:9, (b) 1:1, and (c) 9:1, respectively. (d and e) Two adjacent silver lines with line space (center to center) set to 75 and 50 μm, respectively (silver ink to EG ratio of 1:9).

triangular cross-section. Thus, to fabricate a silver pattern with good uniformity, the distance between each laser scan (center to center) was set to half the line width, i.e. 25 μm. Figure 5 shows images of the resulting silver patterns. As can be seen from Figure 5a, the metal pattern after two scans shows the formation of a very thin silver layer. As the scan keeps repeating, the silver film becomes thicker and more solid. Silver patterns after 10, 15, and 20 scans show no significant difference in appearance. It should be pointed out that the thickness of the silver patterns yield in the current LDSP configuration can be adjusted with layer-by-layer laser scans until the limit of the film thickness is reached (cf. Figure 5). Therefore, it is possible to realize nanoscale 2.5D fabrication by LDSP. Figure 5b shows the SEM images of the silver pattern that resulted from ten scans. The “lines” in the pattern indicate the path of the scanned laser beam. The wavy profile of the line is typical for a laser direct writing process in liquid.[7] In addition, pure silver element the pattern fabricated by the present LDSP process is confirmed by performing EDS (Phenom ProX, Phenom-World) analysis as shown in Figure 5c.

Figure 6 shows the variation of electrical resistance of the fabricated silver lines with respect to the number of scans measured using a micro resistance meter (Hioki RM3544−01, range 30 mΩ−3 MΩ, accuracy ±0.02%). The resistance decreases with increasing number of scans as the thickness of the film increases. However, after ten scans there is no significant difference in resistance (cf. Figure 6). This is due to the fact that the film thickness does not increase significantly after more than ten scans as previously discussed. The average resistance obtained from ten scans is about 2.1 Ω. In addition, a peeling test using Scotch tape on the silver pattern surface does not result in any noticeable change in electrical resistivity even after many repeated peelings. This clearly demonstrates and confirms the sturdiness of a conductive silver pattern produced on a polyimide substrate by the LDSP process described here.

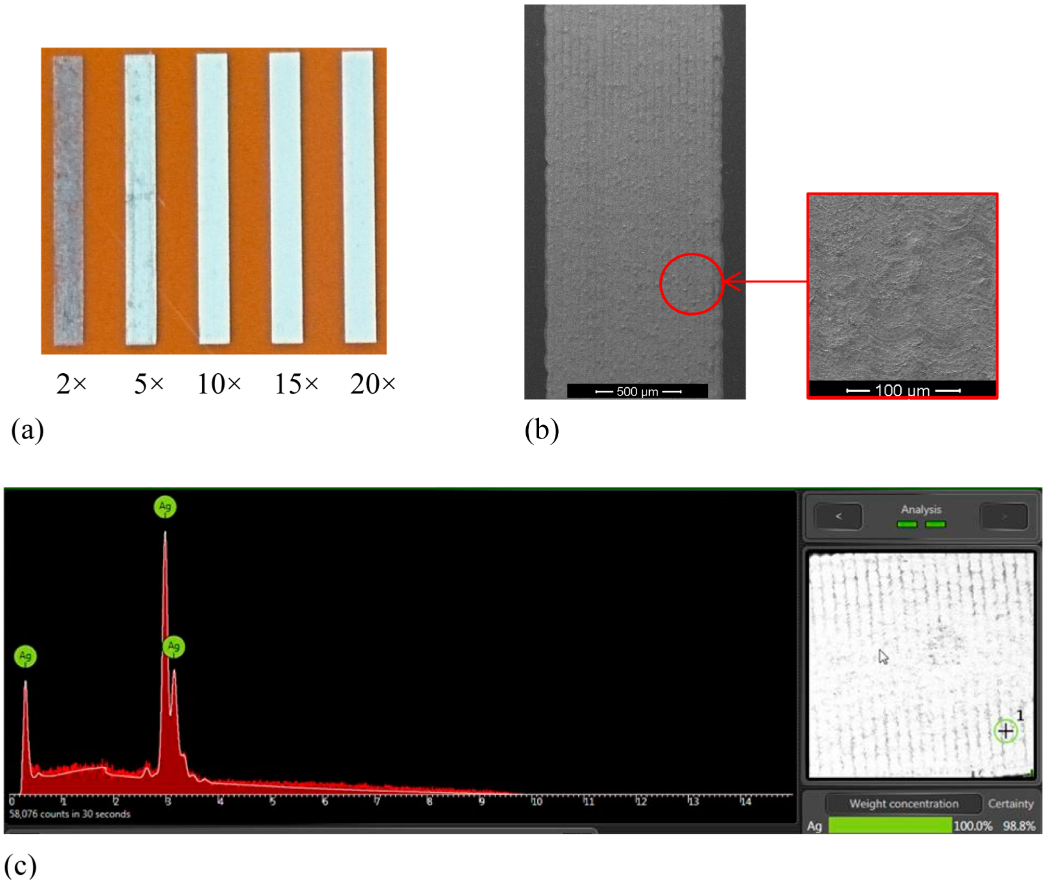


Figure 5. Silver pattern fabricated by LDSP. Process parameters: (a) laser power 200 mW, scanning speed 3 cm/s, number of scans from left: 2× , 5× , 10× , 15×, and 20× , respectively. (b) SEM images of sample shown in part a after 10 scans. (c) Energy dispersive spectrometer (EDS) results of the metal pattern.

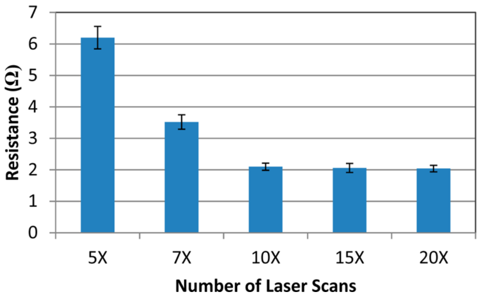


Figure 6. Resistance of the silver patterns versus number of repeating laser scans.

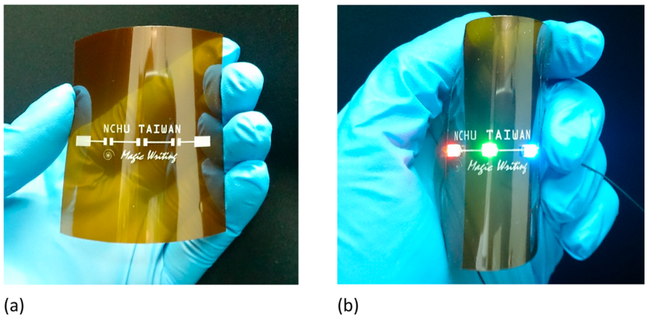


Figure 7. Flexible electrodes (a) and a display with a miniature RGB LED array (b) on polyimide substrate fabricated by LDSP technology.

From Figure 3, the average thickness of the silver pattern with ten and above laser scans is estimated to be between 100 and 200 nm. With this thickness, the resistivity of the silver patterns fabricated in the present study is from 2.1 $\mu\Omega$ cm (taking 100 nm as the average thickness) to 4.2 $\mu\Omega$ cm (taking 200 nm as the average thickness), which is about 131% to 262% of the resistivity of bulk silver (1.6 $\mu\Omega$ cm), respectively. As can be seen from the SEM images (Figures 2 and 5) of the resulted silver patterns obtained by the LDSP process, there are some miniature porous structures in the silver film which might contribute to the increase in electrical resistivity. Nevertheless, it is clear that the presented LDSP technology can be applied to the rapid fabrication of electronic devices on flexible polymer substrates. Figure 7 shows flexible electrodes fabricated by the LDSP process. The stability of the silver electrodes was confirmed by multiple Scotch tape peeling tests and bending tests as shown in Figure 7. This LDSP technology does not require the costly and time-consuming synthesis of nanoparticles that are spin coated or inkjet printed on the substrate for conventional laser direct writing process. Furthermore, the LDSP process can be readily combined with inkjet printing of the reactive ink on the substrate, which will further reduce the waste of precious metal inks. It will also reduce processing time comparing to the conventional inkjet printing process since silver patterns can be quickly formed by the laser instead of needing to be slowly heated in an oven. This new LDSP technology allows simple, fast, direct, low temperature, digitally programmable metal patterning without the need for any vacuum metal deposition, expensive photomask preparation or the complex synthesis of metal nanoparticles.

4. CONCLUSION

In the present study, a novel approach for fabricating electronics on flexible substrates using modified continuous wave (CW) laser direct synthesis and patterning (LDSP) of transparent reactive ink was successfully demonstrated. The patterned film properties are controlled by the LDSP processing parameters such as laser power, scanning speed and number of scans. Silver patterns with electrical conductivity comparable to bulk material can be produced. In additional to the advantages of a simple, direct, low temperature, digital metal patterning process, this novel technique greatly reduces the time and complexity of conventional laser direct writing processes that require the synthesis and deposition (spin coating or inkjet printing) of metal nanoparticles. Silver patterns on a large flexible polyimide substrate with remarkably low resistivity (~2.1 $\mu\Omega$ cm) were achieved by this LDSP process and were demonstrated as LED arrays on the polyimide substrate. This digital programmable LDSP process can rapidly produce high resolution arbitrary patterns of hundreds nanometer in thickness. It also offers great design flexibility and allows changes in the electronics without the need for the preparation of new expensive photomasks. Development of this LDSP process represents a huge leap toward the ultimate realization of next generation maskless, nonvacuum, low temperature laser direct metal patterning technology for high quality flexible electronics.

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Notes

The authors declare no competing financial interest.

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