Selective Laser Sintering of Ag Conductive Inks with a Real-Time Non-uniform Rational Basis Spline Curve Interpolator

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Abstract: A method is proposed for the fabrication of Ag patterns on plastic substrates by printing Ag conductive inks, followed by selective laser sintering (SLS). The printing and sintering processes were realized by a motion control system with a real-time non-uniform rational basis spline (NURBS) curve interpolator. The proposed approach achieves a constant laser scanning speed along the curve path. Ag patterns fabricated by a NURBS curve interpolator and compared to those produced using a linear interpolator.

Keywords: NURBS Curve Interpolator; Selective Laser Sintering; Silver Nanoparticle

Introduction

In recent years, the emergence of flexible circuit boards has presented interesting opportunities and raised the issue of how to best fabricate circuits on 3D surfaces with good electrical conductivity. Unlike traditional ink-jet printed circuit boards confined to a plane, recent efforts have used aerosol-jet printing to print Ag nanoparticle (NP) circuits on the substrate surface [1] and fabricate antenna circuits on a 3D substrate [2]. On the other hand, a ball-point pen filled with Ag NP ink can directly draw on paper [3] allowing for the quick production of required circuits.

Sintered structures usually have lower resistivity, but, due to the thermal limit of the heat sensitive substrate, the conventional oven heat treatment method presents a thermal obstacle. Heat treatment using laser irradiation may be able to reduce the thermal damage to the substrate or surrounding material. A variety of different lasers have been investigated for the sintering of printed Ag NP inks [4-6]. Recently, a method that simultaneously combines direct ink writing with a focused laser and sintering silver ink has been presented [7].

However, conventional laser machining controllers provide only line or arc interpolators, and the curve paths are approximated with piecewise line or arc segments. For example, the 3D Bezier curve is approximated with

piecewise line segments in [7]. This may introduce a velocity discontinuity at the junction of the two connected line segments, resulting in a non-uniform laser density irradiated on the sample. The NURBS curve has attracted particular interest since it provides a common mathematical form for representing standard analytical shapes. Although NURBS interpolators have been shown to be efficient in milling machining, little related work has been presented in laser machining study.

This paper reports on the selective laser sintering (SLS) of silver conductive ink on a heat sensitive substrate through a laser processing system with a real-time NURBS curve interpolator, allowing for a constant laser scanning speed along the curve path. Selective laser sintering of an Ag pattern on a 2D/3D surface with constant laser energy density could also be realized.

Experiment

Figure 1(a) shows a photograph of the laboratory 3D SLS system. The SLS system was composed of a diode-pumped solid-state laser (SDL-532-200T, Shanghai Dream Lasers) with a wavelength of 532 nm, a continuous mode, a beam diameter of 2.4 mm (at $1/e^2$), and maximum available laser power of 2 W. The laser beam was passed through a beam expander (2x magnification) and a series of reflective mirrors, and then subsequently entered an

objective lens (numerical aperture 0.28, M Plan Apo, Mitutoyo) and was incident in the normal direction on the sample mounted on an XY stage. The position of the objective lens was adjusted in the vertical direction (i.e., the z-axis). The laser sintering pattern was fabricated by translating the sample using a positioning stage (i.e. the x-y axis) and a laser-focused spot (i.e., the z-axis). For the purpose of alignment, a co-axial charge-coupled device (CCD) vision system was installed. A dichroic mirror (LPD02-532RU, Semrock) was selected to reflect the laser beam (>98% at 532 nm) and transmit white light (>93 % at 534-700 nm) to enable visualization of the reflected laser-focused spot and sample surface for alignment purposes.

Before the SLS process, the objective lens was replaced with a conductive pen to print the Ag pattern. Figure 1(b) shows a photograph of the silver-based conductive pen (AgIC Inc.) installed in the Z stage and the Ag pattern printed on the PET substrate. The conductive pen contained silver NP (size 60-100 nm, 15%wt), water, and an ethanol solution. After the printing process, as shown in Figure 1(c), the conductive pen was replaced with the objective lens for the SLS process. The co-axial CCD vision system (Figure 1(a)) was used to align the position of the laser-focused spot on the printed Ag pattern. In the present experiment, the Ag pattern was printed on the PET substrate (thickness 100 μm) using a printing speed of 250 mm/min. Figure 1(d) shows the cross-sectional SEM image of the printed Ag pattern. The thickness of the Ag pattern was $\sim 25 \mu\text{m}$ and attached well to the PET substrate.

To generate an Ag pattern in a 3D space, the path could be described by an NURBS curve $P(u)$ [8]. To achieve a constant scanning speed along the curve path, the increment of the parametric u for each time interval T (the interrupt of the controller) will not always be a constant. Accordingly, a method to determine successive values of u was needed to accurately generate an appropriate increment length for the desired scanning speed. A real-time NURBS curve and surface interpolators for cutter machining were developed in our previous studies [9, 10]. The method using Taylor's interpolator was adopted in this study. The NURBS curve interpolator for generating u_{k+1} is given by:

$$u_{k+1} = u_k + \frac{TV_k}{\left\| \frac{dP(u)}{du} \right\|_{u=u_k}} \quad (1)$$

where u_k denotes the value of u at the k th sampling time instant kT , V_k is the speed along the curve path, and T is the sampling period.

A PC-based system with a motion control card was used to realize multi-axis synchronous motion of the three-axis stage. The servomotors of the stages were driven by SSCNET (servo system control network)

networked drivers. An embedded XP operating system with a real-time kernel was used to implement the NURBS curve interpolator and the SSCNET communication protocols.

The surface characteristics of the printed and laser sintered specimens were observed using an optical microscope (OM) and a scanning electron microscope (SEM). The surface resistivity was measured using a four-point probe station.

Figure 1. Photograph of the experimental setup: (a) laboratory 3D SLS system; (b) conductive pen and Ag pattern printed on PET substrate; (c) laser irradiation; (d) cross-sectional SEM image of the printed Ag pattern.

Results and Discussion

Figure 2 shows a schematic drawing of the laser scanning process, in which the laser beam is focused on the surface of the sample. The laser scanning path was perpendicular to the direction of the as-printed Ag pattern. The lateral displacement was the distance between two adjacent scanning paths.

In the area sintering process, the sintered line width depends on the laser parameters and must be determined. Figure 3(a) shows the top-view microscopic image of the sintered line pattern using different laser parameters.

Each three-line pattern, i.e., the marked area, was formed at the same laser power with different scanning speeds of 100, 200, and 300 mm/min (from left to right). The laser irradiated area differs slightly from the as-printed region. Figure 3(b) shows the SEM images of the three-line patterns formed at a laser power of 500 mW. The width of the sintering line pattern decreased as the scanning speed increased. Figure 3(c) shows the magnification of the SEM images of the as-printed and laser sintered area using scanning speeds of 100, 200, and 300 mm/min. The grain size of the laser sintered area (~ 500 - 600 nm) was much larger than the as-printed area (~ 60 - 100 nm), and the average grain size increased as the scanning speed decreased.

Figure 2. Schematic drawing of the laser scanning process.

Figure 3. Image of the sintered line pattern by different laser parameters: (a) microscopic; (b) SEM; (c) magnified image of the marked area in (b).

Figure 4 shows the magnified SEM images of the sintered single-line pattern using a scanning speed of 300~600 mm/min with a varying laser power of 300~700 mW. The average grain size increased as the laser power increased or scanning speed decreased. At a laser power of 600 mW, it was found that the Ag NPs were completely sintered into large grains. If the effective laser power density was sufficiently high and the particle temperature

was higher than the NPs' melting point, a thin surface layer of NPs could be partially melted. If the effective laser power density was much higher, the molten material would move toward the center region of the particle and the particle could be fully melted.

Figure 5 shows the sintered line width (measured from SEM data) for a scanning speed of 300~600 mm/min with varying laser power of 300~700 mW. At the same scanning speed, the sintering line width clearly increased with laser power. At the same laser power, the sintering line decreased with the scanning speed.

Figure 4. Magnified SEM images of sintered single line pattern using a scanning speed of 300~600 mm/min with varying laser power of 300~700 mW.

Figure 5. Sintered line width for a scanning speed of 300~600 mm/min with varying laser power of 300~700 mW.

For the area sintering process, as shown in Figure 2, in addition to the laser power and scanning speed, lateral displacement is an important parameter which controls the surface characteristics of the sintered pattern. To investigate the effect of lateral displacement, three rectangular areas (5×4 mm²), as shown in Figure 6(a), were fabricated at a laser power of 500 mW, a scanning speed of 300 mm/min, and different overlapping ratios (20%, 30%, and 40%). The overlapping ratio was defined

as the ratio of the lateral displacement distance and the sintered line width (Figure 5). There were no obvious morphology differences among the three area patterns. However, from the back-view magnified images, as shown in Figure 6(b), it was observed that the damaged substrate area (marked by the arrow) increased with the overlapping ratio.

In Figure 7, different sintered rectangular areas ($5 \times 4 \text{ mm}^2$) were fabricated using a laser power of 300~700 mW, a scanning speed of 300~600 mm/min, and a fixed overlapping ratio of 20%. The sheet resistance of these sintered patterns was measured, as shown in Figure 8. The sheet resistance at the laser power of 600 mW had the minimum value of $\sim 209.8 \text{ m}\Omega/\text{sq}$ at a scanning speed of 400 mm/min, which was lower than that of the as-printed pattern, at $\sim 670 \text{ m}\Omega/\text{sq}$. At a laser power range of 300~500 mW, the NPs were partially melted (see Figure 4) and resulted in medium sheet resistance. At a laser power of 600 mW, the NPs could be fully melted (see Figure 4) and resulted in low sheet resistance. However, at a laser power of 700 mW and a low scanning speed of 300 mm/min, the sheet resistance was very high (not shown). Since the irradiated effective laser power density was higher than the ablation threshold of the printed Ag, the material at the scanned path was ablated, resulting in a damaged area (marked with an arrow) shown in Figure 7.

Figure 6. Area sintering using different overlapping ratios: (a) top-view; (b) magnification of the back-view.

A 2D NURBS butterfly curve [11] was tested to compare the SLS process by the NURBS and linear interpolators. Figure 9 shows the top-view OM image of the NURBS sintered pattern and the magnified images for the nine large curvature areas. Figure 10 shows the magnified image of area 4 by the linear and NURBS interpolator. The NURBS interpolator has a smaller change in the sintered line width than the linear interpolator at the corner. Table 1 shows the measured results of the sintered line width for the nine areas using the linear and

NURBS interpolators. The variation of the sintered line width was defined by:

$$\Delta L = \frac{L_{\max} - L_{\min}}{L_{\text{ave}}} \quad (2)$$

where, $L_{\max}$ and $L_{\min}$ are respectively the measured maximum and minimum line width from the magnified image, and L_{ave} is the average line width.

In Table 1, it could be seen that ΔL for the nine corner areas by the NURBS interpolator were all smaller than the linear interpolator. The average line width variation of the linear and NURBS interpolators was respectively 17.6 % and 9.2 %. This corresponds to an improvement of about 8.4% for the NURBS curve interpolator.

Figure 7. Sintered rectangular areas under different laser parameters.

Figure 8. Sheet resistance of sintered areas in Figure 7.

To demonstrate the 3D structures' fabrication capability, Figure 11(a) presents a 3D NURBS curve with control points (circles) for performance evaluation. The associated order, knots, control points, and weight vectors of the curve are listed in Table 2. Figure 11(b) and Figure 11(c) respectively show the measured position and tracking responses. The rise tracking error in Figure 11(c) could have been caused by the the two large degree of

curvatures in the curve, possibly due to the servo controller. The actual scanning speed shown in Figure 11(d) closely followed the desired value of 400 mm/min. Note that the command scanning speed agreed well with the desired value and the vibration of the actual scanning speed, possibly due to the servo controller.

Table 1. Measured results of the sintered line width for the nine areas using the linear and NURBS interpolators.

	Linear interpolator				NURBS interpolator			
Area	L_{max} (μm)	L_{min} (μm)	L_{avg} (μm)	ΔL (%)	L_{max} (μm)	L_{min} (μm)	L_{avg} (μm)	ΔL (%)
1	79.6	71.0	74.9	11.4	76.2	72.9	75.1	4.5
2	81.9	63.9	73.7	24.4	78.2	64.2	73.0	19.2
3	76.7	63.6	68.7	19.1	68.5	66.3	67.5	3.3
4	68.8	60.4	65.4	13.0	74.5	68.5	70.9	8.5
5	72.4	60.3	65.4	18.6	73.6	64.6	70.7	12.8
6	78.6	63.0	72.6	21.5	74.6	63.3	70.2	16.2
7	78.3	64.0	68.9	20.8	70.4	66.8	68.1	5.3
8	73.8	64.3	69.1	13.9	73.0	67.4	69.7	8.1
9	76.7	65.8	70.3	15.5	71.1	67.9	71.1	4.6
	Average of the ΔL			17.6	Average of the ΔL			9.2

Figure 9. Images of the NURBS sintered pattern and the magnified images for the nine large curvature areas.

Figure 10. Magnified image of area 4 by (a) linear and (b) NURBS interpolator.

Figure 11. (a) 3D NURBS curve; (b) position responses; (c) tracking error; (d) actual scanning speed along the curve path.

Table 2. Associated parameters of the 3D NURBS curve.

Order	3
Knots	(0, 0, 0, 0.25, 0.5, 0.5, 0.75, 1, 1, 1)
Control points (x, y, z) _{mm}	Weights
(0, 0, 7.765)	1.0
(3.75, 26.25, 0.731)	0.5
(48.75, 18.75, 2.741)	0.5
(45, 0, 7.765)	1.0
(41.25, -11.25, 10.78)	0.5
(26.25, -3.750, 8.77)	0.5
(30, 0, 7.765)	1.0

Figure 12(a) and 12(b) respectively show the as-printed and laser sintered Ag patterns on the PET film. In Figure 12(b), the NURBS area was then sintered at a laser power of 600 mW, with a scanning speed of 400 mm/min and an overlapping ratio of 20%. An LED was lighted for simple evaluation and showed that the sintered pattern (Figure 12(d)) had better performance than the as-printed pattern (Figure 12(c)).

Figure 12. Ag patterns on the PET film: (a) as-printed; (b) laser sintered; Evaluation by LED lighting: (c) as-printed; (d) laser sintered Ag patterns.

Conclusions

This study presents an approach for the fabrication of Ag patterns on a plastic substrate using a selective laser sintering (SLS) system with a real-time NURBS curve interpolator. The SLS with constant scanning speed along the path enabled the fabrication of a sintered Ag pattern with no discernible damage to the underlying plastic substrate. It was found that the SLS process significantly improved the structure and electrical characteristics of the as-printed Ag pattern. The grain size could be increased from ~60-100 nm to ~500-600 nm, and the sheet resistance decreased from 670 mΩ/sq to 209 mΩ/sq. The experimental results confirm that the proposed SLS system with a real-time NURBS curve interpolator provided a highly precise means of fabricating advanced 3D circuits.

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