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Fabrication of Ag micro-patterns by electrohydrodynamic jet printing

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Abstract. Electrohydrodynamic jet printing is a rapid manufacturing method in additive manufacturing fields, which is employed to generate micro-nano patterns, functional structures, sensors and electronics in recent years. It is a rapid manufacturing, low-cost, mask-free route to manufacture one dimensional to three dimensional structures by nanoink. In this paper, silver dots, lines and designed patterns are printed by electrohydrodynamic jet printing. The results are stable and uniform, which can be adjusted by printing parameters. With high voltage, large pulse width or small stand-off distance, the size of dots increase. By increasing frequency or decreasing shifting speed, the distance between dots becomes short, then the structures are getting into lines from dots. Multi-layer silver lines are characterized by X-ray imaging and exhibit good absorption of X-ray, leading to the significant radiation attenuation effectiveness. The printed silver structures are good candidates for radiation shielding in electronics and circuit boards.

1. Introduction

Electrohydrodynamic jet (e-jet) printing is a rapid manufacturing method in additive manufacturing fields, which can generate many kinds of micro-nano structures from metal to polymer [1-5]. There are many advantages of e-jet printing, such as rapid manufacturing, low-cost, mask-free and pattern variation, thus, many functional structures can be fabricated on glass, flexible films and silicon [6-9]. The nanoink for printing are prepared by nanomaterials and typical solvent, resulting in the good property for printing with silver nanoparticles [9], quantum dots [10], silver fibers [11], even carbon nanotubes [12] and graphene [13]. Compared with the traditional manufacturing methods, e-jet printing provides a green, low environmental approach to generate micro-structures, which has great potentials in electronic sensors, bio-sensors and circuit boards.

The property of printed results is greatly influenced by printing parameters, such as voltage, shifting speed, frequency, stand-off distance, needle size, etc. Han *et al* [14] reported high aspect-ratio 3D structures of sub-10 µm resolution by e-jet printing, which showed high resolution of this method. AC-pulsed voltage was used to manufacture the transparent electrode [15], electrical features and connectors [16,17]. Qin *et al* [18] fabricated a functional touch sensor with high sensitivity via e-jet printing using silver nanoink. Many composite materials were employed to manufacture multi-layer structures, including WO₃-Ag [19,20], Ta [21], WO₃ [22], which were good candidates of electron devices. In addition to traditional substrate, flexible films were employed for printing, such as polydimethylsiloxane (PDMS) and Polyethylene terephthalate (PET) [23,24]. In the previous reports, the researchers focused on improving printing quality through different approaches by controlling the

relevant printing parameters, but the printing mechanism and quality control were still challenges for manufacturing functional structures.

One of the potential applications for printed metal structures is radiation shielding. The electronic components and circuit board used in a high-radiation environment always cause operational errors of the system because of heavy intensity radiation. X-ray absorbed metals are good selections for radiation-hardening techniques, which requires special manufacturing processes and tailored electronic design. Furthermore, it was difficult to realize particular part radiation protection, because the micro/nano fabrication of given shape metal is complex. Fortunately, with the development of nanotechnology, many metal nanoparticles were synthesized and commercialized. These nanoparticles can be made into nanoink for printing with a particular additive solvent to generate different patterns on the substrate.

In this paper, silver micro-structures in dots, lines and other designed patterns were fabricated by e-jet printing. The influence of voltage, pulse width, frequency, shifting speed and stand-off distance on the size of printed results were discussed. With multiple printing processes, multi-layer silver lines were generated, which showed good absorption of X-ray by characterizing them with X-ray topography imaging. The printed silver structures are good candidates for radiation shielding in electronics and circuit board.

2. Methods and materials

2.1. E-jet printing system

The schematic e-jet printing system is shown in figure 1(a). A nozzle with a micro-needle in the tip is employed to contain the ink. There is a shifting platform (Aerotech A3200), which moves freely in xyz directions to control the designed patterns. A high voltage generated by the wave generator and amplifier is applied between the metal needle and the plate electrode. The substrate is on the electrode, which moves by program control in xy plan. The distance between the needle tip and substrate is adjusted by moving nozzle positions along z axis.



Figure 1. (a) Schematic of e-jet printing. (b) Optical image of the needle of the printing process. (c) Scanning electron microscope (SEM) image of printed silver dots.

The whole system is set on a flat stable platform to avoid vibration. In order to get the printing results in real-time, a charge-coupled device (CCD) camera coupled with a lens system is added in the system [25]. Figure 1(b) shows the needle shape and size, as well as the printed line. Different size patterns are generated by controlling the stand-off distance and needle size. In the printing process, the nanoink is added to the nozzle, then it is jetted by the high voltage, then deposited on the substrate, resulting in functional patterns. The nanoink used in this research is silver nanoink from Sigma Aldrich, in which the ~50 nm silver nanoparticles are solved in the solvent Triethylene glycol monomethyl ether (TGME) at 50 wt%.

2.2. Characterization

The printed patterns were characterized by optical microscope (Hirox RH-2000). The microscope

obtained both the surface morphology and film thickness. The largest magnification was 5000X. A scanning electron microscope (SEM, FEI Quanta 250) was employed to estimate the details of printed patterns. With the characterization results, the printing control and patterns optimization were realized. An X-ray imaging system (figure 7(a)) was employed to characterize the radiation absorption property. It includes X-ray source, rotating platform, focus system, detector, and image process program. The X-ray topology image was recorded by the detector, which shows different gray scale to estimate the absorption ability of X-ray [26].

3. Results and discussions

The control of parameters in the e-jet printing process is significant to get designed patterns. By altering these parameters, the target results change in size and shape. Voltage is one of the important parameters in e-jet printing. The nano ink is jetted by electrical force in the electrical field generated by high voltage. Different from gas-driven jet printing, e-jet printing is better to control the droplet by voltage. Direct current (DC) [27] and alternating current (AC) [28] were both employed to drive the printing process in the previous reports. AC voltage is controllable by frequency, positive and negative value, pulse width, resulting in charges removing of nanoink, which benefits on printing results. An amplified AC voltage is applied with variable voltage amplitude, frequency and pulse width. Figure 1(c) shows the SEM of the printed dot, which is composed of dense silver nanoparticles, indicating that the stability of nanoparticles is not destroyed in the e-jet printing process.

Figure 2(a) shows the optical microscope image of printed silver dots with different voltages. The size of dots becomes large as the increase of voltage amplitude. By the curve of dots areas as a function of printing voltage shown in figure 2(b), the change rule meets the function of S=-0.0073 u^2 +17.976u-8598.2. In the equation, S is the mean area of the dots, u is the voltage. It indicates that the dot diameter linear changes as the voltage altering. The area of the dots represents the volume of the droplet of e-jet printing. With large voltage, the electrical field force becomes large, resulting in large quantity size volume. There is another advantage of high voltage used in ink-jet printing, good stability of the printing process. The program can control the voltage and set a given value, which leads to regular and high-quality printing structures. We can see from figure 2(a) that, while the voltage reaches 900 V, there is a tip of each dot. That's because the ink split under high voltages, resulting in small satellite droplets and tip-dots on the substrate.



Figure 2. (a) Optical microscope image of printed dots with different voltages. (b) The dots areas as a function of voltages.

By changing the stand-off distance, the size of the dots is changed gradually, shown in figure 3. The stand-off distance here is the distance between the needle tip and the substrate, which is usually 10-100 μ m. The mean area of dots changes from 2250 μ m² to 420 μ m², as the stand-off distance changes from 10 μ m to 45 μ m, respectively. When the stand-off distance becomes short, the electrical force applied to the droplet decreases. Thus, small volume droplet is generated, and deposited on the substrate, resulting in small dots. The needle and printing results are both in micrometer level, so that

it is important to control the stand-off distance accurately. With the application of e-jet printing in flexible electronics, the substrate surface is no longer flat, such that the program should adjust the constant stand-off distance. The selection of stand-off distance is also affected by the size of the needle. In our experiment, a needle with $\sim 28 \ \mu m$ is used to generate dots and lines.



Figure 3. (a) Optical microscope image of printed dots with different stand-off distance. (b) The dots areas as a function of printing stand-off distance.

Pulse width is the time period in the open status of the voltage switch, which allows the supply of high voltage for printing. It affects droplet volume, resulting in size control of printed structures. The printed lines and dots at different pulse width are shown in figure 4. By controlling printing speed, we obtained lines (0.2 mm/s) and dots (4 mm/s). The results show an increase of line width and dot diameter with the increase of pulse width. With very large pulse width, there are also tip-dots patterns because of the droplet split, shown in figure 4(b).



Figure 4. Optical microscope image of printed silver (a) lines and (b) dots with different pulse width.





Lines and dots are generated by changing the printing speed or frequency. It affects the distance of two nearby dots by the time period of droplet deposited onto the substrate. Once a small frequency or large speed are applied in printing, separate dots are printed, shown in figures 5(b) and 5(d). With the

increase of frequency and decrease of speed, the dots become close to each other, forming a dense dots arrays. Due to the constant voltage, pulse width and stand-off distance, the size of the dots don't change. Lines are fabricated while two or more adjacent dots overlap with each other, shown in figures 5(a) and 5(c). At this condition, the width of lines is changed with frequency and speed. The droplet is large and aggregates together during the printing process, which results in different widths of lines at a low solidified rate of nanoink. The shifting speed is changed by moving the platform in our experiment, where the electrical field is also changed. Many defects will appear at high moving speed during the printing process, especially in manufacturing some complex functional patterns.

With computer design, many functional patterns are realized by e-jet printing. Figure 6(a) is a micro-glass composed of silver lines and circles. The linewidth is about 30 to 35 μ m. It is noticeable the linewidth of the circle is larger than the line, which is caused by the circle route of printing at a small speed. With the spread of nanoink deposited on the substrate, the outline of the circle becomes wider. The line patterns connected together as circuit candidates in electronics are shown in figure 6(b). Both circles and lines are fabricated by e-jet printing with silver nanoink, which indicates the good printing performance in manufacturing most functional patterns on the substrate. The letters of 'QUST' grouped by micro silver dots are generated in figure 6(c). The amplified optical image is shown in figure 6(d). The diameter of the dot is 36 μ m, almost the same as the diameter of the needle. The dot is very uniform and regular, which is the high-quality results of optimizing printing parameters.



Figure 6. Optical microscope image of printed designed silver patterns. (a) micro-glass, (b) circuit, and (c) letters with dots. (d) is the magnified image of one dot in (c).

Multi-layer silver lines are printed for X-ray absorption analysis by multiple e-jet printing. The lines were deposited layer by layer at a small shifting speed. The previous layer became solid partly while the new layer deposited. Thus, high density and thickness silver line are generated to form the X-ray image in the system of figure 7(a). A 30 kV, 1000 μ A X-ray source was employed for scanning the samples. The exposure time was 6500 ms to get a high-quality image. The detector with resolution 3072×3888 was used to get the X-ray transmitted data. Each pixel has position information with grey value to indicate the absorption ability of X-ray. Figure 7(b) shows the amplified optical image of silver lines 1, 10, and 50 layers. The mean width is 18.64 μ m, 19.56 μ m and 28.43 μ m, respectively. The width difference is caused by the spread of printed nanoink. The more number of layers are, the wider of the lines generate. The different layers represent single layer line, medium layer line and thick layer line. Furthermore, other different layers between 1 and 200 layers can also be printed according to the requirements.



Figure 7. (a) Schematic of the X-ray imaging system. (b) Optical microscope and (c) X-ray image of multi-layer silver lines.

The X-ray image is shown in figure 7(c). The lines are clear with a different gray value which is obtained with image processing in Matlab. The gray value ratio $G=I/I_0$, where I and I_0 are gray value of the substrate and printed silver lines, separately. The dark color in the image refers to the small gray value. Thus, a small gray value ratio means high X-ray absorption ability. With the printing layer increase, the color of the lines in the X-ray image becomes dark. It is due to the larger absorption rate of X-ray of 50 layers than 10 layers and a single layer. The X-ray shielding efficiency is determined by the density and thickness of the structure. In e-jet printing, larger number layers result in higher density and more thickness. They have much more atoms at the direction X-ray passed through, leading to better absorption ability. However, it is still a challenge to get sufficient thick layer for radiation shielding, because of the flow of ink during the printing process. In the future, we will focus on building several grating masks and print silver nanoink into them to enhance the X-ray shielding ability.

4. Conclusion

To summarize, we have printed functional silver micro-structures of different typical dots and lines using an e-jet printing. The influence of printing parameters on results was discussed. With high voltage, large pulse width or small stand-off distance, the size of dots increase. By increasing frequency or decreasing shifting speed, the distance between dots becomes short, then the structures are getting into lines from dots. The printed silver structures show good absorption of X-ray by an imaging system measuring, resulting in application potentials in electronics radiation shielding. The research provides a significant method of fabricating functional micro-structures of e-jet printing and could pave a way for the applications in electronic radiation shielding.

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