Study of aerosol jet printing with dry nanoparticles synthesized by spark discharge

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Abstract. A new method of aerosol jet printing utilizing dry (solvent-free) airborne nanoparticles generated by spark discharge is proposed. This method was applied to fabricate thin conducting lines (60–160 μm) composed of silver nanoparticles on the surface of glass substrates. It has been demonstrated that the line width is determined by a sheath flow rate, while its thickness and cross-sectional area can be scaled up by a number of printing runs. The resistivity of printed lines after the annealing was found to be five times higher than that of bulk silver that is attributed to the porosity and the interparticle contact resistance. The proposed method holds promise for the application in technologies of printed electronics.

1. Introduction
In recent years there is an active development of new methods for the production of cheap electronic devices by printing equipment [1]. Aerosol jet printing is one such method. The conventional approach of aerosol jet printing is based on the selective deposition of focused beams of microdroplets on a substrate with nanoparticles inside. The use of nano-ink causes some significant problems, such as environmental pollution due to the use of organic solvents and necessity of removing and recycling solvent and surfactant after deposition. In this regard, researchers are developing and investigating the new environmentally friendly and versatile source of nanoparticles for aerosol jet printing, which does not require the use of inks with solvents. For example, the spark discharge generator [2] is a promising source of dry nanoparticles for aerosol jet printing. The spark discharge generator does not require the use of solvents and is a great alternative for pneumatic and ultrasonic atomizers. However, the use of the spark discharge generator for aerosol jet printing is insufficiently investigated due to the complexity of the design of the spark discharge generator and the novelty of the approach. In this work we used the spark discharge generator and investigated the characteristics of the lines formed in different modes of aerosol jet printing.

2. Experimental
The experimental setup consisted of a multi-spark discharge (m-SDG) generator and a commercial system for the particle deposition AJ 15XE with coaxial nozzle 100 μm in outlet diameter (figure 1a). Aerosol nanoparticles were synthesized by the m-SDG as a result of electrical erosion of silver electrodes in air [2]. The aerosol flow $Q_a$ entered the coaxial nozzle through the inner cylindrical channel, while the sheath flow $Q_{sh}$ was inserted through the outer conically converging axisymmetrical channel. The distance between the nozzle and substrate were fixed in the experiment as 0.5 mm. Then the focused aerosol beam was directed to the glass substrate for deposition. In the process of moving the substrate relatively to the focused aerosol beam, we formed the line of deposited silver nanoparticles on the substrate.
Characteristics of the lines were studied depending on changes in sheath flow rate (from 35 to 100 sccm), number of printing runs (from 9 to 36) and speed motion of the substrate (from 3 to 40 mm/min). Printed lines were annealed in a muffle furnace at 450°C for 1 hour at air atmosphere. Aerosol nanoparticles were characterized by the aerosol spectrometer SMPS 3936 before their entering the nozzle. Figure 1b demonstrates the particle size distribution of aerosol nanoparticles measured before their entering the nozzle. It has been found that while entering the nozzle the size of agglomerates is in the range from 15 to 100 nm, and their mean size is about 44±6 nm. These particles have high inertia due to the high density and high velocity values at the nozzle exit more than 150 m/s.

The width of formed lines was measured by using the optical microscope KH-7700. The microstructure, cross-sectional profile and thickness of the line were studied using scanning electron microscope (SEM) JSM-7001F and profilometer DektakXT. Electrical resistivity of the printed and sintered lines was measured by four-probe method.

3. Results and discussions
It is found that an increase of the sheath flow rate \(Q_{sh}\) from 35 to 100 sccm at a constant flow rate of aerosol \(Q_a\) leads to a decrease in the diameter of the aerosol beam and as a consequence a decrease of the line width \(W\) from 160 to 85 μm (figure 2a).

Figure 1(a, b). (a) The scheme of the aerosol jet printing with dry nanoparticles; (b) Particle size distribution of aerosol nanoparticles measured before their entering the nozzle by the aerosol spectrometer.

Figure 2(a, b). (a) The image of the printed lines in the optical microscope related to the sheath flow rate \(Q_{sh}\); (b) The dependence of the width of the line \(W\) from the sheath flow rate \(Q_{sh}\).
It was found that the dependence of the line width \( W \) on the flow rate is described by the following expression:

\[
W \sim k \cdot D_n \sqrt{\frac{Q_a}{Q_a + Q_{sh}}}
\]

(1)

where \( k \) – is the function of increasing the line width due to the diffusion displacement of the nanoparticles [3] and the spreading of the material on the surface during the deposition process [4]; \( D_n \) is nozzle outlet diameter.

Equation (1) shows that an increase of the sheath flow rate \( Q_{sh} \) at a constant flow rate of aerosol \( Q_a \) leads to a decrease in the line width \( W \). Experimental confirmation of this dependence is presented in figure 2b. The minimum line width is reduced up to 60 \( \mu m \) at high values of sheath flow rate.

The cross-section profile of the printed line has a bell-shaped according SEM image of the cross-section of the line and data surface profilometry see figure 3a and b, respectively. We found that the average thickness \( t \) and cross-sectional area \( A_s \) of the lines can be raised more than 2 times by increasing the number of printing runs \( N_p \) from 9 to 36 at \( Q_{sh} = 90 \) sccm, \( V_s = 10 \) mm/min (figure 3b). A similar dependence was observed by decreasing the speed of motion of the substrate \( V_s \) at \( Q_{sh} = 90 \) sccm, \( N_p = 6 \) (figure 4a). These both results are explained by the growth amount of material which is deposited per unit time onto the substrate.

**Figure 3 (a, b).** (a) Cross-sectional SEM image of a sintered line formed by aerosol jet printing with dry nanoparticles; (b) Effect of number of printing runs on cross-sectional profile, average thickness and line width measured by surface profilometer at \( Q_{sh} = 90 \) sccm, \( V_s = 10 \) mm/min.

It is known that the amount of material exiting from nozzle and deposited on a substrate is determined by the following equation taken from [4]:

\[
Wt \approx A_s = \left( \frac{\rho_e}{\rho_s} \right) \frac{V_e A_s}{V_s}
\]

(2)

where \( A_s \) – cross-sectional area of the printed line, \( w \) and \( t \) – width and thickness of the as-printed line, respectively, \( \rho_e \) and \( \rho_s \) – densities of the aerosol beam and the coalesced as-printed material, respectively, \( V_e \) and \( V_s \) – exit velocity of the aerosol beam and stage speed, respectively.

Thus, decreasing the stage speed \( V_s \) at a fixed aerosol \( Q_a \) and sheath flow rate \( Q_{sh} \) or exit velocity \( V_e \) leads to an increase in the line width \( W \) and thickness \( t \), as illustrated in figure 4a. Moreover, figure 4b shows that the width of lines \( W \) changes significantly at low stage speed of 3-10 mm/min and become almost constant at high stage speed. Thus, it has been found that at low stage speed \( V_s \), the effect of
spreading the line in the lateral direction is observed. The spreading effect of the line disappears at high speed of substrate of more than 20 mm/min and the line width $W$ depends mainly on the diameter of the aerosol beam (figure 4b).

![Figure 4. (a, b). Effect of speed substrate on cross-sectional profile, average thickness, line width and cross-sectional area measured by surface profilometer at $Q_{sh} = 90 \text{ sccm}$ and $N_p = 6$.](image)

Using the results of measurements of cross-sectional area, the length and line resistance, the electrical resistivity of the formed lines, which amounted to about 7.5 $\mu\Omega\cdot\text{cm}$ was determined. Thus, electrical resistivity of sintered lines of silver nanoparticles is 5 times higher than that of bulk silver is determined by the results of electrical measurements. This result is due to the presence of pores in lines and the high contact resistance between the nanoparticles. The obtained results indicate the need for new optimization research of the sintering lines.

4. Conclusion
This work presents a study on the characteristics of silver lines printed at various modes of new solvent-free method of aerosol jet printing. It has been established that when controlling parameters of aerosol jet printing one can form functional lines in a wide range of width values from 60 to 160 $\mu$m. The same printed lines can be used in printed electronics devices.

Acknowledgments
This work was supported by a grant from the Russian Science Foundation (project № 15-19-00190).

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