Laser sintering of silver nanoparticles deposited by dry aerosol printing

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Abstract. This work is devoted to the sintering of silver nanoparticle arrays in the form of lines by the local treatment with laser radiation with wavelengths of 527, 1054 and 1064 nm in pulsed and continuous laser modes. The silver nanoparticle lines were formed by the dry aerosol printing, free from organic solvents and surfactants. To form the lines with a width of 25–300 μm and a thickness of 0.1–15 μm a focused stream of nanoparticles with an average size of about 60 nm was used. It is shown that when using continuous laser radiation with a wavelength of 1064 nm, the minimal specific resistance of silver nanoparticle lines was achieved 3 times higher than that for the bulk material was reached.

1. Introduction

In a large number of microelectronic components it turned out to be more cost effective to refuse from lithographic technologies and develop printing technologies that use direct material delivery to form microstructures. Currently, the most promising technology in printed electronics is the aerosol printing based on the selective deposition of aerodynamically focused nanoparticle beams on a substrate [1]. With this method it would become possible to produce microstructures on curved surfaces, transistors [2], solar cell elements [3], multilayer ceramic capacitors [4], microheaters [5], and other elements. Previously, the authors proposed to use aerosol spark discharge generator to form nanoparticle flows for aerosol printing [1]. In this way aerosol nanoparticles are synthesized by electrical erosion of electrodes of required material in the processes of repetitive spark discharge in a gas flow [6]. This allows to obtain a stream of dry aerosol nanoparticles from metals, their oxides and semiconductors [7, 8]. Additionally, the shape and size distribution of the particles is controlled using a tube furnace [9] or electrostatic precipitator [10]. The dry aerosol nanoparticles stream is then focused and delivered to the substrate. The use of dry nanoparticles is preferable, as in the following sintering process there is no need to preliminary remove solvent [11, 12].

An important advantage of the aerosol printing method is the possibility of further sintering of the deposited structures at lower temperatures due to the small particle size. Consequently it is possible to print conductive microstructures on heat-sensitive substrates, for example, on plastic [13]. Actually, the sintering of nanoparticle arrays deposited on a substrate is efficient to produce by laser radiation heating as this method delivers energy to the sample locally without damaging the substrate material [11, 14].

The sintering process result was evaluated by measuring the specific electrical resistivity of the final micro-sized samples. Thus, in [11, 14] the resistivity of sintered samples was 3–15 times higher than the resistivity of bulk silver. This means that the challenging task is to find the optimal conditions for laser
sintering of nanoparticle arrays which may depend on both as material and size of particles and so as on the parameters of laser radiation. In the present work, this problem is solved for laser sintering of silver nanoparticle arrays formed by the dry aerosol printing method.

2. Experimental

The experiment was carried out in two processes separated in time: in the first process a layer of silver nanoparticles was formed by the dry aerosol printing and its local laser sintering was accomplished during the second pass.

The scheme of experimental setup for forming nanoparticle arrays in the form of lines is shown in figure 1 (a). It includes a spark discharge nanoparticle generator, (the operation principle is given in the article [7]), a thermal optimizer in the form of a tube furnace which changes nanoparticles shape and size [9], a coaxial nozzle for nanoparticles depositing and a coordinate table which moves the substrate at a given speed. To form the lines with a width of 25 – 300 μm and a thickness of 0.1 – 15 μm a focused stream of silver nanoparticles with an average size of 60 nm was used. The shape of the coaxial nozzle and the parameters of the gas flows were chosen on the basis of the previous theoretical and experimental studies [15 - 17]. Nanoparticles were deposited on a substrate between two previously applied conductive contacts necessary for measuring the specific resistance.

![Figure 1(a, b).](image)

Figure 1(a, b). (a) The sketch of the experimental setup for forming lines of silver nanoparticles; (b) Optical scheme for laser sintering of silver nanoparticles deposited lines.

For sintering of the formed nanoparticle lines an optical scheme shown in figure 1 (b) was constructed. Laser radiation was delivered to the substrate with a sample mounted on the same moving coordinate table. The sintering processes of nanoparticle arrays were studied by using laser radiation with wavelengths of 527, 1054 and 1064 nm. At the same time the input energy was varied by changing the average power of laser radiation and the movement speed of the laser spot over the array of nanoparticles in the range up to 10 W and 520 mm/s respectively. Additionally the sintering process quality was studied and compared in continuous (CW) and pulsed laser modes. Sintering in a pulsed mode was performed at a pulse repetition rate of 4 kHz with a pulse duration of 20 ns.
In the sintering processes the laser spot diameter in the sample plane was controlled using a Duma Optronics BeamOn HR laser beam profile meter and the power of incident radiation on the sample using an Ophir F150A-BB-26 power meter.

The sintering process results were estimated by the electrical resistivity of the lines. The absolute resistance was previously measured using a Fluke 287 multimeter and the cross section profile with the aid of an optical profilometer Leica DCM 3D.

3. Results and discussion

The conducting lines were formed by nanoparticles, their images from the transmission electron microscope (TEM) JEM-2100 (JEOL) are shown in figure 2 (a). Due to the spherical shape of the deposited nanoparticles the green samples of lines have a low porosity and a high density of contacts between the particles which ensures a high conductivity. Figures 2 (b - f) show images from a scanning electron microscope (SEM) JSM 7001F (JEOL) for characteristic green sample and samples sintered by continuous and pulsed lasers with wavelengths of 527, 1054 and 1064 nm.

Figures 3 (a - d) show the experimental dependences of the specific electrical resistance \( \rho \) of sintered nanoparticle lines for different lasers as a function of the specific energy coming to the sample per second and the speed of the laser spot moving along the array of nanoparticles \( v \) in logarithmic scale. Almost in all dependences (figure 3 (a - d)) for a given radiation power density there is a weakly expressed line resistivity minimum near the moving speed of the laser spot along an array of nanoparticles of about 1 m/s. This speed corresponds to the best result of resistivity 3 times higher in comparison with bulk silver as it shown in figure 3 (d). Sintering regimes in this area are close to optimal. In figure 3 there is an increase in the lines resistivity to the left of the minimum at low scanning speeds, effecting in overheating and evaporation of the sintered material as the dose of delivered laser radiation increased. The growth of the lines resistivity to the right of the minimum at high scanning speeds, where the dose of delivered laser radiation on the contrary decreases, is logically associated with the incomplete sintering of nanoparticles.

Sintering by laser radiation with a wavelength of 527 nm required less energy consumption than by radiation with wavelengths of 1054 and 1064 nm and led to 30-50% greater values of the silver lines resistivity. This feature is explained by the fact that silver nanoparticles better absorb radiation at a wavelength of 527 nm due to the excitation of plasmon effects on them and the absorption efficiency decreases with increasing wavelength [18].
Figure 2(a–f). (a) TEM images of nanoparticles; (b) SEM images of the surface of the green sample; (c–f) SEM images of samples surface sintered by laser radiation: (c) pulsed 527 nm, (d) pulsed 1054 nm, (e) CW 527 nm, (f) CW 1064 nm.
Figure 3(a – d). Dependencies of specific electrical resistivity as a function of the specific energy coming to the sample per second and the speed of the laser spot moving along the array of nanoparticles for four types of lasers.

4. Conclusion

By the example of laser sintering of conductive silver nanoparticle lines there has been demonstrated the advantage of combining the method of dry aerosol printing with laser sintering due to beneficial properties of the local delivery of nanoparticles and laser energy. The best results in laser sintering of conductive silver lines were obtained by continuous laser radiation with a wavelength of 1064 nm. In addition, the results obtained within the study demonstrate that continuous radiation provides more efficient sintering of nanoparticle arrays than pulsed, and radiation with wavelengths of 1054 and 1064 nm is more preferable than with a wavelength of 527 nm for obtaining lines with minimal specific resistivity. However, infrared laser radiation sintering requires greater energy costs than for short-wave radiation. This feature is explained by a higher silver nanoparticles absorption coefficient at a wavelength of 527 nm, which is associated with the excitation of plasmon effects at the resonance absorption at a wavelength of 450 nm, thereat the absorption efficiency decreases with increasing wavelength.
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