Laser sintering of oxidized copper nanoparticles deposited by dry aerosol printing

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Abstract. Sintering of oxidized copper nanoparticles arrays in the form of lines by the local treatment of laser radiation with wavelengths of 527 nm and 980 nm was studied. To form lines with a width equal to 40–150 µm and a thickness equal to 0.5–4 µm focused aerosol jets with average nanoparticle sizes of 110 and 65 nm were used. The production of semiconductor arrays from oxidized copper nanoparticles with a specific electrical resistance of $2 \cdot 10^{-3} \, \Omega \cdot m$ using laser radiation with a wavelength of 980 nm was demonstrated.

1. Introduction
Nowadays, the field of printing technologies for the production of electronic devices (solar cells [1], gas sensors [2]) is actively developing. New methods for the formation of functional microstructures are emerging, which are aimed at simplifying, reducing the cost and minimizing hazardous waste. One of these methods is aerosol printing. It is based on the deposition of aerodynamically focused beams of nanoparticles on substrates. Earlier, the authors of [3-4] demonstrated the possibility of forming arrays of nanoparticles using the dry aerosol printing method.

It is advisable to sinter arrays of nanoparticles formed on a substrate with laser radiation, since this method of energy transfer is local and does not damage the substrate material [5]. Therefore, an urgent task is to find the optimal conditions for laser sintering, which depends on the shape and size of nanoparticles and the laser radiation parameters. In this work, we explore the optimal conditions for sintering by laser radiation of oxidized copper nanoparticles arrays formed using the method of dry aerosol printing.

2. Experimental
To form the nanoparticles arrays in the form of lines used the experimental setup shown in figure 1a. It includes the following key elements: a spark discharge generator of nanoparticles [6-10], a thermal nanoparticles optimizer [11] to control the size and shape of nanoparticles, a coaxial micro-nozzle to deposit nanoparticles on a substrate, a coordinate table to move the substrate at a given speed.

Nanoparticles arrays are formed in dry form without the use of solvents and surfactants [12-14]. Nanoparticles obtained as a result of electrical erosion of copper electrodes are generated and deposited on the substrate in an atmosphere of gas Ar+H2(5%).

The morphology and elemental composition of nanoparticles are studied using a transmission electron microscope (TEM) and an aerosol spectrometer. The structural properties of nanoparticles arrays are studied using a scanning electron microscope (SEM) and an optical profilometer.
Nanoparticles arrays are formed in the form of lines with a width equal to 40–170 µm and thickness equal to 0.4–6 µm. The control of size and shape of the nanoparticles is realized by varying the operating modes of the thermal nanoparticles optimizer.

The processes of sintering by laser radiation were carried out using a fixed optical stand, in which the formed arrays were attached to the same coordinate table [15]. The continuous laser radiation with wavelengths of 527 nm and 980 nm used to study the sintering of the arrays. The laser spot moving over the arrays of nanoparticles and the laser radiation power were also varied in the experiments. The diameter of laser spot in the sample plane and the power of incident radiation on the sample in the sintering processes were controlled using a Duma Optronics BeamOn HR laser beam profile meter and an Ophir F150A-BB-26 power meter, respectively.

The estimation of the sintering processes was realized by the measuring of the electrical resistivity of the lines on a heating plate with temperature of 300°C. The absolute resistance and the cross section profile were measured using a Fluke 287 multimeter and an optical profilometer Sensofar S-neox, respectively.

3. Results
Microstructures formed by primary nanoparticles (PNPs) and thermally optimized nanoparticles (TNPs) have different porosity. It was found that microstructures formed by TNPs have a higher density of contacts between the particles and lower porosity than microstructures consisting of PNPs. The TEM images of PNPs and TNP are shown in figure 1(b, c).

Figure 1. (a) The scheme of the experimental setup; (b) TEM images of PNPs; (c) TEM images of TNP.

Figure 2 (a - d) show images from a profilometer Sensofar S-neox and scanning electron microscope (SEM) JSM 7001F (JEOL) for samples, formed by PNPs and TNPs, sintered by continuous laser radiation with wavelengths of 527 and 980.

The experimental dependences of the specific electrical resistance $\rho$ of sintered lines as a function of the specific power coming to the sample and the speed of the laser spot moving along the array of nanoparticles $v$ in logarithmic scale for two types of lasers are shown in figure 3(a-d). Almost in all dependences for a given radiation power density there is a line resistivity minimum near the moving speed of the laser spot along an array of nanoparticles of about 10 mm/s. Sintering regimes in this area are close to optimal. The best result of resistivity was obtained at the scanning speed of laser spot about 0.28 mm/s as it shown in figure 3(d). There is a resistivity increasing of the lines to the left of the minimum at low scanning speed in figure 3. This is due to overheating and evaporation of the sintered material as the dose of delivered laser radiation increased. High scanning speeds, where the
dose of delivered laser radiation decreases, lead to the growing lines resistivity due to the incomplete sintering of nanoparticles.

Sintering by laser radiation with a wavelength of 527 nm was less energy intensive led to 100-500% greater values of resistivity, than by radiation with wavelengths of 980 nm.

![Figure 2](image)

**Figure 2.** Images from an optical profilometer of microstructures formed by PNsPs (a, b) and TNsPs (c, d), sintered at optimal sintering modes of two lasers. Inset: SEM images of the surface of microstructures.

![Figure 3](image)

**Figure 3.** Dependencies of specific electrical resistivity as a function of the specific power coming to the sample and the speed of the laser spot moving along the array of (a, b) PNsPs and (c, d) TNsPs for two types of lasers.
4. Conclusion
The advantage of combining the method of dry aerosol printing and laser sintering was demonstrated by the example of sintering arrays of oxidized copper nanoparticles. The minimum resistivity at a heating plate temperature of 300°C was observed for arrays formed from TNPs and sintered by laser radiation with wavelength 980 nm near the speed of 0.28 mm/s and equal to $2 \cdot 10^{-3}$ Ω·m. In addition, the results obtained show that continuous radiation sinters arrays of nanoparticles more efficiently than pulsed radiation, and radiation with a wavelength of 980 nm is more preferable than with a wavelength of 527 nm for obtaining lines with minimal resistivity. It was found that with an increase in the scanning velocity of the laser spot, a monotonic decrease in the specific resistance of the printed lines occurs.

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