The influence of the morphology of oxidized copper nanoparticles on the electrical properties of microstructures obtained by dry aerosol printing

D V Kornyushin¹, A A Efimov¹, K M Khabarov¹ and V V Ivanov¹

¹Moscow Institute of Physics and Technology (National Research University), Dolgoprudny 141701, Russia

Abstract. The influence of the morphology of oxidized copper nanoparticles on the deposition efficiency, packing density, and resistivity of microstructures obtained by dry aerosol printing was studied. It has been established that the thermal treatment of aerosol nanoparticles allows to vary their morphology from branched submicron agglomerates to compact spherical nanoparticles with a size of 20-50 nm. It is shown that the use of spherical nanoparticles in comparison with agglomerates allows one to obtain densely packed nanoparticles on substrate. Moreover, obtaining of semiconductor microstructures from oxidized copper nanoparticles on a plastic substrate with a resistivity of 0.01 Ohm • m was demonstrated.

1. Introduction
Currently, printing technologies that use direct delivery of material to form microstructures are actively developing. These methods are more efficient and cost effective. 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]. This method is the most optimal for the production of electronic devices (RFID tags [2], flexible displays, solar cells [3] and others) on flexible plastic substrates. It is expected that these devices will have low cost, low weight and flexibility. The formation of electronic devices on plastic substrates [4] is a difficult task, since plastic substrates have a high sensitivity to thermal treatment. In this regard, the formation of functional elements on plastic substrates is carried out using nanoparticles having a lower sintering temperature than bulk material [5]. At the same time, the use of nanoparticles leads to additional difficulties associated with their low deposition efficiency on the substrate and high oxidative ability, which changes the electrical properties of the microstructure. For this reason, the establishment of the formation of microstructures from nanoparticles on plastic substrates requires multifactorial research. So in this paper, we study the influence of the size and shape of oxidized copper nanoparticles on the electrical properties of microstructures obtained using the dry aerosol printing method on substrates of polyimide and silicon.

2. Experimental
The experimental setup for the formation of microstructures from nanoparticles in the form of lines includes the following key elements: a gas-discharge nanoparticles generator [6-11], a thermal optimizer for controlling the size and shape of nanoparticles [5], a coaxial micro-nozzle for focused deposition of
nanoparticles on a substrate and a coordinate table with the possibility of moving the substrate from a given speed relative to the micro nozzle, see figure 1a. The formation of microstructures from nanoparticles is carried out in dry form without the use of solvents or surfactants [12-15]. The generation and deposition of nanoparticles obtained by electrical erosion of copper electrodes is carried out in an atmosphere of a gas mixture Ar+H2(5%).

The size, shape and elemental composition of the nanoparticles is studied using a transmission electron microscope and aerosol spectrometer. The geometry of the microstructures of the nanoparticles is measured using a scanning electron microscope and an optical profilometer. To form microstructures in the form of lines with a width and thickness equal to 100-200 μm and 0.1-8 μm, respectively, a focused stream of nanoparticles generated from copper electrodes was used. The parameters of the gas flows and the shape of the coaxial nozzle were chosen on the basis of the previous theoretical and experimental studies [16-18]. By varying the operating modes of the thermal optimizer, the size and shape of the nanoparticles are controlled. At the same time, the efficiency of the deposition of nanoparticles on the substrate, their packing density is qualitatively investigated, and the resistivity of microstructures [19] on substrates of polyimide and silicon is measured.

Figure 1(a, b). (a) Experimental setup for the formation of microstructures from nanoparticles on substrates of polyimide and silicon; (b) Median particle size of the agglomerates vs the sintering temperature. Insets: TEM micrographs of typical particles at 25 °C, 100 °C, 500 °C and 1000 °C.

3. Results

Figure 1b shows that with an increase in the sintering temperature of nanoparticles from 25 °C to 1000 °C, the median size of nanoparticles decreases from 108 to 65 nm, respectively. Moreover, from the analysis of TEM images of unsintered (25 °C) and sintered (1000 °C) nanoparticles shown in the inset in figure 1b, it is shown that branched fractal agglomerates >100 nm in size are transformed into compact spherical particles of the order of 20-50 nm.

From analysis of the efficiency of deposition of nanoparticles on polyimide and silicon substrates, it was found that both agglomerates and spherical nanoparticles are more efficiently deposited on a polyimide substrate, see table 1. In this case, spherical nanoparticles have a lower deposition efficiency on a silicon substrate in comparison with agglomerates, see figure 2. This result is probably associated with a higher coefficient of rebound of spherical nanoparticles from a solid silicon substrate.
Table 1. Comparison of the efficiency of deposition of agglomerates and spherical nanoparticles on a silicon and polyimide substrates.

| Morphology of nanoparticles | Type of substrate | Cross-section area, μm² | Deposition efficiency¹ |
|-----------------------------|-------------------|-------------------------|------------------------|
| Agglomerates²               | Polyimide         | 196                     | 4,4                    |
|                             | Silicon           | 135                     | 1,6                    |
| Spherical nanoparticles³    | Polyimide         | 122                     | 4,1                    |
|                             | Silicon           | 65                      | 1,4                    |

¹ deposition efficiency is the dimensionless ratio of the number of nanoparticles deposited on the substrate to the number of nanoparticles emitted from the nozzle;
² agglomerates - a set of primary (single) nanoparticles held together by the forces of Van der Waals, having a branched shape;
³ spherical nanoparticles - agglomerates that have passed through heat treatment in the optimizer and acquired a spherical shape.

Figure 2(a, b). (a) Cross-section areas of microstructures formed by agglomerates; (b) spherical nanoparticles.

The packing density of microstructures of nanoparticles deposited on a silicon substrate depending on the morphology of the nanoparticles was studied using scanning electron microscopy, see Figure 3. It was found that microstructures formed from deposited spherical nanoparticles have lower porosity than microstructures consisting of agglomerates.

The dependence of the electrical resistivity of microstructures formed from agglomerates and spherical nanoparticles on the ambient temperature was studied, see table 2. For this the substrates on which microstructures of agglomerates and spherical nanoparticles were formed were placed on a heating plate and measurements of electrical resistance were made in the temperature range from 25 °C to 300 °C. Taking into account the measurement error, it was found that at 300 °C the resistivity of microstructures formed from spherical nanoparticles is less than the resistivity of microstructures made form agglomerates. This is probably due to the lower porosity of microstructures formed from spherical nanoparticles.
Figure 3(a, b). (a) SEM images of cross-sectional profiles of microstructures from deposited agglomerates; (b) spherical nanoparticles.

Table 2. Temperature dependence of the electrical resistivity of microstructures formed from agglomerates and spherical nanoparticles.

| Morphology of nanoparticles | Resistivity of microstructure ($\rho$), Ohm*m | at 25°C | at 50°C | at 100°C | at 150°C | at 200°C | at 250°C | at 300°C |
|-----------------------------|---------------------------------------------|---------|---------|----------|----------|----------|----------|----------|
| Agglomerates                |                                            | ± 172,13 | ± 59,28 | ± 2,87   | ± 0,34   | ± 0,13   | ± 0,06   | ± 0,04   |
| Spherical nanoparticles     |                                            | 8,21    | 5,49    | 0,31     | 0,04     | 0,03     | 0,02     | 0,01     |
|                             |                                            | ± 74,52 | ± 3,12  | ± 0,07   | ± 0,04   | ± 0,01   | ± 0,01   |
|                             |                                            | ± 6,28  | ± 0,25  | ± 0,02   | ± 0,01   | ± 0,01   |

4. Conclusion
It was found that the deposition efficiency and the packing density of nanoparticles on the substrate significantly depends on the size and shape of the nanoparticles and the type of substrate. From analysis of the efficiencies of the deposition of nanoparticles on polyimide and silicon substrates, it was found that both agglomerates and spherical nanoparticles are more efficiently deposited on a polyimide substrate. At the same time, microstructures formed from compact spherical nanoparticles have higher values of the packing density of nanoparticles and, as a result, the minimum resistivity.

Acknowledgments
This work was supported by the Russian Science Foundation (project # 19-79-00375).

References
[1] Efimov A A, Potapov G N, Nisan A V and Ivanov V V 2017 Results in Physics. 7 440-3
[2] Singh R, Singh E and Nalwa H S 2017 RSC advances. 7 48597-630
[3] Yang C, Zhou E, Miyaniishi S, Hashimoto K and Tajima K 2011 ACS Appl. Mater. Interfaces 3 4053–58
[4] Efimov A A, Minkov K N, Arsenov P V, Protas N V and Ivanov V V 2018 IOP Conf. Ser.:
\[ J. \text{Phys.} \ 1124 \ 081041 \]

[5] Lizunova A A, Efimov A A, Arsenov P V and Ivanov V V 2018 IOP Conf. Ser.: Mater. Sci. Eng. 307 012081

[6] Arsenov P V, Efimov A A, Protas N V and Ivanov V V 2018 IOP Conf. Ser.: Mater. Sci. Eng. 324 012016

[7] Mylnikov D, Efimov A and Ivanov V 2019 Aerosol Sci. Tech. 53 1393–403

[8] Ivanov V V, Efimov A A, Myl’nikov D A and Lizunova A A 2018 Russ. J. Phys. Chem. 92 607–12

[9] Lizunova A A, Mylnikov D A, Efimov A A and Ivanov V V 2017 J. Phys.: Conf. Ser. 917 032031

[10] Mylnikov D, Lizunova A, Borisov V, Paranin S and Ivanov V 2018 Orient J Chem 34 5

[11] Mylnikov D A, Urazov M N, Efimov A A, Lizunova A A and Ivanov V V 2017 AIP Conf Proc 1858 040007

[12] Theodorakos I, Zacharatos F, Geremia R, Karnakis D and Zergioti I 2015 Appl. Surface Sci. 336 157-62

[13] Efimov A, Arsenov P, Kornyushin D, Lizunova A, Volkov I and Ivanov V 2020 Materials 13 730

[14] Arsenov P V, Efimov A A, Khabarov K M, Kornyushin D V and Ivanov V V 2020 Key Eng. Mater. 834 37-41

[15] Efimov A A, Arsenov P V, Protas N V, Minkov K N, Urazov M N and Ivanov V V 2018 IOP Conf. Ser.: Mater. Sci. Eng. 307 012082

[16] Protas N V, Efimov A A, Zemlyanoy V K and Ivanov V V 2018 IOP Conf. Ser.: J. Phys. 1124 081033

[17] Arsenov P V, Efimov A A and Ivanov V V 2018 Key Eng. Mater. 2018 779 159-64

[18] Khabarov K, Kornyushin D, Masnaviev B, Tuzhilin D, Saprykin D, Efimov A and Ivanov V 2020 Appl. Sci. 10 246

[19] Arsenov P V, Efimov A A and Ivanov V V 2020 Key Eng. Mater. 834 10-5