Analysis and 3D modelling of percolated conductive networks in nanoparticle-based thin films

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5 Abstract

A methodology to model the percolated conductive network in nanoparticle-based thin films, synthesized by means of a magnetron-based gas aggregation source, was developed and validated. Two differently sized copper oxide nanoparticles were produced by varying the diameter of the exit orifice. Comprehensive characterization of these films was performed using scanning electron microscopy, transmission electron microscopy, small-angle X-ray scattering and X-ray diffraction to determine particle morphology, size distribution, porosity, vertical density profiles, and phase composition. Using the experimental data, virtual films were generated through a data-driven stochastic 3D microstructure model that is based on a sphere packing algorithm, where the particle size distribution, porosity and vertical density profile are taken into account. The generated 3D structures have been then refined to cover the effect of oxidation of as-deposited nanoparticles and non-zero roughness of real films. A computational model incorporating a simplified adsorption model was developed to simulate the effects of oxygen adsorption on the surface conductivity of the nanoparticles. Then, the electrical conductivity of the percolated networks in these virtual structures was computed using the finite element method for various partial oxygen pressures. Simulated resistivity values were compared with experimental measurements obtained from four-point probe resistivity measurements conducted under varying oxygen partial pressures at 150 °C. A discussion of the validity of the model and its ability to cover qualitatively and quantitatively the observed behaviour is included.

Keywords: 3D microstructure modelling, Nanoparticle-based thin films, Percolated conductive networks, Magnetron-based gas aggregation cluster source, Adsorption model

1. Introduction

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Nanostructure-based materials have been in the scope of material scientists for decades. Compared with their bulk counterparts, nanomaterials exhibit unique properties related mainly to their high surface-to-volume ratio, enormously large specific surface area and specific electronic structure modified due to characteristic nanometric dimensions. All these properties are exploited when nanomaterials are used as conductometric gas sensors – so-called chemiresistors [1, 2].

Enormous effort has been devoted to the synthesis of chemiresistive nanomaterials formed by various types of nanostructures, such as nanowires, nanotubes, nanodots, etc. [3, 4, 5, 6, 7]. Among others, nanoparticle-based materials are of great importance since there are numerous available methods of their

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synthesis, including liquid-phase-based methods (e.g., sol-gel, sonication, hydrothermal) and gas-phase-based methods (e.g., spray pyrolysis, electrospraying, sputtering) [4, 8, 9].

- Magnetron-based gas aggregation source (MGA) of nanoparticles (NPs) is based on the aggregation of the nanoparticles from a gas phase of magnetron-sputtered material, which is supersaturated in an aggregation chamber by a high-pressure working gas (typically Ar). The formed NPs are then carried by the working gas out of the aggregation chamber through an exit orifice. The main advantage of NPs prepared by MGA is their high purity since they are produced without any precursor. Moreover, the NPs can be produced from many various sputterable materials or their compounds (*e.g.*, Cu[10], Au[11],
- Ag[12], TiO₂[13, 14], CuO[15], WO_x[15]). Recently, we have shown [10] that the size of NPs produced by the MGA can be efficiently varied by controlling the exit-orifice diameter or by a mass filter integrated into the MGA [16]. In recent years, numerous publications have focused on the appearance and structure of MGA NPs, including the inner structure of NPs [14, 17, 18]. However, little attention has been paid to the collective behaviour of these particles [19]. Even if we have successfully employed CuO NPs for
- ³⁰ hydrogen gas sensing [20], not enough is known about how the particles interconnect with each other and behave when they form a continuous film. This knowledge would be beneficial for the preparation of new NP-based materials and would also boost the research of composite NP-based materials (combining NPs of different materials [15]). However, such a task is demanding to be performed purely experimentally. Thus, the present study presents a methodological workflow that combines data-driven stochastic 3D
- ³⁵ microstructure modelling and finite element simulations to compute the electrical resistivity. Therefore, a broad range of virtual but realistic 3D structures of CuO NPs can be generated in the future just at the cost of computer simulations. This lays the ground for an approach called virtual materials testing, where quantitative process-structure-property relationships can be established. This approach has been applied - among others - to open-cell foams [21], fiber-based materials [22] or lithium-ion batteries [23].
- ⁴⁰ To address the described lack of understanding, we characterize NP-based thin films synthesized by MGA by various analytical methods (mainly scanning electron microscopy (SEM), small angle X-ray scattering (SAXS) and X-ray diffraction, XRD)) and, at the same time, characterize individual NPs via SEM and transmission electron microscopy (TEM). The resulting information is used as input for modelling the stochastic 3D microstructure of the film. Subsequently, virtually generated structures are
- ⁴⁵ used to compute the electrical conductivity of the percolating network of the simulated nanoparticles. At the same time, the conductivity measurements are performed on real structures, and the results are compared.

The main contribution of the presented work is in the construction and verification of the methodology, which enabled us to create a 3D model of the thin films formed by NPs. The novel model constructed for synthesized NP-based films will enable a faster development of functional materials based on MGA NPs. There are only a few publications on percolating networks of NPs describing mostly monodisperse NPs [24]. To the best of our knowledge, none of these focuses on particularly MGA NPs, which naturally exhibit a polydisperse distribution.

2. Methodology

In Figure 1, the overall strategy employed in this work is depicted. NP-based thin films were prepared using an MGA (Synthesis) in various configurations and on different substrates to enable various analytical measurements. The applied methods provided the information to generate model structures (Virtual synthesis) based on a sphere packing algorithm. In the next step, the resistivity of the model structures was determined (Virtual experiment) and compared with the measured resistivity of real samples.



Figure 1: Schematic flow chart of the overall strategy. The individual subsections of Methodology section can be linked to individual process parts.

In the following, the individual steps are described in detail and closely mirror the structure illustrated in the flow chart in Figure 1.

2.1. Synthesis



Figure 2: Schematic diagram of the whole deposition system.

A custom-built high-vacuum deposition system equipped with an MGA (HVM Plasma Ltd.) depicted in Figure 2 was used for the synthesis of nanoparticles. The MGA consists of a cylindrical magnetron (equipped with an in-situ axial movement) placed inside a grounded cylindrical aggregation chamber of a diameter of 100 mm terminated by a conical ending with a replaceable exit orifice (cylindrically-shaped orifices with a diameter of 1.5 and 4 mm and a length of 3 mm were used in this work). For clarity, throughout the text, the films/particles will be referred to as "Large NPs" for those prepared with ⁷⁰ the 1.5 mm orifice and "Small NPs" for those prepared with the 4.0 mm orifice due to the various size distributions specified later.

The aggregation chamber was baked out to ~100 °C prior to each deposition and water-cooled during the deposition. The base pressure before each deposition in both the main and aggregation chambers was below 5×10^{-5} Pa. The working pressure of Ar in the aggregation chamber was 120 Pa. The magnetron was equipped with a circular Cu target (50 mm in diameter, 3.2 mm in thickness) and the target-toorifice distance was set to 150 mm. The magnetron was driven by a DC power supply at a constant average target power density of 5 W/cm^2 . More details about the system can be found in [10].

The NP-based films were primarily deposited on 12.5 μm thick Kapton foil (Kapton 50HN, Dupont) stuck to ultrasonically cleaned Si substrates with the aid of carbon tape. These substrates were used
due to their low background signal during small-angle X-ray scattering (SAXS) analyses. The equivalent depositions were also carried out on pre-scratched silicon substrate enabling subsequent break of substrate to acquire cross-sectional views of films. Depositions with a scarce concentration of nanoparticles were performed on Si substrate as well as transmission electron microscope grids. These samples were used for microscopic investigations of the particle size distribution and the internal structure of NPs, respectively.

Due to the much lower and wider flux of NPs with the 1.5 mm orifice compared to the 4 mm orifice (see [10]), two different substrate holder configurations were used to get sufficiently thick films with a reasonable thickness homogeneity. For the 1.5 mm orifice, close-to-orifice depositions were performed using an additional substrate holder positioned at a distance of 50 mm from the exit orifice. With the

- ⁹⁰ aid of in-house designed software, the holder could be rotated along an axis parallel to the axis of the beam of nanoparticles spanning the diameter of the aggregation chamber. The holder was without a shutter, but the controlled movement of the holder allowed for voltage stabilization at a far-off spot before actual deposition. In the case of the large orifice, a rotating (40 rpm) standard substrate holder positioned at the standard distance of 400 mm from the exit orifice was used.
- After the SAXS analyses were completed, the same samples were cut to a size of $9 \times 9 \text{ mm}^2$ and equipped with a square platinum electrode of approximately $3 \times 3 \text{ mm}^2$ at each corner to investigate their resistivity by the four-point method. The electrodes covered the substrate area from the edges towards the centre, leaving an uncontacted cross-shaped area in the middle with an approximately 1500 µm pitch.

100 2.2. Analyses

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In this section, the individual analytical methods are described, some of them are used for deriving multiple quantities at once playing a role in subsequent processes.

2.2.1. Shape and internal structure of NPs

The appearance of the particles was checked by a scanning electron microscope (SEM) Hitachi SU-70. ¹⁰⁵ The deposition duration was adjusted to get incomplete coverage of the surface and individual particles can thus be distinguished in SEM micrographs.

To examine the internal structure of individual nanoparticles, the Thermo Fisher Talos L120C Transmission Electron Microscope with a LaB₆ cathode was utilized. The acceleration voltage is given by 120 kV. Particles were deposited on TEM grids with thin graphitic foil. Afterward, the particles were 110 coated with 5 nm thick graphite film to prevent them from leaving the grid.

The internal structure of NPs was also examined by means of X-ray diffraction (XRD) using Rigaku SmartLab diffractometer equipped with 9 kW Cu rotating anode X-ray source (Cu K_{α} radiation $\lambda = 0.15418$ nm) in a parallel beam geometry with a constant incidence angle of the primary beam $\omega = 1^{\circ}$.

2.2.2. Size distribution and porosity

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SAXS technique was employed to analyse the size distribution and inert structure of nanoparticles, as well as the mean porosity of the samples. The measurement in the transmission geometry was done in Xenocs Xeuss 2.0 SAXS instrument with the Cu X-ray source ($\lambda_{CuK\alpha} = 0.15418 \text{ nm}$) with the sample to the detector (Dectris Pilatus 200) distance of 2500 mm. Acquired data were masked, integrated, normalized to the absolute scale in intensity (using a standard glassy carbon sample) and corrected for background. The final data were fitted in the IRENA package [25] in the IGOR Pro software by the model of diluted core-shell spheres. The X-ray scattering length densities were used as follows, copper core (10^{10} cm^{-2}) and copper(I) oxide shell ($44 \times 10^{10} \text{ cm}^{-2}$). For analysis with SAXS, the particles were deposited on Kapton, forming films thicker than 500 nm.

The size distribution from the SAXS method was compared to the one derived from SEM imaging. ¹²⁵ For this purpose, the above-described sample on silicon substrates with a low concentration of NPs was prepared. SEM micrographs, each targeting hundreds of NPs, were binarized, and the size distribution of assumed circular grains was fitted by a log-normal distribution. For more details, we refer to [10].

2.2.3. Layer thickness and vertical density profile

Since the deposited layer of nanoparticles is highly inhomogeneous (the particles form a circular pattern on the substrate), it was necessary to accurately determine the deposited spot's profile. For this 130 purpose, samples were inspected after completing all other measurements. The films were scratched with a sharp tip in six different areas of the covered region to expose the substrate. These areas were then scanned using atomic force microscopy (AFM, AIST-NT SmartSPM) in a semi-contact mode and the thickness of the layer at those locations was determined from the measured profiles (not shown). The positions of all measured thicknesses relative to the corners of the platinum electrodes were determined 135 using the calibrated optical microscope on the AFM. Subsequently, the measured points (their exact positions relative to the electrodes and the thickness of the layer) were fitted with a rotational Gaussian model. This approach allowed us to determine the shape of the deposited material. Such fitted Gaussian is depicted in Supplementary Data S.1. With the precise positions of the electrodes known, it was possible to use the finite element method (FEM) to determine the "equivalent thickness of the material", which 140 expresses how thick a homogeneous layer of material would be to have the same sheet resistance as the measured circular spot.

The vertical density profile, *i.e.*, the probability of finding a NP at a certain distance ("altitude") from the substrate, was determined from cross-sectional micrographs of broken samples with thick films, which were deposited along with the films for SAXS measurements. SEM micrographs were carefully acquired in a low-depth-of-focus regime. This enabled a manual highlighting of particles that were on the very edge of the exposed break. Several skylines of such exposed layers were manually obtained, and the resulting vertical distribution was produced by averaging and normalizing these records. The reader is referred to Figure 8 in Results section for more details.

150 2.2.4. Sheet resistance measurements

Resistance measurements were carried out using a custom-built system, which allows for conductivity measurements using the four-point probe (4PP) method. The spring-loaded gold-coated contact tips of the measuring system are arranged in a square pattern with a spacing of 8 mm. The NP-based films are easy to tear off, so the Kapton foil used as a substrate was equipped with platinum contact electrodes prior to the nanoparticle deposition.

The custom-built 4PP system enables measuring resistivity in defined conditions, including elevated temperature (from room temperature to 500 °C) and defined atmosphere. For measurements of presented



Figure 3: Scheme of four-point resistance measuring system. Four clamps contacting the specimen in the corners are visible in the cutout.

samples, the various concentrations of oxygen gas in nitrogen gas were used (commented later). The mixing was done using two flow controllers (Alicat Scientific) connected to pure gases (O_2, N_2) , keeping a constant flow of 0.203 Pa·m³·s⁻¹ (120 sccm). The scheme of the 4PP system is depicted in Figure 3. It is important to mention that it was not possible to measure the resistance of the NP-based films

at room temperature in an as-deposited state due to their very low conductivity. For this reason, the films were heated in the 4PP system in the presence of air to 300 °C for two hours while still measuring the resistance. After stabilization of the measurement output, the temperature was lowered to 150 °C at which the final measurements were conducted. This procedure, of course, altered the appearance and composition of the particles, as discussed later.

2.3. Virtual synthesis

The NP system is modelled in 3D using spherical core-shell particles, where the core and shell correspond to copper and the copper oxide layer, respectively. This corresponds to the findings of TEM imaging. First, a hard-sphere packing algorithm is used to generate a system of non-overlapping copper particles as it is during deposition. A subsequent swelling mimics the formation of the oxide layer once the film is exposed to the ambient air. This creates connections (necks) between overlapping particles. Finally, a homogeneous compact structure is selectively trimmed to achieve a realistic vertical distribution of NPs. The resulting 3D structure of connected particles (described parametrically using positions and core-shell radii) serves as 3D geometry input for the computation of conductivity described in Section 2.4.2, where for each input data pair (size distribution and porosity), ten structures were generated, enabling statistical evaluation.

2.3.1. Hard-sphere packing algorithm

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At first, a system of (non-oxidized) overlapping core particles is generated by placing spheres, whose radii are drawn from the number-based particle size distribution determined by SEM measurements, inside a predefined sampling window W according to a uniform distribution on W. This process is repeated until the sum of sphere volumes corresponds to 60% of the volume of W, which typically leads to a highly connected sphere system. To obtain such a system of non-overlapping core particles, a force-biased collective rearrangement algorithm is used [26, 27], where periodic boundary conditions are applied in x-direction. Note that the porosity at this point equals 40% and does not yet correspond to the experimentally determined target porosity, which will be achieved in Section 2.3.3.

2.3.2. Swelling, meshing

The swelling of the non-overlapping core particles is carried out by increasing the radii of the previously generated spheres. The amount of this swelling is not given directly by the oxide thickness derived from TEM observation, but it is calculated by considering the extra volume that is gained when particles are oxidized. This was estimated by simple algebraic reasoning taking into account the different densities of the deposited metallic material ($\rho_{Cu} = 8.96 \text{ g} \cdot \text{cm}^{-3}$) and copper oxide ($\rho_{CuO} = 6.32 \text{ g} \cdot \text{cm}^{-3}$). So it is estimated that a 1.5 nm thick surface layer of each particle is oxidized, and due to an addition of oxygen, it gains a volume forming an oxide shell with a thickness of 2.2 nm (value observed approximately by TEM and fitted in SAXS).

Without this step, (i) the generated structure would clearly not correspond to those observed in SEM cross-sectional views, (ii) there would be no necks enabling calculating the resistivity of the structures.

2.3.3. Trimming to target vertical distribution

The core-shell system is now converted to a weighted graph G, where each node corresponds to a NP and thus a spherical core-shell particle. The distance between two NPs corresponds to the shortest distance between the outer shell of those NPs, taking periodic boundary conditions in x-direction into account. Next, the minimum spanning tree, denoted by T_0 of this weighted graph, is computed via Prim's algorithm [28]. Moreover, the path with the smallest weights from the vertex with the lowest zcoordinate to the vertex with the highest z-coordinate is computed. This shortest path is now extended iteratively, leading to the trees $T_1, T_2, ..., T_N$, where $N \in \mathbb{N}$ is the smallest index $i \in \mathbb{N}$ for which the sum of the volume of each core-shell particle belonging to T_i is larger than the target volume fraction determined by the SAXS method. In each iteration, a sphere is chosen randomly according to the target vertical density distribution obtained from cross-section SEM micrographs. In step $i \in \mathbb{N}$, this randomly selected sphere is connected to the tree from the previous iteration T_{i-1} such that the newly added edges have minimal weight and are a subset of the edges of G.

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2.4. Virtual experiment

The final step of our proposed workflow is to assess whether the virtually generated structures correspond to the real ones. For this purpose, we validate the model with regard to the sheet resistance, as it can be measured on real films and determined via numerical simulations based on virtually generated 3D structures.

The sheet resistance of NP-based percolating films is determined by the shape of the structure and the resistivity of the material. If we had a well-defined material resistivity, we could directly compare results for structures that were prepared and generated with different shapes, *i.e.* with various particle size distributions and/or thicknesses. However, it turns out that the absolute value of resistivity for nanoparticles is a very difficult parameter to find out, as discussed in more detail later. Therefore, it was necessary to include an additional parameter beyond particle size that could be varied in both the measured and modelled data.

For this purpose, we selected the resistance at different partial pressures of oxygen (in carrying nitrogen). The adsorption of oxygen causes noticeable changes in the material's resistivity, and in the following text, we describe how this is modelled and used for comparison. This approach provided us with a series of measured points for each sample, which, despite increasing the number of fitted parameters, helped to assess the realism of our generated structures.

2.4.1. Adsorption model

The effect of the adsorption of gases to the surface of the metal oxide semiconductors has been studied for decades [29] and is often described in textbooks, *e.g.* [2, 30]. Usually, these approaches model the potential bending of the material's band structure and sometimes try to estimate the change of the free-charge-carriers density in the adsorbate. In the present study, we need to use a simplified adsorption model for two reasons: (i) we need to be able to calculate the current transport through complex geometrical shape (NP-based thin films), (ii) it is difficult to get a large variety of materials and conditions, which would be needed if someone would like to use models which employ numerous material properties. The simplified model of electrical conduction considering surface adsorption is as follows:

Nanoparticles are considered to be homogeneous with an intrinsic resistivity ρ_{core} corresponding to the conductivity

$$\sigma_{\rm core} = \frac{1}{\rho_{\rm core}}.\tag{1}$$

On the surface, a layer influenced by oxygen adsorption can be formed, which removes electrons from the surface, thus changing the concentration of free charge carriers at the surface, commonly denoted as surface charge region (SCR). The change in surface conductivity can be considered directly proportional to the concentration of oxygen on the surface (θ_{O_2}). The conductivity of the surface affected by adsorption (the shell) can therefore be expressed as

$$\sigma_{\text{shell}} = \sigma_{\text{core}} \left(1 + k_{\text{s}} \cdot \theta_{\text{O}_2} \right), \tag{2}$$

where k_s is the dimensionless proportionality constant representing the changing of the conductivity.

We assume a sharp boundary between the unaffected material with resistivity ρ_{core} and the surface with ρ_{shell} . The thickness d of this affected layer in our simplified model is also considered directly proportional to the concentration of adsorbed oxygen:

$$d = k_{\rm d} \cdot \theta_{\rm O_2},\tag{3}$$

where k_d is the proportionality constant with the dimension of length. Such a model can be simply used in further calculations and its validity is discussed later.

From now on, we will refer to this SCR, where the change is manifested as the "shell" and the unaffected region inside the particles as the "core". This is to keep the notation consistent with the more general model described in Section 2.4.3. Readers are asked to pay attention to the fact that this is a different shell than the oxide shell described in Section 2.3.

255

Last but not least, it is necessary to estimate the concentration of oxygen on the surface. For this purpose, the well-known Langmuir isotherm is used, as applied in theoretical calculations on similar materials, for example, in [31], which relates the gas pressure p (in our case, we consider this parameter as the partial pressure of oxygen in the O₂ and N₂ mixture) and the surface coverage θ_{O_2} :

$$\theta_{\mathcal{O}_2} = \frac{p}{p+p_0},\tag{4}$$

where p_0 is another fitting parameter with the dimension of pressure.

Overall, we are looking for several material parameters (ρ_{core} , k_s , k_d , and p_0) that we can determine using the modelling described below and by comparing with the measured resistances at various oxygen pressures.



Figure 4: Illustration of the mathematical model for conductivity calculation: a) Top view of the modelled structure of particles including a highlighted network of neighbouring particles (black lines), a few highlighted connections between neighbouring particles, so-called *nodes* (red lines) and boundary conditions (blue and red lines) applied to calculate sheet resistance of the structure. b) A single particle with its neihgbours showing the core-shell structure, electric currents passing through the particle and electrostatic potentials associated with the nodes and the centre of the particle.

2.4.2. Sheet resistance calculation

The sheet resistance of the thin film of nanoparticles is calculated using FEM [32]. The individual spherical particles are the finite elements from which the whole structure is constructed. The connection points between the particles are called *nodes* in this work. In Figure 4a), the network of connected particles is visualized: the blue dots represent the elements, and the blue lines represent the nodes (connections) between the elements.

To calculate the sheet resistance, the 3D structure is subject to an electrostatic potential difference along one axis perpendicular to the film thickness and the total electrical current through the structure must be evaluated. The solution to the problem is decomposed into two steps. First, the electrostatic potential distribution is calculated for each particle, assuming perfect spheres with boundary conditions prescribing current flowing in and out of the sphere at the nodes, see Figure 4b). Note that the particles can differ in size, the thickness of the shell, the resistivity of the core and the shell domains and the relative position of the nodes. From the potential distribution, the potential difference between each pair of nodes (as a function of the current flowing through the nodes) is calculated. In other words, the electrical conductance of the element between each pair of nodes is evaluated.

In the second step, a system of linear equations is assembled for the whole structure. The primary unknowns are the values of the electrostatic potential at the nodes. After the application of the boundary conditions, which fix the potential of the elements intersecting the boundary planes, the system can be solved. The currents at the nodes are then calculated using the known conductance of the individual elements, and the total resistance of the structure is evaluated.

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Note that a single-step (direct) solution of the electrostatic potential distribution in the whole structure has proven to be inefficient. The solution of the corresponding partial differential equation requires sufficiently fine discretization (meshing) in order to resolve the relatively narrow connections between the particles. However, this has proven to be too computationally demanding for the whole 3D structure. In the following sections, the two steps of the used method are described in more detail.

2.4.3. Conductance of core-shell particles

As mentioned above, in the first step, the conductance of each spherical particle is calculated. The task is to determine the electrostatic potential in the particle, V, for a given current passing through the nodes representing connections with neighbouring particles, see Figure 4b). The particle contains two domains with different resistivity, ρ_{core} and ρ_{shell} , corresponding to the core and shell domains, respectively. We denote by R the radius of the particle and by R_c the radius of the core domain. Thus, we can obtain V in spherical coordinates from two contributions, $V_{\text{core}}(r, \theta, \phi)$, valid for $0 \le r \le R_c$, and $V_{\text{shell}}(r, \theta, \phi)$, valid for $R_c \le r \le R$.

In general, the electrostatic potential, V, obeys the Laplace's equation

$$\nabla^2 V = 0, \tag{5}$$

which follows from the equation for the current density (Ohm's law)

$$\boldsymbol{j} = -\frac{1}{\rho} \nabla V \tag{6}$$

and the current conservation equation $\nabla \cdot \boldsymbol{j} = 0$, where ρ is the resistivity of the material. The solutions of (5) in spherical coordinates are the regular and irregular solid harmonics, $R_{lm}(r,\theta,\phi) = r^l Y_{lm}(\theta,\phi)$ and $I_{lm}(r,\theta,\phi) = r^{-l-1}Y_{lm}(\theta,\phi)$, respectively, where $Y_{lm}(\theta,\phi)$ are the real spherical harmonics [33]. Therefore, we can express the core and shell potentials as

$$V_{\text{core}}(r,\theta,\phi) = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} C_{lm} r^{l} Y_{lm}(\theta,\phi) \quad \text{and}$$
(7)

$$V_{\text{shell}}(r,\theta,\phi) = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} (A_{lm}r^{l} + B_{lm}r^{-l-1})Y_{lm}(\theta,\phi).$$
(8)

The coefficients A_{lm} , B_{lm} , C_{lm} need to be calculated from boundary conditions to obtain a particular solution. Note that we have omitted l = 0 from the summation, *i.e.*, we have set $A_{00} = B_{00} = C_{00} = 0$ which sets V = 0 at the centre of the spherical particle. This is a necessary Dirichlet-type boundary condition required to constrain the solution, given the Neumann-type boundary condition on the outer surface, where a given current density $j_{\text{shell}}(R, \theta, \phi)$ is prescribed. A positive value of j_{shell} means the current is flowing into the sphere while a negative value means the current is flowing out of the sphere. Of course, to ensure current continuity, the integral of j_{shell} over the whole sphere surface must be zero. The boundary condition then takes the form

$$\rho_{\text{shell}}^{-1} \frac{\partial V_{\text{shell}}}{\partial r} (R, \theta, \phi) = j_{\text{shell}} (R, \theta, \phi) \,. \tag{9}$$

³¹⁰ Apart from this, the solution must fulfil two more boundary conditions:

$$V_{\text{core}}(R_{\text{c}},\theta,\phi) = V_{\text{shell}}(R_{\text{c}},\theta,\phi), \qquad (10)$$

$$\rho_{\rm core}^{-1} \frac{\partial V_{\rm core}}{\partial r} (R_{\rm c}, \theta, \phi) = \rho_{\rm shell}^{-1} \frac{\partial V_{\rm shell}}{\partial r} (R_{\rm c}, \theta, \phi) , \qquad (11)$$

These conditions ensure potential and current continuity at the core-shell interface, respectively. All these conditions are sufficient to fully define the values of the A, B and C coefficients for a given j_{shell} . Moreover, given the orthogonality of the spherical harmonics, the coefficients corresponding to different l and m values can be separated from the sums in (7) and (8) and directly calculated as

$$A_{lm} = \frac{\rho_{\text{shell}}}{R} \frac{1 - p_l}{l(1 - p_l) - (l + 1)p_l(R_c/R)^{2l+1}} I_{lm} , \qquad (12)$$

$$B_{lm} = (R_c/R)^{2l+1} \frac{p_l}{1-p_l} A_{lm} , \qquad (13)$$

$$C_{lm} = \frac{A_{lm}}{1 - p_l},\tag{14}$$

³¹⁵ where p_l was defined as

$$p_l = \frac{l}{2l+1} \frac{\rho_{\rm core}/\rho_{\rm shell} - 1}{\rho_{\rm core}/\rho_{\rm shell}} \tag{15}$$

to simplify the formulas and

$$I_{lm} = \int_0^{2\pi} \int_0^{\pi} j_{\text{shell}}(R,\theta,\phi) Y_{lm}(\theta,\phi) \sin\theta d\theta d\phi \,.$$
(16)

To summarize, the potential distribution is calculated by repeated evaluation of the spherical surface integral (16), involving the current density and the spherical harmonics function, for increasing l values (and corresponding m values) and then by summing the individual terms in the series (7) and (8). The iteration over l is stopped when the relative error between the left-hand-side and the right-hand-side of (9), integrated over the whole sphere surface, is less than the tolerance 10^{-4} .

According to Figure 4b), the current in and out of the sphere is non-zero only at the connections between neighbouring particles. This connection is represented by the circular intersection, with radius R_n , of the two spheres and by the node, i.e., the centre of this circle. The location of the node with respect to the particle centre can be specified using the spherical coordinates by two angles, θ_n and ϕ_n . For the simplicity of the following discussion, at first, we assume that the particle has only two nodes $(n \in \{1, 2\})$.

To ensure that the series (7) and (8) converge for reasonably small l, j_{shell} must be smooth and, thus, we have to avoid sharp changes of j_{shell} at the edge of the connection between the particles. Therefore, ³³⁰ a Gaussian distribution in the form

$$j_{\text{shell},\theta_{n},\phi_{n}} = j_{0} \exp\left(-\frac{\alpha(\theta,\phi)}{2\sigma^{2}}\right), \qquad (17)$$

is used to model the current density distribution at the junction. In (17), α is the angle between the vector pointing to the coordinates (θ, ϕ) on the sphere surface and the vector pointing to the node (θ_n, ϕ_n) and σ is the "width" of the current density distribution, corresponding to the radius of the connection, R_n , as

$$\sigma = \frac{2}{\pi} \arcsin(R_n/R) \,. \tag{18}$$

- To verify this approximation, we have performed numerical calculations (using the finite element method) of the potential distribution in spheres with spherical caps cut off and fixed potential boundary conditions applied to those spherical surfaces. This should more closely simulate the conditions near the connection between two spherical particles. The above-mentioned value of σ provided excellent agreement between the potential distribution calculated by both methods for a wide range of R_n . The normalization constant j_0 ensures that the absolute value of the total current over the spherical surface (corresponding to one applied to the potential distribution for a spherical surface (corresponding to one between the potential distribution for the total current over the spherical surface (corresponding to one between the potential distribution for the total current over the spherical surface (corresponding to one between the potential distribution for the total current over the spherical surface (corresponding to one between the potential distribution for the total current over the spherical surface (corresponding to one between the potential distribution for the total current over the spherical surface (corresponding to one between the potential distribution for the total current over the spherical surface (corresponding to one
- node) is unity and takes the form

$$j_0 = s_n \left(2\pi R^2 \sqrt{\pi/2} \,\sigma \exp(-\sigma^2/2) \,\operatorname{erfi}(\sigma/\sqrt{2}) \right)^{-1} \,, \tag{19}$$

where 'erfi' is the imaginary error function and $s_n = \pm 1$ (it is positive for the node with current flowing into the particle and negative for the node with current flowing out of the particle). In other words, the total current flowing through the particle via the two nodes, denoted by I_{12} , is unity. The integral (16) is evaluated numerically using product Gaussian quadrature [34] with at least 200 integration points (for the smaller R_n) centred at the node locations (θ_n, ϕ_n). The calculation was implemented in the Python programming language using the Scipy numerical algorithms package [35]. The implementation allowed the calculation of spherical harmonics up to l = 85, which ensured convergence with strict tolerances for $R_n > 0.05R$.

Once the potential distribution is calculated, the node potentials are evaluated at the midpoints of the spherical intersections of the two neighbouring spheres, *i.e.*, $V_n = V_{\text{shell}}(r_n, \theta_n, \phi_n)$ where $r_n = R(1 - \sqrt{1 - R_n^2})$. Then, the conductance between the nodes is expressed as $G_{12} = I_{12}/(V_1 - V_2)$.

If the particle has K nodes, the potential distribution is calculated gradually for the current passing through K - 1 independent combinations of node pairs. For each pair, the voltages at all nodes are evaluated. After combining all these calculations, we obtain a conductance matrix, G_{nk} , which expresses

the node currents I_n for a general combination of node voltages V_k using matrix-vector multiplication as

$$I_n = \sum_k G_{nk} V_k \,. \tag{20}$$

The symmetric matrix G_{nk} contains complete information about the electrical conductance of the particle, and in the framework of the finite element method, it represents the basic element from which the model of the whole structure is constructed.

2.4.4. Assembly and solution of structure equations

The structure of connected particles is described by the positions and radii of particles, from which a global list of nodes (i.e., connections between the particles described by their centre points and radii) is constructed. We denote by N_i the total number of (internal) nodes. Each node is connecting exactly two particles and a map between the global and local node indices is kept: $i \to (p, n)$, *i.e.*, a node with global index *i* corresponds to a local node *n* of particle *p*. The current flowing out of one particle must be equal to the current flowing into the other particle. Therefore, we have equations of the form

$$I_{p_1,n_1} + I_{p_2,n_2} = 0 (21)$$

After substitution of (20), we obtain

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$$\sum_{j} (G_{ij}^{p_1} + G_{ij}^{p_2}) V_j = 0, \qquad (22)$$

where the conductance matrices corresponding to the two particles, p_1 and p_2 , sharing the node j were mapped to the global node indices. In addition, N_b nodes at the intersection of particles with the boundary planes are created, see blue and red lines in Figure 4a) for the V = 0 and V = 1 boundaries, respectively. For these nodes, the equations take the form

$$V^p = \sum_j M_j^p V_j = V_{\rm b} \,, \tag{23}$$

where V^p is the potential at the centre of the particle, and M_j^p is a vector of coefficients that relate the centre potential with the node potentials and the boundary potential $V_b = 0$ or 1 depending on the location of the particle.

Thus, together we have a linear system of $N = N_i + N_b$ equations for the node voltages V_j where j = 1, ..., N. This system is solved numerically by the iterative GMRES method implemented in the Scipy library [35]. From the calculated values V_j , we can again obtain the currents at nodes, I_i , using (20). By summing the currents at the nodes associated with one of the fixed-voltage boundaries, we



Figure 5: SEM cross-sectional micrographs of NP-based films. TEM insets show individual particles in an as-deposited state. The *Large NPs* in a) were prepared using 1.5 mm orifice in MGA, *Small NPs* in b) were prepared using 4.0 mm orifice.

obtain the total current through the simulated structure, denoted by I. The resistance of the structure is then $R_s = 1/I$, and since the simulated structure has a square base, it is the *sheet resistance* of the thin-film structure. Its resistivity can be obtained from it upon multiplication by the film thickness.

It follows from the Buckingham π theorem that the film resistivity can be expressed as $\rho = \rho_{\text{core}} g(d, \rho_{\text{shell}}/\rho_{\text{core}})$, where g is a function representing the complex dependence of resistivity on the arrangement of the NP structure, including the inherent dependence on the shell thickness, d and the normalized shell resistivity, $\rho_{\text{shell}}/\rho_{\text{core}}$. Therefore, using the FEM method, it is sufficient to calculate $g(d, \rho_{\text{shell}}/\rho_{\text{core}})$ as the normalized film resistivity ρ/ρ_{core} .

2.4.5. Final fitting

In the final step, it was necessary to combine the parameters from the adsorption model with the results of FEM modelling. For this purpose, a look-up matrix of values of the g function corresponding to a range of normalized shell resistivities, $\rho_{\text{shell}}/\rho_{\text{core}}$, and a range of shell thicknesses, d, was calculated by FEM for each of the virtually synthesized structures. Then, for any given values of the parameters ρ_{core} , k_d , k_s and p_0 (providing the values of ρ_{shell} and d through θ_{O_2} , as defined in Eqs. (2), (3) and (4)), the modelled film resistivity is obtained by interpolation from values in the generated matrix. The optimal values of these parameters were determined by fitting the model to the measured dependence of film resistivity on the oxygen partial pressure, p, using the non-linear least squares algorithm implemented in the Python SciPy package [35].

3. Results

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3.1. Analyses of synthesized structures

400 3.1.1. Particle appearance and size distribution

Two different diameters (1.5 and 4.0 mm) of the orifice of our MGA were utilized to prepare NPbased films characterized by significantly different size distributions of NPs, denoted as "Small NPs" and "Large NPs". Figure 5 shows SEM micrographs displaying cross-sectional views of the prepared films (prepared on silicon for this purpose). It is evident that NPs prepared with the larger orifice are much smaller than those prepared with the smaller orifice. This phenomenon is well documented in the literature [10].



Figure 6: a) An example of a TEM image used for deriving size distribution. b) and c) show the number-based particle size distribution functions derived both from multiple micrographs (together with the multimodal log-normal fit) and distribution from the SAXS model for *Large NPs* and *Small NPs*, respectively.

Figure 6 illustrates the process of determining the number-based size distribution of the particles. Short depositions were performed on a silicon substrate or a TEM grid with a graphite film, allowing individual particles to be identified using TEM or SEM. Histograms obtained from image analysis were aggregated, and in Figure 6b) and c) number-based particle size distribution of *Large NPs* and *Small NPs* are shown, respectively. The distribution can be fitted with a multimodal log-normal distribution. For *Large NPs*, there are two modes (with maxima at 9.2 and 50 nm). The bi-modality was observed and described in [10]. The *Small NPs*' distribution (with main peaks at 1.1 and 5.0 nm) shows an extra third peak (at 13 nm). However, this is likely because image analysis is not able to separate very small particles, which sometimes aggregate together, and thus, this peak is considered instrumental. The shape of the distribution generally fits with our previous experience.

From the point of view of the SAXS measurements, the data cannot be reasonably fitted with a two-mode distribution as too many parameters would be involved in the model (considering also the oxide shell thickness), but a reasonable fit was achieved using a single mode. In Figure 6, the SAXS and microscopy results are compared, and their overlap is evident. Finally, we decided to use both the size distribution and the porosity information provided by the SAXS method.

It should also be clarified that the distribution needed to be truncated at a certain particle size. The largest particles were, therefore, omitted. The criterion for truncation was the exclusion of 5% of the total volume formed by the largest particles. Without this step, the hard-sphere packing algorithm ⁴²⁵ would randomly generate extremely large particles that we have never observed microscopically. In other words, the large-radius tails of the log-normal distribution are not realistic.

3.1.2. Film porosity

The SAXS model provided information about the porosity of the films. For *Small NPs*, the porosity was found to be 59%, and for *Large NPs*, 77%.

430 3.1.3. Particle composition

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The composition of the particles was examined using X-ray diffraction. Figure 7 shows the X-ray diffractograms of the films of *Large NPs* and *Small NPs*, both in the as-deposited state and after thermal stabilization in a 4PP device. The as-deposited particles consist of a metallic copper phase (fcc, PDF 00-004-0836) and partially copper oxide, mainly Cu_2O (cubic, PDF 00-005-0667). This correlates well with the TEM insets in Figure 5, where a core-shell structure of the particles is clearly visible, characterized

by a denser (and therefore darker in the bright-field image) metallic core and a lighter oxidized shell.



Figure 7: XRD diffractograms of NP-based films. The as-deposited films show a prevailing metallic phase with a small amount of Cu₂O oxide. After stabilization at 300 °C films contain only the CuO phase.

After stabilizing the films at 300 °C in 4PP system, complete transformation into oxide occurs, leading to a fully oxidized and stable CuO phase (monoclinic, PDF 01-089-5897).

3.1.4. Film thickness and vertical profile

To create the model of NP-based films, it was necessary to determine the thickness of the prepared films. More details on determining the thickness of the highly inhomogeneous spot-like deposits prepared by MGA can be found in Sections 2.2.3. The samples for which resistivity was measured had an equivalent thickness close to 400 nm. Specifically, 380 and 340 nm for *Large NPs* and *Small NPs*, respectively. ("Equivalent thickness" means the thickness at which a homogeneous layer would have the same sheet resistance as the actual Gaussian spot, considering its real position relative to the electrodes.)

As a final input for the modelling, it was necessary to determine the vertical distribution of the particles. NP-based films are not abruptly terminated by a plane, but rather, in some areas, the particles pile up to a greater height (from the substrate) than elsewhere. One can also imagine that the outer envelope of the film has its own 'roughness.' This vertical distribution of particles (or profile) is an important input for the modelling, as a high roughness of the layer causes a significant increase in resistivity.

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To estimate the vertical distribution, fractures of the prepared films were detailedly imaged using SEM with a slightly varied focal distance. The resulting images were then analyzed and the separate layers were marked. This process is illustrated along with the resulting vertical distribution curves in Figure 8. It was also assessed how much the shape of the profile depends on the thickness of the layer

⁴⁵⁵ Figure 8. It was also assessed how much the shape of the profile depends on the thickness of the layer (since it is not uniform everywhere and is replaced by a single equivalent thickness). It turned out that for films that are not too different in thickness, the obtained profile can be normalized (shrunk) to



Figure 8: a) Cross-sectional SEM micrograph of synthesized NP-based thin films. An example for Large NPs shows the approach to vertical distribution estimation by manually selecting planes of various focus depths. b) Measured on various positions of samples (symbols and solid lines) and adjusted distributions used as input for virtual synthesis (faded lines).

the desired thickness. This is evident in the presented curves, where the blue curve with empty discs represents the analyzed profile for the thicker region of *Large NPs*, and the green curve represents the profile at a thinner part of the very same sample. The shrunk profile from the first, thicker region (semitransparent blue line) matches very closely with the directly measured profile. Therefore, the measured profiles from different spots were simply shrunk and averaged to provide input vertical distribution for subsequently coming virtual synthesis.

It is also apparent that the profiles for Large NPs and Small NPs differ significantly. Small NPs are terminated quite sharply, whereas films made from Large NPs are noticeably 'rougher'.

3.2. Virtually synthesized structures

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In the previous sections, the process of obtaining inputs for the algorithms generating virtual structures was described. Finally, ten structures with the desired properties (porosity, size distribution) were generated for both orifice diameters. These structures were created to have a thickness of 400 nm and contain approximately 4000 particles. For the Large NPs, the structures were laterally larger $(3.8 \times 3.8 \,\mu\text{m}^2)$ than for the Small NPs $(0.2 \times 0.2 \,\mu\text{m}^2)$. Subsequently, the vertical profile was trimmed to match the observed vertical distribution, which decreased the number of particles by approximately 20%. This results in a porosity of 77% for the 1.5 mm orifice and 59% in case of the 4.0 mm orifice, which corresponds to the values obtained by SAXS analysis. An example of final virtually synthesized structures for each size is shown in Figure 9, where the electrical potential as well as the electrical current are also visualized.



Figure 9: Example of final generated structures used for FEM modelling. The potential distribution is visualized by colors of individual NPs, current flows are depicted by color-coded arrows. In between the spherical NPs, there are black circles drawn to highlight the contact area. Mind the different spatial scales for a) Large NPs and b) Small NPs.

Table 1: Fitted parameters of the model. In the first case, the resistivities of thin films formed by Large NPs and Small NPs were fitted independently. Then some of the parameters were fitted together.

		Independent fit		Coupled fit		Error	
		Large NPs	Small NPs	Large NPs	Small NPs	(0	$\sigma)$
p_0	$[10^5 \mathrm{Pa}]$	0.106	0.177	0.13		0.001	
$k_{\rm d}$	[nm]	50.0^{*}	18.2	23.0		0.1	
$k_{\rm s}$	[1]	0.446	0.543	0.508		0.001	
$\rho_{\rm core}$	$[\Omega \cdot \mathrm{cm}]$	3.6	0.22	3.5	0.29	0.2	0.01

^{*}Fitted parameter restrained to this value.

3.3. Resistivity calculations and experiment

3.3.1. Resistance measurements

- The resistance of the prepared samples was measured using the 4PP technique. Samples were first heated to 300 °C for approximately two hours in synthetic air until the resistance stabilized. The resistance increases during this time due to particle oxidation, eventually reaching a stable value. Subsequently, resistance measurements were taken at various oxygen concentrations in a nitrogen mixture. The oxygen ratio was varied from 0% to 75%. The measurements were conducted at various temperatures, here we present data for 150 °C for both types of samples.
- In Figure 10, the measured values of electrical resistivity (determined by recalculating using the geometrical factor obtained from the sample thickness measurements) are shown with symbols. The resistivity of thin films for Large NPs and Small NPs differs by two orders of magnitude, with values around $2 \cdot 10^2$ and $2\Omega \cdot cm$, respectively, for 0% oxygen (100% nitrogen).

3.3.2. Fitting resistivities with model

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The measured values were further used to fit the physical model employed for evaluating the resistivity of virtual structures using FEM. The fitted dependencies are also plotted in Figure 10.

The dotted lines display the situation when the films with Large NPs and Small NPs are fitted independently. The solid lines are the fits with some of the parameters coupled together. In an ideal



Figure 10: Resistivities of thin films, *Large NPs* (blue) and *Small NPs* (red). The data was fitted by a presented model with fitting parameters independent for each sample or with some of the parameters coupled among samples, details provided in the text. Values of fitted parameters are listed in Table 1.

case, all of the parameters could be fitted together for the joint data of Large NPs and Small NPs. In this case, it is necessary to fit the logarithm of resistivity to minimize the relative error between experimental data and the model (considering the order of magnitude differences between the two datasets). Anyway, it was not possible to get a reasonable fit in such a case. Therefore, $\rho_{\rm core}$ was fitted independently for each material. Further details can be found in the next section.

The fitted values of p_0 , k_d k_s and ρ_{core} are provided in Table 1. Note that the presented errors were derived here solely from the fitting of various realizations of virtual structures.

4. Discussion

The virtual 3D structures generated by the procedure described above are visually very similar to real structures as observed in 2D SEM images. However, the detailed assessment of our model's suitability is based on resistivity measurements. A simple linear model was used to describe how adsorbed oxygen affects the conductivity of the system, and still, it was possible to qualitatively capture the shape of the measured dependence of resistivity vs. relative oxygen concentration in the surrounding atmosphere.

In p-type semiconductors like cupric oxide, oxygen adsorption increases the number of free charge carriers (holes) in the material [36], thus reducing resistivity. The adsorbed oxygen (mostly O_2^- and partially O⁻, typical at 150 °C [37]) simply removes an electron from the material and creates a hole near the surface. Our model captures this drop in resistivity well. The study [38] investigated the kinetics of oxygen adsorption on CuO nanowires and reached similar qualitative conclusions. The magnitude of the constant p_0 is in the expected range for this class of materials (0.1–0.01 bar).

Discussion of the values of k_s and k_d is difficult since all accessible models describe accepted voltage bending near the surface [2, 29] in contrary to the simplified sharp transition between the surface charge layer and the bulk. However, the order of magnitude of the constant k_d , which indicates how thick the layer near the surface is affected by oxygen adsorption, is reasonable. Earlier studies [39, 40] generally mention values in the range of nanometers, consistent with our findings. The constant k_d is in the low tens of nanometers, which, combined with the coverage factor, results in a surface layer only a few nanometers thick being affected by adsorption.

The downside of our model is that the correlation to individual constants varies. In the case of 520 Large NPs, when they were fitted independently, the parameter $k_{\rm d}$ increased during optimization, though this had minimal impact on the fitting results. This phenomenon did not occur when seeking an optimal solution with joint data, where three of the material constants were fixed, and the average value of $k_{\rm d} = 23.0\,\rm nm$ was found. Unfortunately, a good fit to the measured data could not be achieved when all constants were coupled. The best fit was achieved with ρ_{core} parameters fitted independently. 525 Values differ by more than an order of magnitude: 0.29 and $3.5 \,\Omega \cdot \mathrm{cm}$ for Large NPs and Small NPs, respectively. Since the resistivity values at $0\% O_2$ differ by two orders of magnitude for the samples, the model captures the changes in these values only partially. We believe this is due to a combination of two effects. The first is the fact that the real oxygen coverage at $0\% O_2$ is not zero, as assumed in Equation (2). This could be caused by the system's design or simply by the large desorption time 530 constant of oxygen from both the samples' surfaces and the inner part of the aperture. The second, more significant effect is the oversimplification that particles remain spherical after stabilization/oxidation. As the material volume increases due to the oxidation, more coalescence of the spheres likely occurs. This effect is especially evident in Smaller NPs, where the formation of broader necks between the nanoparticles leads to a resistivity two orders of magnitude lower than that of Large NPs. Our model 535 does not account for this effect and therefore compensates by reducing $\rho_{\rm core}$.

It is challenging to determine which of $\rho_{\rm core}$ values is closer to that of the bulk material. Like all oxides, copper oxides are highly sensitive to the number of vacancies. In [41], the reported resistivity for various films of monoclinic CuO ranges from 0.01 to $1\Omega \cdot \text{cm}$. Additionally, for CuO, crystallinity plays an important role, as discussed in [42]. Here, the authors examined various Cu_xO films, yielding 540 resistivity values on the order of $10^2 \Omega \cdot \text{cm}$ (at room temperature). The measurements in [43] reported values for sintered CuO materials similar to our findings, around $0.17 \,\Omega \cdot \mathrm{cm}$ (measured at 150 °C).

Finally, our model qualitatively described the behaviour of the measured materials and provided reasonable estimates for the magnitudes of those constants that are measurable by other methods. To better understand the behaviour of the presented NP-based thin films, mainly it will be necessary to i) 545 incorporate a more complex model of surface layer conductivity affected by adsorption and ii) improve the geometric representation of sphere coalescence.

5. Conclusion

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This study presents a complex and comprehensive methodology to model the percolated conductive networks in nanoparticle-based thin films. The process involved several key steps: synthesis of copper oxide nanoparticles, detailed analyses, virtual synthesis through modelling, and virtual experiments to simulate electrical resistivity. By varying the diameter (1.5 and 4.0 mm) of the exit orifice of the aggregation chamber of magnetron-based gas aggregation source, two types of NP-based films were prepared. They were characterized by significantly different size-distributions of NPs. The Large NPs had a bimodal size distribution with dominating radius families of approximately 50 nm and 10 nm, while the Small NPs predominantly measured around 5 nm in radius. Subsequently, the films were stabilized in air at 300 °C, when the particles turned into fully oxidized CuO.

Using the acquired experimental data, virtual films were generated through a hard-sphere packing algorithm that accounted for the size distribution and measured porosity. Further, oxidation-induced swelling of particles was mimicked, which led to increased necking between nanoparticles. In addition, 560 some of the top particles had to be stripped in order to match the non-zero roughness of the film.

A comprehensive computational model was developed, incorporating a simplified adsorption model to simulate the effects of oxygen adsorption on the surface conductivity of the nanoparticles. The elec-

trical resistivity of the percolated networks in these virtual structures under various oxygen exposures was calculated using the finite element method. While the model qualitatively captured the conductive 565 behaviour of the nanoparticle-based thin films and provided reasonable estimates for key material parameters, some drawbacks were identified. The model did not fully account for the increased necking between nanoparticles upon oxidation, which significantly affects conduction pathways. Future improvements should focus on incorporating more accurate geometric representations of particle coalescence and a more complex adsorption model. 570

Despite these limitations, this work represents an important step forward as it is, to the best of our knowledge, the first attempt to analyze and model the 3D structure of percolated conductive networks in nanoparticle-based thin films. It provides a valuable framework which can be used for further optimizing the electrical properties of NP-based nanomaterial films for applications in conductometric sensing. This is essential to fulfil the goal of developing functional sensing materials based on mixtures of different MGA NPs. It will enable the leveraging of heterojunctions at material interfaces to enhance the sensor response.

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CRediT authorship contribution statement

Stanislav Haviar: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Supervision. Benedikt Prifling: Investigation, Writing – original draft, Writing 580 - review & editing. Tomáš Kozák: Conceptualization, Methodology, Investigation, Writing - original draft, Writing – review & editing. Kalyani Shaji: Investigation. Simon Kos: Methodology. Volker Schmidt: Conceptualization, Writing - review & editing. Jiří Capek: Investigation, Writing - review & editing, Supervision.

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Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT in order to get style and grammar recommendations for the draft text. After using this service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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