Morphology versus conductivity of nanocomposite films

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Abstract. A computer experiment for the study of transport and morphological properties of composite/nanocomposite films is presented. Features based on the theory of mathematical morphology describe the film morphology. The electrical transport in composite films is simulated stochastically near the metal-dielectric transition, where the basic mechanism of charge transport is the tunnel effect. The results of morphological and transport analysis of modelled composite structures are compared and discussed.

1. Introduction
Composite and nanocomposite metal/dielectric films consisting of metal particles embedded into an oxide or polymer matrix represent class of promising materials. The properties of prepared composite films are strongly influenced by used technologies – thermal evaporation, ion-beam sputter deposition, laser deposition and above all by plasma deposition techniques [1].

The structure of metal-containing composite films depends on the metal volume fraction of the system. The films consist of individual metal particles embedded into a dielectric matrix at low filling factors. The percolation structure with the two components intermixed is observed with the increase of metal fraction, and at high filling factors the structure is converted into metal films with dielectric inclusions. Morphological analysis of composite films is important for the prediction of their properties. However, a theoretical approach often leads to the nearly invincible difficulties; therefore, a computer experiment would be more suited for that purpose.

In the contribution, a computer experiment for the study of both transport and morphological properties of composite/nanocomposite films is presented. The main task of this simultaneous analysis is to find correlation between film morphology and its electrical conductivity [2] and in such way to bring another source of information for the partial three-dimensional reconstruction of composite/nanocomposite structures from two-dimensional (2D) information only on one side and to show strong dependence of the electrical properties on the type of structure on the other side. If the film is thin enough, it is possible to use as input information either the projections or planar sections of composite/nanocomposite structures, both obtained from Transmission Electron Microscope. The study of the film morphology leads to application of image analysis techniques.
2. Computer Experiment

All models used and computer experiments completed are self-made prepared in our laboratories. The computer experiment performed was divided into four levels: (i) generation of model structures of composite films followed by (ii) morphological and (iii) transport properties analyses and in conclusion (iv) comparison of results of these two analyses with a view to find correlations between transport and morphological characteristics.

The composite structures were simulated by spherical objects of constant radius spaced out in a three-dimensional (3D) working area. Dimensions of the area were set from 1000×1000×100 to 1000×1000×500 pixels with c. 10% margins. The usual number of objects to be generated was between $1\times10^3$ and $1\times10^4$ in order to guarantee the reasonable precision of our results.

The simulated composite structures were generated by the hard-sphere model [3] technique. The main parameter of this model describing morphology is so called diffusion zone $D \in <0, D_{\text{max}}>$, or $D_{\text{rel}} = D/D_{\text{max}}$, $D_{\text{rel}} = <0,1>$. The value of $D$ denotes the minimal distance between object’s edges; $D_{\text{max}}$ is the maximal usable value of $D$ preserving the metal volume fraction. The objects are generated randomly and $D$ enables to set up the degree of arrangement of the structure. $D_{\text{rel}} = 0$ holds for wholly random structure and $D_{\text{rel}} = 1$ for maximally ordered one. More sophisticated methods of film generation were suggested in case that hard-sphere model does not fit sufficiently to various types of experimental data [4].

In spite of that one of the main task of our computer study is to find a technique for electric transport analysis of 3D structures, these structures are not so sufficient both for the algorithms development and for the visualization of results. Because of that 2D analogies of composite films were prepared (see Fig. 1). The parameters of 2D structures were set to 1000×1000 pixels with margins, objects were circular with constant radii and were generated by the help of hard-disk model with the same parameter $D$. Simulations were performed for both types of models, 3D and 2D, but the results are presented in following figures for 2D analogies only.

3. Results

Studying morphological properties of the 3D composite and nanocomposite structures we have used the 3D model structures. Then we have applied a random section of the structure to get possible information similar to real conditions. The standard morphological algorithms are well used in case of 2D structures. However, the applicability and the interpretation of the results are more difficult when we are trying to apply the same morphological method to study of the 3D composite and nanocomposite structures. It means we need to reconstruct morphological properties of a 3D structure from 2D information only (a section or a projection). It is well practicable provided that we have some additional information about the 3D structure tested (knowledge of the form of objects or information about some electrical properties etc.). First results of the computer experiments have showed that our effort is worthy and can help to improve diagnostic methods for composite and nanocomposite films.

![Figure 1](image1.png)

**Figure 1.** Results of morphological analysis of 2D analogies of composite structures with $D_{\text{rel}} = 0, 0.33, 0.67$ and 1.0 (from left to right). Used method: Voronoi tessellation. Main figures – VT cells, inner figures – distribution of their areas $A_{WS}$. 

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Concerning suitable morphological methods for this purpose we used Voronoi tessellation (VT) method [5, 6] by which means the area is divided into cells. The VT cell surrounding an object consists of all points from the area which are closer to this object than to the others. In Fig. 1 we see sections of four structures with various degree of randomness and the corresponding distributions of cell areas $A_{WS}$. The distribution is broader for the random structure ($D_{rel} = 0$) and the narrower distribution is typical for well-arranged structure ($D_{rel} = 1.0$). This behaviour can be quantified by a morphological feature derived from normalized second moment of the distribution of $A_{WS}$.[7]

**Figure 2.** Infinite ‘fuzzy’ clusters representing currents flowing between electrodes. Diffusion zones $D_{rel} = 0.25, 0.5, 0.75$ and $1.0$ (from left to right). The positions of metal particles are depicted by the dots. The values of the electric current are proportional to the shade of lines (100 % corresponds to maximal value of the current between two particles in the structure).

The low conductivity of the composite film with low metal volume fraction can be caused either by high resistivity of the dielectric matrix or by tunnel effect between metal objects situated close to each other in case we have structures below percolation threshold [8]. However, after the percolation threshold is reached, the dielectric-metal transition occurs and the individual metal clusters form the connected structure. The situation is much more complicated when the tunnel transport dominates and the individual objects are connected (from electrical point of view) by larger number of bonds with different intensities. There exist several ‘fuzzy’ clusters instead of the only one infinite cluster and they can partially form a network. We concentrate on their analysis in our paper because the detailed description of the ‘fuzzy’ clusters is still an open question.

**Figure 3.** The distribution of values of electric currents flowing between objects in simulated composite structures (in arbitrary units) for various degrees of object arrangement characterized by relative diffusion zones $D_{rel}$.

We are using the Monte Carlo technique for the calculations of current passing through the composite structure. From experiments performed on similar structures it is known that the voltage differences between individual objects are typically of the order of tens millivolts only, so the electron tunnelling in a low voltage approximation was chosen. Due to this assumption it was possible to introduce the resistivity of the whole composite structure and according to the distances between individual objects to calculate the probabilities of various transitions. The complete transport algorithm consists of emission of electrons from negatively biased electrode, tunnel transport of
electrons between individual objects causing their charging and finally the collecting of electrons by positively biased electrode. All these processes were treated stochastically. In every time step the given number of electrons originating from negative electrode was divided into various conduction paths according to corresponding tunnel probabilities and actual potential of objects. The simulation was very time consuming, as the simulation had a form of iterative process.

Results of the simulation are shown in Fig. 2. The paths of charged particles are strongly dependent on both the distances between objects and the electric potential of each object. There are shown ‘fuzzy’ clusters formed by the path of electric current in structures with different degree of arrangement. The distribution of values of electric currents flowing between objects in the structures with various degree of randomness can be seen in Fig. 3.

4. Discussion
The simultaneous morphological and transport analyses show a close connection between morphology and conductivity of the composite and nanocomposite films. The distribution of areas of VT cells gets narrow with increasing of $D_{rel}$ (see Fig. 1), so the dispersion of distances between each object and it’s nearest neighbour decreases and the structures become more arranged. From Fig. 2 it can be derived that the number of electric current paths grows up and the current paths become shorter and better arranged with increasing degree of arrangement of the composite structures. Structures with low value of $D_{rel}$ represent interesting behavior in situations when some of the objects are very close to each other. One can observe a switching of the polarity of the objects causing a noise in electric current measurements. This noise can bring additional information about structural parameters of the films. Fig. 3 shows one of the possible quantitative analysis of the “fuzzy” clusters and it can be seen that the number of electrical connections between objects increases with increasing structure arrangement. One can also claim that the representation of individual currents was redistributed – the number of darker current paths is greater for more ordered structures than for random ones. That means more uniform distribution of current values in the structure. Computer study enables to find some of above-mentioned conclusion that could be hardly obtained in the other way because the processes take place inside the composite materials. A possible explanation how the morphology of the film influences electric current paths and therefore conductivity was done.

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