Simulation of the structure formation in alloyed silicon-carbon materials

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Abstract. The formation of alloyed thin-film coatings on the basis of a dielectric matrix of silicon-carbon compounds in terms of the assumption on the fractal nature of the formed structures was simulated. Having studied the evolution of two- and three-layer aggregates with increasing temperature by quantum chemistry methods, it is determined that at the initial stage of the structure growth, the hydrogenated aggregates are looser, which contributes to the penetration of metal ions into the interlayer space and access to oxygen and nitrogen atoms. The formation of oxides and nitrides of metals is possible with the addition of a system for obtaining more energy while maintaining the sp3-hybridization of most of the carbon atoms. The possibility of reorganization of the primary structure and analysis of the formed structures for the presence of percolation clusters was implemented when modelling the growth process of a doped silicon-carbon film. It was established that the concentration of the alloying component of 0.2 mol % is sufficient to form a percolation cluster.

1. Introduction
Films based on a silicon-carbon matrix are amorphous materials. Nanocomposites with the specified electrophysical, optical, and mechanical properties can be created by alloying silicon-carbon films with metal atoms. The concentration of metal atoms in films can reach tens of percent. By varying the composition and concentration of metal atoms, the values of electrical conductivity in films in the range 10^{-4}-10^{14} \, \Omega \cdot \text{cm} can be specified [1]. Materials based on a silicon-carbon matrix are used to create gas sensors [2] and electrodes of supercapacitors [3].

The production of new silicon-carbon materials with the desired properties is possible using experimental methods and computer simulation of various crystalline and composite structures at the molecular level [4].

Various quantum mechanical methods of calculation are used to determine the possibility of embedding metal atoms into a silicon-carbon matrix, to obtain the spatial characteristics of particles (molecules) and Hartree-Fock energy [5-6]:

– non-empirical methods (Hartree-Fock method with different basis sets, multiparticle theory, discrete Fourier transform, inverse discrete Fourier transform);
– semi-empirical methods (MNDO, PM3, AM1, TM1, ZINDO, etc.).

Computer simulation based on certain algorithms of particle motion and interaction allows creating a virtual fractal surface and analysing the properties and nature of the growth of real systems.
The formation of the structure is determined by the nature of the process, of the motion and of the particle or cluster pooling. The diffusion-limiting model (DLA) allows one to explore the aggregation of clusters and particles limited by diffusion by implementing the Witten–Sander model, which assumes the presence of an aggregation centre and a free particle that carries out a Brownian motion from infinity and adheres to the aggregation centre when collides with it. The cluster-cluster aggregation model (SSA) accounts for the diffusion controlled cluster-cluster aggregation and implements the possibility of movement of clusters themselves, not only free particles. The reaction limited cluster aggregation model (RLCA) is based on a chemically limited aggregation of clusters with clusters. This model describes the interaction of clusters with a small coefficient of adhesion. There are also "cluster-cluster" aggregation models taking into account the long-range effect of attraction and the "cluster" model with extended detailing of the growth mechanism [7].

2. Methodology
The process of creating silicon-carbon coatings by electrochemical deposition was chosen as the object of modeling. Tetraethoxysilane (TEOS) and hexamethyldisiloxane were used as the source of silicon. Ethanol and methanol were used as carbon sources. Manganese, nickel, zirconium and copper were used as alloying additives to set the functional properties of materials for gas sensors and electrodes of supercapacitors [8]. These metals, according to preliminary experiments, enable the materials to acquire the necessary functional properties. The concentration of dopant varied in the range from 0.1 to 0.5 mole %.

Quantum chemistry methods were used to determine the energy and geometric parameters of the precursor particles. HyperChem software products (preliminary ab-initio calculations by the PM3 method) and Gaussian 03 (semi-empirical calculations by the HF method in the 3-21G basis) were used in the calculation of complex nanostructures and the dynamics of their behavior depending on time and temperature.

To model the growth of the dielectric matrix structure, the Witten-Sander diffusion–limited aggregation model and the RLCA ("cluster" aggregation limited chemically) model were used, taking into account the possibility of rotation of the clusters relative to the contact point and aggregate movement [9]. The Monte Carlo method [10] for the implementation of the Wang-Landau algorithm was adopted as the basis for modelling [7].

The modeling of film structures was carried out in the MatLab software environment. In this work, a four-connected square lattice with the number of initial particles up to 10^6 was used for modeling. A certain number of free nodes were determined, which are randomly distributed over a given bounded surface. Among the free reachable nodes, a certain initial set was formed. For each of the initial nodes, a set of neighbors was allocated (the perimeter of the set) and those nodes that were reachable and did not belong to any other set were attached to the initial one. Then the perimeter was built for the new initial set, and the process was repeated until the free nodes were exhausted or until the node from the given set was reached. Each initial particle was labeled as metal-containing or containing only a polymer base. The ratio of such particles was chosen based on experimental capabilities. In addition, in order to take into account the influence of the chemically aggressive medium, the pH of the medium was set in the form of so-called "interfering" points.

3. Results
Geometrical and energy parameters of complexes with the selected metals are calculated by quantum chemistry methods (figure 1). The use of manganese was the most profitable, therefore at the second stage of modelling manganese was taken as a metal.

Figure 2 shows the simulation results for two-layer (figure 2a) and three-layer (figure 2b) structures. Information on the distances between atoms is summarized in table 1.

The Si-C bond length in two-layer aggregates increases in the presence of hydrogen atoms to 1.87 Å, while in three-layer aggregates the Si-C bond length slightly increases from 1.94 to 1.98 Å with an increase in the number of hydrogen atoms. The length of the C-C bond is approximately the
same for two-layer and three-layer aggregates and is 1.36 Å for less hydrogenated structures, which corresponds to the value of the double bond and 1.53 Å for hydrogenated structures (single Sigma bond). Between the layers, the C-C bond ranges from 1.53 to 1.68 Å. The Si-Si bond length in three-layer aggregates is approximately the same and is 2.66 ± 0.02 Å. For bilayer aggregates this relationship is shorter than for the hydrogenated structures (of 2.53 Å). The distance between the atoms in the layers for two-layer structures reaches 3.79 Å, for three-layer 3.85 Å, in three-layer hydrogenated - 3.45 Å.

![Figure 1. Hexamethyldisilane complex with manganese](image1)

**Figure 1.** Hexamethyldisilane complex with manganese

![Figure 2.](image2)

**Figure 2.** The computer model of the structure of the unit: a) Si₈C₂₀H₁₂O₄; b) Si₁₄C₂₇H₂₆O₇

| The distance between the atoms (Å) | Si₁₄C₂₇N₇H₁₂ | Si₁₄C₂₇N₇H₄₃ | Si₁₄C₂₇H₂₆O₇ | Si₁₄C₂₇H₃₆O₇ |
|-----------------------------------|-------------|-------------|-------------|-------------|
| Si-N(O)                           | 1.66219     | 1.64510     | 1.78600     | 1.69457     |
| Si-C                              | 1.93675     | 1.95313     | 1.94512     | 1.97750     |
| C-C (between layers)              | 1.52171     | 1.63092     | 1.68332     | 1.62945     |
| C-C (in one layer)                | 1.35792     | 1.50653     | 1.35631     | 1.54063     |
| Si-Si (between layers)            | 2.66568     | 2.64633     | 2.64826     | 2.68012     |
| N…N (between layers)             | 3.40688     | 3.16203     | -           | -           |
| O…O (between layers)             | -           | -           | 3.28573     | 3.15433     |

**Table 1.** The distance between the atoms in three-layer units.
At the second stage of modeling, the possibility of reorganization of the primary structure and analysis of the formed structures for the presence of percolation clusters was realized. The search for the lowest concentration at which the formation of percolation cluster is possible is carried out. The presence of a percolation cluster ensures the conductivity of the coating, but high concentrations of the additive lead to a deterioration of adhesion to the substrate. It is determined that the concentration of the alloying component 0.2 mol % is sufficient for the formation of the percolation cluster.

Figure 3 shows the simulation results for different substrate dimensions (blue color indicates particles containing metal, red color indicates a silicon-carbon matrix). These results show that as the dimension of the substrate increases, the visual perception of the structure of the material is blurred, it is perceived as a continuous film, details are not visible.

Figure 3. Simulation results for the concentration of the alloying additive 0.2, the dimension of the substrate t: a) 100×100; b) 150×150; c) 200×200. Blue colour indicates particles containing metal, red colour indicates a silicon-carbon matrix.

The experiment on the calculation of dimension was carried out on a four-connected lattice of size $n \times n$, at $n=100$ and more. According to the simulation results, with an increase in the number of particles per unit surface, the value of the fractal dimension increases uniformly, which may be due to an increase in the number of particles distributed over the surface area.
The modeling was implemented taking into account three different concentrations of ions hindering the growth of clusters. The concentration of ions interfering with the growth of clusters was chosen in relation to the total number of particles (for particles in the amount of 100n the concentration of interfering ions was 15n, 25n, 35n). The results obtained allow us to speak about the dependence of the onset of percolation, i.e. the probability of cluster formation, on the number of particles at different pH. According to experimental data, it can be concluded that the probability of percolation does not depend on the pH of the medium at the number of initial particles 20n. At a lower concentration of the initial particles with increasing pH, the formation of a percolation cluster occurred earlier than in the case when the medium is not taken into account.

### 4. Conclusion

Quantum chemical studies have shown the possibility of embedding metal atoms in a silicon-carbon matrix, which will subsequently determine the modes of the process in the formation of doped silicon-carbon coatings.

After studying the evolution of two- and three-layer aggregates with increasing temperature using quantum chemistry methods, it was determined that at the initial stage of the structure growth, hydrogenated aggregates are looser, this will contribute to the penetration of metal ions into the interlayer space and access to oxygen and nitrogen atoms. Further, the communication of additional energy to the system allows the formation of metal oxides and nitrides while maintaining sp$^3$-hybridization of most carbon atoms than in the absence of an alloying component.

On the basis of standard models and algorithms for determining fractal and percolation clusters, the influence of input data on the final structure of the films is determined. It was also found that the pH of the medium significantly affects the density of the film structure, the growth of the percolation cluster and the fractal dimension.

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