Modeling the process of formation of fractal structures in thin films

A I Fedosimova, E A Dmitrieva, I A Lebedev, A T Temiraliev, T Temiraliev, M E Abishev, B A Baitimbetova, Yu A Ryabikin and A S Serikkanov

1Institute of Physics and Technology, Satbaev University, Almaty, Kazakhstan
2Al-Farabi Kazakh National University, Almaty, Kazakhstan

E-mail: abzal.temir@yandex.kz

Abstract. This paper presents the results of modeling the features of the formation of fractal structures in thin films of tin dioxide \( \text{SnO}_2 \) obtained by the sol-gel method. The process of hydrolysis of tin tetrachloride \( \text{SnCl}_4 \) leads to the formation of tin acid \( \text{Sn(OH)}_4 \), which has a gel-like structure. Unstable tin acid decomposes to form water and tin dioxide. The formation of cluster structures is considered depending on the "competition" of these two processes. The nonlinear evolution of sol-gel stochastic processes leads to a fractal structure of the film clusters. The peculiarities of the formation of fractal clusters and the morphology of a thin film are estimated depending on the control (technological) parameters.

1. Introduction

The ability of thin layers of \( \text{SnO}_2 \) to change the electrical conductivity during gas adsorption became the basis of their application in semiconductor sorption sensors along with other applications [1]. At present, several methods for the production of tin dioxide based on sol-gel technology have been developed [2-4]. The most interesting for gas sensitive sensors are layers with a controlled porous structure. Moreover the fact of occurrence of fractal cluster structures of colloidal particles of the dispersed phase is essential.

Models of formation of fractal structures differ clustering mechanisms: model the diffusion-limiting aggregation [5] where with high probability the cluster of random nature grows at the expense of adhesion particles/clusters to the original fractal cluster and pattern cluster-cluster aggregation [6], when combined formed small clusters. Small probability of particles/clusters sticking leads to deep penetration of clusters into each other and small fractal clusters are formed [7-10]. In the theory of diffusion-limited aggregation, particles experience thermal Brownian chaotic motion by clustering and diffusion processes dominate the system. The extension of this model is considered to be a cluster-cluster aggregation model in which, together with particles, clusters can move. For the study of diffusion because of the duration of the process cannot be applied the methods of molecular dynamics and used approximate methods Monte-Carlo.

When the number of particles is huge in the scale of the Avogadro number, the system has new collective properties when any local disturbance affects the entire condensed medium. The nature of collective excitations determine the different properties of the system. The interaction between the particles leads to the creation of nanostructured ensembles. Nanoparticles are nanoclusters with a large surface area, having excess energy and high chemical activity. Therefore, activation energy is not
required for aggregation processes and reactions with other compounds for the appearance of substances with new properties.

The classical Hamiltonian approach with generalized coordinates and pulses is not applicable. It is problematic to formulate/generalize and solve the quantum Schrödinger equation accurately even within the framework of the quantum field theory for a multi-partial system of interacting particles.

It is effective to apply the methods of nonlinear theory of dynamical systems, when instead of differential equations the mappings are used. From the knowledge of elementary microscopic processes, we can proceed to the identification of a global collective organization of the entire macroscopic cluster. The well-known phenomenon of self-organization in living and inanimate nature is associated with the correlated collective interaction of a large number of structural units of the ensemble. It is the nonlinearity of the random processes in sol-gel evolution that leads to a self-organizing self-similar fractal structure of the thin film. Methods of fractal and multifractal analysis characterized by the structure of the surface of a thin film SnO$_2$ and fractal knowledge of fractal dimension $D_f$ determined by the algorithm of construction of fractal aggregates. Self-organizing structures become fractal clusters during cluster aggregation, the fragment of which is repeated at different scales.

We model and solve the problem of structure formation in sol-gel processes using the methods of nonlinear theory of dynamic systems. The dynamics of interacting particles is reduced to a qualitative nonlinear approach of the known Poincare mapping method. Algorithms of evolution programs are developed and numerical computer calculations of model representation of formation of nanostructured clusters are carried out. Changing the initial data of the evolution process and, accordingly, the parameters of the cluster fusion and decay of clusters allows controlling the distribution of matter in the form of fractal structures of different dimensions. The expected characteristics of a thin film of tin dioxide are determined mainly by the fractal dimension of the clusters and are controlled by the parameter of evolution of a deterministic chaotic dynamic system.

The behavior of deterministic chaotic systems at long times is not predictable and statistical description is required. Then equilibrium systems are considered at times when fast nonequilibrium processes have ended and slow processes occur at such large times that they can be neglected. The thermodynamic system eventually comes to an equilibrium state. At equilibrium, each configuration of the microscopic system is given by the probability described by the Gibbs distribution for the state with the least energy in the limiting cases.

We model the formation of structures in the sol-gel process by considering the fusion and separation of chemical reaction reagents considering Brownian diffusion in conjunction with the so-called dynamically determined chaos. Interacting molecules are in a state of continuous chaotic motion and turn into nanoclusters that do not preserve the chemical properties of molecules. These processes (hydrolysis, condensation, coagulation, aggregation, etc.) are complex with some reversible stages of the process.

The evolution of the dispersed medium is influenced by such factors as the density of the medium, the degree of acidity (pH), the time of temperature exposure when the pressure is proportional to the concentration and temperature. Tunnel transitions of electrons between semiconductor states are also acceptable. Structure formation is accompanied by an increase in the viscosity of the system and depends on the concentration of particles of the dispersed phase. Diffusion plays a significant role in the adhesion of clusters. At the same time, diffusion is affected by the presence of internal cavities, pores. It is also important to assess the degree of diffusion effect (weak, strong).

To identify the dominant processes/mechanisms in the first stage, approximate toy model methods of solving the problem are used. If the binding energy is less than the energy of the Brownian diffusion motion, the Brownian random spatial structure formation dominates. The identification of optimal initial data for the sol-gel process can be done by the known method of "adjustment" in the boundary value problem of the differential equation. The realism of the approximations made and the accuracy of the methods used are estimated, as usual, by testing on an exactly solvable model. It is
required to obtain the programmed material properties. For a system with a large number of interacting particles, the accuracy of the solution depends on the choice of a numerical algorithm.

2. Modeling of stochastic Brownian process

It is possible to consider the formation of spatial structures through a random stochastic Wiener process describing Brownian motion. The interacting molecules are in a state of continuous thermal chaotic and fractal Brownian propagation. On the Brownian particle from the environment acts absolutely unpredictable chaotic force changing its magnitude and direction. For the simulation of the Brownian motion to the coordinates of the particles of the added random variables. The trajectory will be a fractal any part of which after increasing is similar to the whole. The stochastic and diffusion process under the influence of the chemical potential on the reagents and the gradient allows to consider the distribution as normal (Gauss). The difference of coordinate \( s \) at each subsequent step can be set by the normal distribution function \( \text{rnorm}(2.0, \sigma) \) with zero mean and dispersion \( \sigma \), depending on the particle mass and viscosity of the liquid.

The intersection of the trajectories of two particles is considered as a process of their coalescence (formation of a cluster). The intersection of particle-cluster and cluster-cluster trajectories leads to clumping (increase in cluster sizes). Figure 1 shows an example of the formation of structures in a Brownian motion with \( \sigma = 1 \).

![Figure 1. The formation of structures in the Brownian motion.](image)

In Brownian motion, the average force acting on the part of the medium is zero, but the correlation function depends only on the time interval. For time intervals less than the time correlation of the random interaction of the classical evolution is deterministic. In the future, the details of the medium impact on the particle are lubricated and the time-averaged values act as dynamic parameters. Given random stochastic fluctuations, Brownian evolution is described by the Langevin equation when the viscous friction forces proportional to the velocity/temperature according to the Stokes law are essential. At large times random walks of a Brownian particle / cluster acquire the character of a diffusion process. When the process becomes Markov (the future of the system is determined only by the present and does not depend on its background), the evolution of the system is determined by the Fokker-Planck equation.

As it was shown by Einstein, simultaneously with the special theory of relativity, the dispersion of the Brownian signal increments depends only on the observation time interval, and not on the values of the times themselves. The changes in the position of a Brownian particle determined by a random function \( r(t) \), as well as the increments of the function \( \Delta r = r(t) - r(t_1) \), have a Gaussian distribution. The variance of the increments of the Brownian distribution is \( \sigma^2 t \), where \( t \) is the time difference. Increments have the property of statistical self-similarity of distributions with the same
mathematical expectation and variance. The confirmation of this in the processing of data indicates that its structure belongs to a fractal with a dimension $D \approx 1.5$ as in the Brownian motion.

Combining the molecules into cluster structures reduces the surface area of the nanoparticles and thus reduces the surface tension. However, the decrease in surface energy is partially compensated by the presence of pores in the gel state.

3. **Modeling the process of formation of fractal structures in thin films**

Non-linear differential equations of the diffusion with dynamically determined randomness can be used for modeling the features of the formation of fractal structures in thin films obtained by the sol-gel method.

We consider thin films of tin dioxide, $SnO_2$, belongs to the group of nonstoichiometric semiconductors with the ratio of $O/Sn < 2$. The $SnO_2$ nonstoichiometry may be a consequence of oxygen vacancies ($SnO_x$) or the presence of interstitial tin atoms ($Sn_{1+y}O_2$).

The process of hydrolysis of tin tetrachloride $SnCl_4$ leads to the formation of tin acid $Sn(OH)_4$, which has a gel-like structure:

$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$

Unstable tin acid decomposes to form water and tin dioxide:

$$Sn(OH)_4 \rightarrow SnO_2 + 2H_2O$$

The formation of cluster structures is considered depending on the "competition" of these two processes.

The presence of a large number of particles can lead to collective correlated behavior of the condensed/dispersed medium. The isolated thermodynamic system over time comes to a state of equilibrium when there is both a direct and an inverse reaction with an arbitrary relaxation time. From the solution of microscopic equations of motion of particles interacting with each other it is possible to obtain macro thermodynamic characteristics of the system, averaging along the trajectories. Using methods of nonlinear dynamics, evolution is alternatively modeled using the Poincare map.

It is possible in diffusion processes, the mass flow is due to the motion of particles involved in the Brownian thermal chaotic motion. Mathematical models of diffusion processes are based on the fundamental laws of substance conservation in the integral or differential form of the Ostrogradsky-Gauss equations. For small differences in the concentration of the substance $u(r,t)$, the Fick law for the diffusion flux: $-d \cdot \text{grad } u(r,t)$ is applicable. In case of significant changes in concentration over time, Fick's law applies: $\dot{u}_t = d \cdot \Delta u + f(u,t)$.

The concentration of reagents depending on the scheme and mechanism of the dynamic process can simultaneously decrease in proportion to the concentration and increase in parallel competing, successive or reversible chemical reactions. Considering that the diffusion process from the concentration of substance $u(x,y,t)$ in the approximation of deterministic dynamic chaos is described by the diffusion equation with dynamically determined chaos. So, a differential equation of the diffusion process in a chemically active medium with dynamically determined randomness, associated with quadratic nonlinearity $u^2$ can be represented in the form: $k_p \cdot \dot{u}_t = d \cdot \Delta u + f(u,t)$ with the porosity ratio $k_p$ [11] or

$$k_p \frac{\partial u(x, y, t)}{\partial t} = d \left( \frac{\partial^2 u(x, y, t)}{\partial x^2} + \frac{\partial^2 u(x, y, t)}{\partial y^2} \right) + f(u,t)$$
This is a nonlinear differential diffusion equation with an incremental nonlinear function \( f(u,t) = \mu(t) \cdot A \cdot (\alpha \cdot u - \beta \cdot u^2) \) with the normalization condition \( A \) and parameter of the evolution \( \mu \). The nonlinear function \( f(u) \) is the density of the internal source of structures in the evolutionary competition of the generation and recombination of elements of the substance (molecules, ions, clusters) of the dynamic system with the coefficient of birth \( \alpha \) and absorption \( \beta \). At certain values of the parameter \( \mu \), the function \( f(u) \) leads to so-called deterministic dynamic chaos.

We use an explicit Euler lattice difference scheme with a uniform time step and spatial coordinate. For the difference scheme, we introduce the time step \( \Delta t = \tau \) and the coordinate step \( \Delta r=L \). Model derivatives in the differential equation of their difference analogies get an approximate solution lattice points:

\[
\begin{align*}
    k_p \cdot \frac{u_{i,j+1} - u_{i,j}}{\tau} &= d \cdot \frac{u_{i-1,j} - 2u_{i,j} + u_{i+1,j}}{L^2} + \mu \cdot u_{i,j}(1 - u_{i,j})
\end{align*}
\]

It is assumed that the concentration density at the \((j+1)\) stage of evolution is proportional to the density of the concentration in the \((j)\)-th generation of the \((\text{linear member})\). The quadratic term describes the decrease in the concentration density as a consequence of the processes of merging into clusters. Introducing the Courant number \( \alpha = \tau d/L^2 \), counting \( k_p = 1 \) and control parameter \( \gamma = \tau \mu \) we solve a system of equations:

\[
    u_{i,j+1} = (1 - 2\alpha) \cdot u_{i,j} + \alpha \cdot (u_{i-1,j} + u_{i+1,j}) + \gamma \cdot u_{i,j}(1 - u_{i,j})
\]

Figures 2 and 3 show the stage of formation of structures in a chemical reaction with diffusion and dynamically determined randomness for different values of \( \gamma \) parameter, connected with the competition of the processes of fusion and decay of clusters. We take the time discreteness \( \tau = 10^{-5} \), which corresponds to \( \alpha = 4 \cdot 10^{-3} \). The difference scheme is stable at the Courant number \( \alpha = \tau d/L^2 < 1 \).

`Figure 2. Formation of structures at \( \gamma \) parameter in interval of \( 0 \leq \gamma \leq 0.97 \)`

`Figure 3. Formation of structures at \( \gamma \) parameter in interval of \( 0.85 \leq \gamma \leq 0.97 \)`

Figures 4, 5 and 6 show the complex nature of dynamic structure formation in the sol-gel physical and chemical processes associated with the absorption and decomposition of reagents in the evolutionary process, the occurrence of diffusion in chemical reactions with deterministic chaotic distribution of matter, the processes of condensation, the transfer of a substance in another layer, etc. Within a dynamically deterministic chaos for different values of the parameter \( \gamma \) of the evolution generated by various fractal structure of a particular fractal dimension. Branching growth exponentially of new fractal clusters is the source of the next generation of fractal spatial formations. The crank-Nicholson difference computational scheme, devoid of instability problems, yields the same results.
Mandelbrot defined a fractal as an object with a Hausdorff-Bezikovich dimension (fractal dimension) greater than its topological dimension. To determine the fractal dimension, we construct an increment of the expectation \( S_m = E[|X_{k+m} - X_k|] = \frac{1}{K-m} \sum_{k=1}^{K-m} |X_{k+m} - X_k| \)

Figure 4. Formation of thin film structure in a sol-gel process at parameter \( \gamma = 0.33 \)

Figure 5. Formation of thin film structure in a sol-gel process at \( \gamma = 0.97 \)

Figure 6. Formation of thin film surface structure in a sol-gel process at \( \gamma = 0.97 \)

Figure 7 shows negative values of the Lyapunov exponent \( \lambda_t = \frac{ln|u_{t+1} - u_{t+2}|}{0.0003} \) and hence the stability. The difference in the behavior of the fractal function at different values of the parameter is shown in figure 8. The presented figures show the presence of multi-fractal structures arising in nonlinear sol-gel processes during the period doubling bifurcation.

Figure 7. Lyapunov’s exponent \( \lambda_t \) at \( \gamma = 0.9 \)

Figure 8. Behavior of structural function \( S_m \) at \( \gamma = 0.9 \)

The expectation of the increment square can be represented by the Hurst parameter \( H \) (0<\( H <1 \)) as: \( E[(r(t)-r(t_0))^2] = \sigma^2 |t-t_0|^{2H} \). The Hurst parameter \( H = 0.25 \) and the dimension of the fractal is \( D = 2 - H \approx 1.75 \), which are determined by the slope of the angle in \( S_m \).

4. Conclusions
In the evolution of nonlinear dynamic systems in sol-gel processes, the dominant mechanism of formation of spatial structures may be the phenomenon of self-organization. By methods of nonlinear dynamics it is possible to show Lyapunov stability of attractor fractal structures, the evolution/growth of which is determined by chemical reactions with diffusion in the approach of deterministic chaos. The formation fractal clusters is determined by the chaotically determined competition of clustering and decay processes depending on the control parameter \( \gamma \) of nonlinear evolution. The combination of
concentrations of reactants in a chemical reaction given molar mass with the variation of the parameters of the modeling process will identify the degree of deviation from a purely diffusion distribution of the clusters.

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References
[1] O’Sullivan M at al. 2018 Scientific Research 8 89
[2] Dmitrieva E A at al. 2014 Glass Physics and Chemistry 40 31
[3] Mukashev B N at al. 2005 Materials Science and Engineering B 118 164
[4] Mukhamedshina D M at al. 2006 High Temperature Material Processes 10 603
[5] Witten Jr T A and Sander L M 1981 Phys. Rev. Lett. 47 1400
[6] Brinker C J and Scherer G W 1985 J. Non-Cryst. Solids 70 301
[7] Moshnikov V A and Alexandrova O A 2015 New nanomaterial. Synthesis. Diagnostics. Modeling (SPb.: Publishing house Etu "LETI")
[8] Pan T at al. 2018 Phys. Rev. Lett. 120 248101
[9] Thai M H, Pan R, Ahn J, Bang J, Quan H T and Li T 2018 Phys. Rev. Lett. 120 080602
[10] Zhang W at al. 2013 J. SCIENCE 342 1502
[11] Martinson L K and Malov Yu I 2002 Differential equations of mathematical physics (M.: MSTU)
[12] Korolenko P V et al. 2004 Innovative methods of analysis of stochastic processes and structures in optics. Fractal and multifractal methods (M.: Moscow state University, SINP)