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BIRTH AND FUSION IN A SOL-GEL PROCESS WITH LOW DIFFUSION

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Based on the developed methods of nonlinear dynamics of the mapping of Poincare sections, a numerical simulation of the formation of thin SnO_2 films in sol-gel chemical reactions against the background of weak diffusion where carried out. Numerical calculations were carried out in the framework of dynamically determined chaos in intense opposing processes of merging and decay. For a chemically active medium in the sol-gel process, the differential diffusion equation with an internal source of nonlinearity is used. The simulation results qualitatively confirm the experimental fact of the emergence of Poisson-stable fractal cluster structures. The presence of fractal structures in the experimental results on thin films means the presence of nonlinear collective phenomena. The method of nonlinear self-organization of stable structures in a multi-particle system with competing internal processes is thought to be interesting for new technologies.

Keywords: Chaos, fractal, thin films, sol-gel process.

Introduction

A significant concentration of a huge number of interacting objects leads to the emergence in the dynamic system of new collective properties when any local perturbation, with a sufficient density of particles, affects the entire condensed medium. The nature of collective excitations determines the various properties of the system and leads to the emergence of various nanostructured ensembles. In complex open systems with a huge number of interacting objects, collective phenomena such as self-organization of structures arise. Such a collective action in the formation of structures G. Haken called "synergetics" [1]. Nanoclusters and particles with a large surface area have excess potential energy and high chemical activity. Therefore, no activation energy is required for aggregation processes and reactions with other compounds for the appearance of substances with new properties.

As A. Poincare once pointed out: in some non-integrable mechanical systems, the evolution of which, although determined by the Hamiltonian approach, may lead to unpredictable chaotic behavior. In real systems, irreversible dissipative processes are present, such as diffusion or a chemical reaction, and entropy grows in them. In this case, it is effective to use the methods of the nonlinear theory of dynamical systems, when instead of differential equations the Poincaré maps with bifurcations and other phenomena of the nonlinear theory are used. Knowledge of elementary microscopic processes will allow to identify the collective organization of a macroscopic cluster. The correlated interaction of a large number of elements of an ensemble can lead to the well-known phenomenon of self-organization.

The thin layers of tin dioxide SnO_2 can change the electrical conductivity during gas adsorption and this became the basis for their use in semiconductor sorption sensors along with other applications. Currently, several methods for producing tin dioxide based on the sol-gel technology have been developed [2–4]. For gas-sensitive sensors, films with a controlled porous structure are of particular interest. Essential is the fact of experimental confirmation of the occurrence of fractal-cluster structures of colloidal particles of the dispersed phase.

Models for the formation of fractal structures differ in clusterization mechanisms: models of diffusion-limited aggregation [5], models of cluster-cluster aggregation [6]. The low probability of particles or clusters sticking together leads to deep penetration of the clusters into each other and the formation of small fractal clusters [7-13].

We simulate a sol-gel process with harsh chemical reactions against the background of slow diffusion by a nonlinear parabolic equation. In diffusion processes, the mass flow is due to the motion of particles participating in Brownian thermal chaotic motion with energy ***kT*** (***T***-absolute temperature, Boltzmann ***k***-constant). Mathematical models of diffusion processes are based on the fundamental laws of conservation of matter in the integral or differential form of the Ostrogradsky-Gauss equations. For small differences in the concentration of the substance u (r, t), we apply the law for the diffusion flux: [$D \cdot grad\ u(r,t)$]. In case of significant changes in concentration over time, the law of diffusion applies: $\dot{u}_t = D \cdot \ddot{u}_{rr}$

1. Modeling the process of formation of fractal structures in thin films

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, sequential or reversible chemical reactions. Given that the diffusion process for the concentration of the substance ***u(r, t)*** in the approximation of deterministic dynamic chaos is described by the diffusion equation with dynamically determined chaos. So, the differential equation of the diffusion process in a chemically active medium with a dynamically determined randomness associated with the quadratic nonlinearity $\boldsymbol{u^2}$can be represented in the form [14]:

$$k_p \cdot \frac{\partial u(x,t)}{\partial t} = \frac{\partial}{\partial \mathrm{x}}\left[D(u)\frac{\partial u(x,t)}{\partial x}\right] + k(t) \cdot \varphi(u),$$

with diffusion coefficient ***D(u)***, porosity coefficient $\boldsymbol{k_p}$ [11] and evolution parameter $k(t)$in a quadratically nonlinear function:

$$\varphi(u) = A(\alpha \cdot u - \beta \cdot u^2)$$

with a normalization coefficient A, which will determine the degree of rigidity of the process.

The nonlinear function ***φ(u)*** is the density of the internal source of the formation of structures in the evolutionary competition of the processes of generation and recombination of the elements of a substance (atoms, ions, molecules, clusters) of a dynamic system with production coefficients ***α*** and absorption ***β***. For certain values of the evolution parameter $k(t)$, the so-called dynamically determined chaos arises. The expected characteristics of a thin film of tin dioxide are determined mainly by the fractal dimension of the clusters, which are determined by the evolution parameter $k(t)$ of the deterministic chaotic dynamical system. The evolution parameter may also depend on the influence of thermal effects on the properties of films$[k(t) \to k(t,T)]$.

We solve the diffusion equation with an internal source with boundary and initial conditions:

$$\begin{cases} \dfrac{\partial u(x,t)}{\partial t} = \dfrac{\partial^2 u(x,t}{\partial x^2} + k(t) \cdot \varphi(u) \\ u(x,0) = \varphi(x), \qquad 0 \le x \le 1 \\ u(0,t) = u(1,t) = 0 \end{cases}$$

After replacing the partial derivatives by their discrete analogues, we obtain a difference scheme:

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$$\frac{(u_{i+1,j}-u_{i,j})}{\Delta t}=\frac{\sigma}{(\Delta x)^2}(u_{i+1,j-1}-2u_{i+1,j}+u_{i+1,j+1})+\frac{1-\sigma}{(\Delta x)^2}(u_{i,j-1}-2u_{i,j}+u_{i,j+1})$$

For σ=1/2, the average of the two central derivatives is obtained (the Crank-Nichols scheme), for σ=0 the usual explicit scheme and σ=1 the implicit scheme.

We rewrite the implicit difference scheme (σ = 1)

$$\frac{(u_{i+1,j}-u_{i,j})}{\Delta t}=\frac{D}{(\Delta x)^2}(u_{i+1,j-1}-2u_{i+1,j}+u_{i+1,j+1})+f(u_{i,j})$$

as:

$$A_j u_{i+1,j-1}-B_j u_{i+1,j}+C_j u_{i+1,j+1}=F_j$$

The value from the lower layer, which is known, we have enclosed in the coefficient F_j. The remaining coefficients are expressed in steps of time, space and D. So we got difference equations that are connected by a system of linear algebraic equations.

2. Results and discussions

The results of computer numerical calculations of the differential equation of evolution of the state of a dynamic system in the sol-gel process are shown in Figures 1.

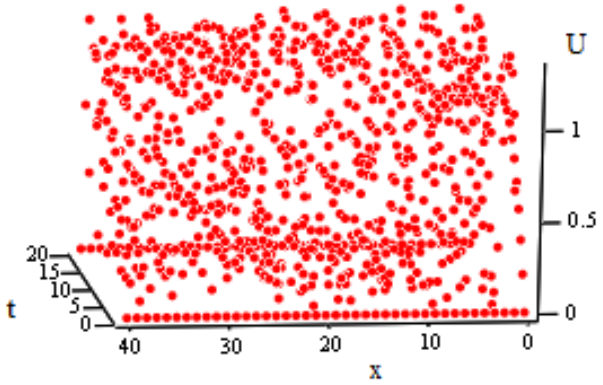


Fig.1. Formation of thin film structure in a sol-gel process at k=0.97

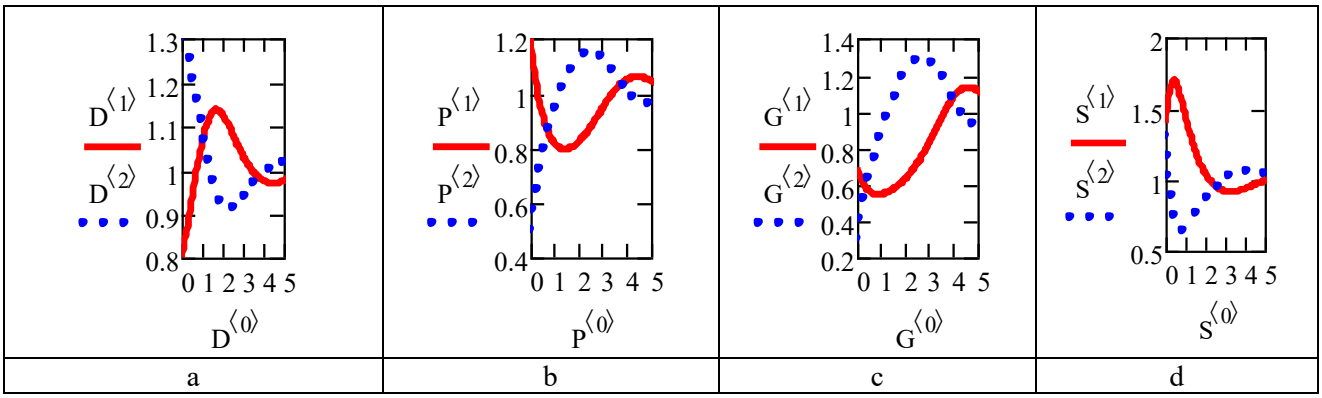
The formation of structures depends on the evolution time, which in our model is determined by the parameter k(t) and is shown in Figure 2. Moderation is programmed by setting several pairs of initial conditions for the concentration of reagents. A combined matrix is formed from separate matrices of solutions of the nonlinear differential equation for different initial conditions. The calculations of the evolution of the dynamic system of a chemical reaction with diffusion of this sol-gel formation of thin films are shown in Figures 1 and 2. The constructed trajectories on the phase plane reflect the dynamics of the concentration of intermediate products of the chemical reaction.

Model parameters are initial concentrations. A study is being made of the solution of a nonlinear differential equation depending on various initial conditions. There is a direct proportion to the ripening temperature of thin films and the evolution time in modeling the sol-gel system. More specifically, this is the number of steps in numerically solving a differential equation. The model is constructed in accordance with the idea of the so-called Prigogine brussellator [15] for solving the system of equations of an autocatalytic chemical reaction with diffusion. Moderation is programmed by setting several pairs of initial conditions for the concentration of reagents.

a b c d

Fig.2. Stages of the formation of U-surface structures of a thin SnO_2 film with parameter: a) k = 0.1; b) k = 0.2; c) k = 0.5; d) k = 0.9.

A combined matrix is formed from separate matrices of solutions of the nonlinear differential equation for different initial conditions. The calculations of the evolution of the dynamic system of a chemical reaction with diffusion - sol-gel formation of thin films are shown in Figures 3 and 4.



a b c d

Fig.3. The graph of the time dependence of the solution of the differential equation: a) for the distribution function D under initial conditions 0.8 and 1.3; b) function P under initial conditions 0.5 and 1.2; c) function G under initial conditions 0.7 and 0.3; d) function S under initial conditions 1.4 and 1.3 .

The constructed trajectories on the phase plane reflect the dynamics of the concentration of intermediate products of a chemical reaction. The parameters of the model are the initial concentration. We present a part of the program code for further calculations presented in Figures 3.

$$F(t,y) := \begin{bmatrix} -(k+1)\cdot y_0 + (y_0)^1 \cdot y_1 \cdot k + 1 \\ k\cdot y_0 - (y_0)^1 \cdot y_1 \cdot k \end{bmatrix}$$

$$D := \text{rkfixed}\left[\begin{pmatrix} 0.8 \\ 1.3 \end{pmatrix}, t0, t1, N, F\right]$$

$$N := 500 \qquad t0 := 0 \qquad t1 := 20$$

$$P := \text{rkfixed}\left[\begin{pmatrix} 1.2 \\ 0.5 \end{pmatrix}, t0, t1, N, F\right]$$

$$G := \text{rkfixed}\left[\begin{pmatrix} 0.7 \\ 0.3 \end{pmatrix}, t0, t1, N, F\right]$$

$$S := \text{rkfixed}\left[\begin{pmatrix} 1.4 \\ 1.3 \end{pmatrix}, t0, t1, N, F\right]$$

From Figure 4 it can be seen that all the trajectories from the solution of the system of differential equations that come from different starting points converge to the so-called attractor

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with coordinates (1.1) from the theory of nonlinear dynamical systems. In this case, this attractor is a “node”. The counteraction of various direct and reverse chemical reactions along with coagulation and peptization in a dispersed medium in sol-gel processes with a stochastic diffusion component leads to the establishment of a certain stationary state with equilibrium concentrations. This will allow obtain optimal parameters.

Conclusion

The presence of fractal structures in the experimental results on thin films means the presence of nonlinear collective phenomena associated with the stochastic process. Fractal dimension is an essential parameter for understanding the properties of film roughness. Algorithms of evolutionary programs were developed and numerical computer calculations were performed for a model representation of the formation of nano-structured clusters of thin films. An interesting review of the fractal analysis of thin films is given in [16]. The formation of structures in dynamically determined chaos [17, 18] provides the key to the development of new nano-structured materials, new quantum technologies.

The method of forming structures within the framework of the introduced nonlinear equation for competing processes of decay and fusion against the background of weak diffusion is new approaches for the mechanism of structure formation. The results of computer modeling indicate the collective effects of self-organization of stable structures. The nonlinear evolution of many-particle sol-gel dynamics with opposing chemical reactions leads to the formation of fractal clusters, which corresponds to the available experimental data on the fractal structure in thin films. The performed numerical calculations within the framework of dynamically determined chaos, like any calculations in deterministic chaos, can be unambiguously reproduced.

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