Peculiarities of ripening and spinodal decomposition of self-organizing fractal systems

I A Pronin¹, N D Yakushova¹, I A Averin¹, A A Karmanov¹
and V A Moshnikov¹,²

¹Department of Nano- and Microelectronics, Penza State University, 440026, Penza, Russia
²Department of Micro- and Nanoelectronics, Saint Petersburg Electrotechnical University “LETI”, 197376, St. Petersburg, Russia

E-mail: nano-micro@mail.ru

Abstract. Qualitative and quantitative patterns for the synthesis of nanostructured films by the sol-gel technology method, established on the basis of theoretical models and experiments, are presented. The effect of annealing temperature, types of solvents and substrates on the morphostructure of the film surface is shown. A technique for the synthesis of films for sensitive elements of gas sensors and vacuum sensors based on orthosilicic acid has been developed.

In recent years, nanostructured films have been considered as promising materials for the creation of gas sensors and adsorption vacuum sensors, based on the principle of changing electrical conductivity of the material under the effect of analyte gases [1–2]. Nanotechnology makes it possible to create new-generation sensors with improved characteristics, such as sensitivity, selectivity, power consumption, as well as small weight and dimensions [3–4]. Using the sol-gel technology, it is possible to create gas-sensitive films with a system of different pores [5]. They include both a quasi-ordered system on the surface and 3D branched porous structure (figure 1).

Figure 1. Pores on the surface of sol-gel composites: a quasi-ordered system of pores on the surface of films (a) and 3D mesh composite (b).
The pore size on the film surface depends on many factors, e.g., type and concentration of the solvent, temperature and annealing time, etc. Pores in the branches of 3D composites play a decisive role in the processes of gas sensitivity. Branches are percolation networks being a product of spinodal decomposition. They are formed by hierarchical structures, which, as a rule, do not reach the percolation spanning cluster. The main contribution to the surface development is made by meso- and micropores, the size of which is less than 10 nm. All of them are beyond the sensitivity of atomic force microscopy, although they are determining the processes of gas sensitivity. Therefore, it is of interest to evaluate porosity and control pore sizes within the framework of the simplified Smoluchowski model. The aim of this work was to assess the influence of factors (viscosity, time and temperature of annealing) on the processes of regular assembly of fractals in sol-gel nanosystems.

In 1916, M. Smoluchowski developed the theory of rapid coagulation, the kinetics of which is determined at the initial concentration of sol particles \( c_0 \) by the following ratio:

\[
\frac{dc}{d\tau} = \xi c_0^2 ,
\]

where \(-dcd\tau\) is coagulation rate; \( \xi \) is coagulation rate constant, which depends on the diffusion coefficient both for temperature \( T \) and viscosity \( \eta \), being defined as:

\[
\xi = \frac{8kT}{3\eta} ,
\]

where \( k \) is the Boltzmann constant.

In turn, the viscosity of a colloidal solution is related to its concentration \( c \) with the Einstein relation [4]:

\[
\eta = \eta_0 (1 + \alpha c) ,
\]

where \( \eta_0 \) is dispersion medium viscosity; \( \alpha \) is a constant for spherical particles equal to 2.5.

Taking into account viscosity correction, the Smoluchowski equation takes the form:

\[
-\frac{dc}{d\tau} = \frac{8kTc_0^2}{3\eta_0 (1 + \alpha c)} .
\]

The following function will be its solution:

\[
c(\tau, T) = \frac{1}{\alpha} (\sqrt{1 + 2\alpha A(\tau, T)} - 1) ,
\]

where \( A(\tau, T) = \frac{\alpha c_0^2}{2} e + c_0 e_1 - \frac{8kTc_0}{3\eta_0} e_2 \tau \), and \( e, e_1, e_2 \) are dimensional factors.

Taking into account that \( c_0/c \) determines the average number of molecules in a cluster \( n \), we rewrite (5) in the form:

\[
n(\tau, T) = \frac{\alpha c_0}{\sqrt{1 + 2\alpha A(\tau, T)} - 1} .
\]

Next, we will consider spatial localization of all particles that make up the cluster. The results of atomic force microscopy have shown that quasi-spherical particles with a porous structure are the product of sol-gel processes. Such objects possess the property of self-similarity; therefore, they can be described quite accurately using the theory of fractals. Three-dimensional Julien fractal is the most suitable one for modeling such nanostructures [6]. The assembly of such fractal structures occurs if we assume that there is no transition to the next stage until the spherization of the previous one at each stage of fractalization.

Let us simulate the assembly of fractal aggregates like Julien fractal taking into account the solution of the Smoluchowski equation. The three-dimensional Julien fractal contains \( \zeta = 13 \)
composite particles, and the growth factor of the aggregate diameter being $\chi = 3$ during the next iteration. After $p$ iterations, the aggregate will contain $n = \zeta^p$ particles, and its radius will be $r = \delta \chi^p$, where $\delta$ is the radius of a single particle. Then the radius of the aggregate, depending on the number of particles therein, will have the form:

$$r = \delta \chi^{\ln(n)/\ln(\zeta)}.$$  \hfill (7)

Substituting (1) into (7), we obtain:

$$r(\tau, T) = \delta \chi^{\gamma},$$  \hfill (8)

where the notation $\gamma = n \left( \frac{\alpha c_0}{\sqrt{1 + 2\alpha A(\tau, T)}} / \ln(\zeta) \right)$ is introduced.

Let us consider the effect of viscosity on coagulation of sol-gel systems. It follows from (1) that the rate of coagulation is inversely proportional to the dynamic viscosity of the dispersion medium. A number of experiments were carried out for experimental confirmation of the pattern. One-component systems based on $\text{SiO}_2$ were studied. Simple alcohols, including ethanol, 1-butanol, and 2-butanol, were used as solvents. Figure 2 shows images of the film surfaces obtained using atomic force microscopy.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Morphostructure of film surfaces obtained by the sol-gel technology using various solvents: TEOS – ethanol (a), TEOS – 1-butanol (b), and TEOS – 2-butanol (c) systems.}
\end{figure}

It is seen that with an increase in the viscosity of the dispersion medium, the sizes of clusters decrease, as does the dispersion of their size distribution. Quantitative characteristics of the cluster size dependence on the medium viscosity are shown in figure 3.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Dependence of the cluster diameter $d$ on solvent viscosity.}
\end{figure}
Equation (8) shows good agreement with theoretical concepts of rapid coagulation and gives the right to assume that the Julien fractal describes the product of the sol-gel synthesis both qualitatively and quantitatively with sufficient accuracy.

Another important factor affecting the surface morphology of the films prior to their annealing is sol maturation time. It can be seen from dependence (6) that the number of atoms in the cluster will be proportional to $\tau^{-1/2}$. It follows that the cluster radius will obey the law of $G(\chi^{-1/2})^{\ln(3)}$, where $G$ is some constant. The resulting dependence curve will be close to hyperbole. This means that in the first minutes of coagulation the process of cluster growth will go on very quickly, being slower later.

This fact is reflected in figure 4, which shows the morphostructure of films being ripened within one hour and a day after the reaction. It is seen that the clusters have gained a diameter of about 100 nm within one hour, and that of about 250 nm after a day.

Figure 4. Film morphostructure at different sol maturation time: one hour (a) and a day (b).

The final stage in the formation of gas-sensitive films is their annealing. At this stage, polymer films turn into silicate films, and hydroxides and dopant metal salts turn into oxides. It is at this stage that it is possible to form a structure most suitable for further use. When creating gas-sensitive elements of nanosensors [7–8], it is necessary to obtain a branched meso- and microporous structure with the maximum value of porosity percentage of the composite.

In general, an increase in heat treatment duration of films contributes to a decrease in the total porosity. The films become smoother, their roughness decreases, pores are practically absent (figure 5). Highly alloyed films have the highest porosity, and the pore size on their surface increases with intense high-temperature annealing. From this point of view, annealing of films with high dopant content at a temperature of 700 K is optimal.

Figure 5. Film morphostructures for different annealing time (annealing temperature is 600 K): 10 minutes, roughness – 540 nm (a), 15 minutes, roughness – 370 nm (b), and 20 minutes, roughness – 100 nm (c).
Besides processes occurring in sol during its maturation and syneresis, the type of substrate plays an important role in the formation of films. To study its effect, three types of substrates were chosen, namely, two amorphous (glass, sitall) and one crystalline (Si (111) KEF 0.3). It was found that it is optimal to use crystalline substrates, since the morphostructure of the films deposited thereon is more uniform and periodic, and the cluster size distribution has a lower dispersion.

Thus, within the framework of this work, models for coagulation and syneresis of thin glassy films were constructed based on the theory of rapid coagulation and the theory of fractals. The resulting models have been confirmed by the outcomes of experiments. Optimal conditions for the synthesis of nanostructured films in the framework of the sol-gel technology for gas sensors and vacuum sensors have been determined.

Acknowledgments

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the research project No. 19-08-00924, as well as the Scholarship of the President of the Russian Federation No. SP-3800.2018.1 and No. SP-84.2018.1.

References

[1] Potyrailo R A, Go S, Sexton D, Li X, Kolmakov A, Amm B, St-Pierre R, Scherer B, Nayeri M, Wu G, Collazo-Davila C, Forman D, Calvert C, Mack C and McConnell P 2020 Nature Electronics 3 280–9
[2] Punetha D, Kar M and Pandey S K 2020 Scientific Reports 10 2151
[3] Pronin I A, Yakushova N D, Averin I A, Karmanov A A, Moshnikov V A and Dimitrov D Tz 2018 Coatings 8 433
[4] Averin I A, Igoshina S E, Moshnikov V A, Karmanov A A, Pronin I A and Terukov E I 2015 Technical Physics. The Russian Journal of Applied Physics 60(6) 928–32
[5] Pronin I A, Averin I A, Yakushova N D, Karmanov A A, Moshnikov V A, Ham M-H, Cho B K and Korotcenkov G 2017 Arabian Journal for Science and Engineering 42(10) 4299–305
[6] Averin I A, Igoshina S E, Karmanov A A, Pronin I A, Moshnikov V A and Terukov E I 2017 Technical Physics. The Russian Journal of Applied Physics 87(5) 780–7
[7] Fedorov F, Vasilikov M, Lashkov A, Varezhnikov A, Fuchs D, Kubel C, Bruns M, Sommer M and Sysoev V 2017 Scientific Reports 7 9732
[8] Kim J, Yoo H, Ba V A P, Shin N and Hong S 2018 Scientific Reports 8 11958