Sol-gel system evolution control for the synthesis of gas-sensitive nanomaterials based on semiconductor oxides

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Abstract. The article analyzes conditions for the occurrence of spinodal decomposition in sol-gel systems based on semiconductor oxide precursors, resulting in labyrinthine structures. Such materials are promising for use in chemoresistive gas sensors with increased sensory response. It is shown that system evolution towards these structures is possible due to sol cooling, or increased its maturation time.

Reducing operating temperatures, and increasing sensitivity and selectivity are the key issues for modern gas sensors [1, 2]. Currently, the industrial production of sensors is based on expensive methods using equipment to create and maintain a certain level of vacuum in the working chamber, magnetron sputtering being the main one. Sol-gel technologies using both centrifugation and dipping in the formation of gas-sensitive layers may serve as an alternative to traditional methods [3, 4]. Flexible control over sensitivity and selective properties of sensors without complicating their production technology is of particular interest. To create chains of quasi-spherical semiconductor grains having small contact area is relevant for this problem to be solved. When gas is adsorbed onto the resulting structure, there is an enrichment or depletion of charge carriers (depending on gas redox properties), which strictly affects conductivity of isthmuses between grains. As a result, it is possible to obtain a new generation of gas sensors with very high sensitivity [5, 6].

The key problem here is to create such semiconductor chains in the sensor substrate matrix. Spinodal decomposition of solutions, which implements labyrinthine structures of a mechanical mixture of phases, is of great interest for solving this problem (figure 1).

Using spinodal decomposition and the sol-gel method, it is possible to obtain a similar structure for semiconductor grains (usually, wide bandgap SnO₂). To ensure a high yield of suitable products, it is necessary to control the mechanism of spinodal decomposition. Therefore, the aim of this work is to establish physical and chemical patterns for spinodal decomposition of solutions, and to study types of phase separation of solutions.

Spinodal and binodal concepts are fundamental in stability theory of solutions. The binodal separates the regions of stable and metastable states on the phase diagram of solutions, and it is specified by the equality to zero of the first derivative of the Gibbs energy of mixing by concentration at constant temperature and pressure:
In the region of metastable states, the system is resistant to low concentration diffusion, but not resistant to high concentration. There is also a region of labile states, where the system is absolutely unstable and disintegrates without the application of energy from outside. This region is separated from the region of metastable states by the spinodal determined by the relation:

\[
\left( \frac{\partial G_{mix}^n}{\partial n} \right)_{T,p} = 0. 
\]  

(1)

Let us consider the change in the Gibbs energy during the dissolution of a polymer in a solvent. The Gibbs energy is determined by the difference between the enthalpy \( H_{mix} \) and entropy \( S_{mix} \) terms by the classical Clausius-Clapeyron relation:

\[
dG_{mix} = dH_{mix} - TdS_{mix}. 
\]

(2)

Since the structure of a semiconductor sensor is created using the sol-gel technology, its product is a polymer that is self-assembled during synthesis. To determine its thermodynamic parameters, we use the Flory-Huggins lattice model [3]. According to this theory, the entire space of the solution is divided into unit cells, filled with either a polymer molecule or a solvent molecule. Considering this, the interaction energy for a two-component system \( \Delta w \) is determined as:

\[
\Delta w = w_{12} - \frac{1}{2} (w_{11} + w_{22}), 
\]

(3)

where \( w_{12} \) is the interaction energy of a monomer chain link with solvent molecules; \( w_{11} \) is the interaction energy of solvent molecules with each other; \( w_{22} \) is the interaction energy of a monomer element of a chain with other elements of the same chain.

Hence, the enthalpy of the polymer dissolution process is as follows:

\[
\Delta H_{mix} = kTN_1 \left( \frac{xN_2}{N} \right) \chi, 
\]

(4)

where \( k \) is the Boltzmann constant; \( N_1 \) is the number of solvent molecules; \( N_2 \) is the number of polymer molecules of polymerization degree \( x \); \( N \) is the total number of interactions; \( \chi \) is the Flory-Huggins parameter.
The entropy value is determined in a similar way, following the Flory-Huggins lattice model, by the Boltzmann relation:

\[ S^{\text{mix}} = k \ln W, \]

where \( W \) is the number of microstates that can be used to implement a given macrostate of the system. Then, following this relationship, we get:

\[ S^{\text{mix}} = -R \left[ x \ln x + (1-x) \ln(1-x) \right], \]

where \( R \) is the universal gas constant.

It should be noted that system configurational entropy decreases to zero while forming a percolation spanning polymer cluster in the solution volume during polymerization. Thus, using (3), (5), (7), we obtain the Gibbs energy function:

\[ G_{\text{polymer}}^{\text{mix}} = kTN \left( \frac{xN_2}{N} \right) \chi + TR \left[ x \ln x + (1-x) \ln(1-x) \right]. \]

This dependence is graphically shown in figure 2.

Let us consider the KS segment. Suppose that the polymer-solvent system is at point \( N \), lying on the dependence up to the inflection point \( M \). The solution can split into two ones: the first being enriched in component \( A \) (point \( K \)), and the second being enriched in component \( B \) (point \( S \)). Then the Gibbs energy of the mixture of these solutions is determined by the straight line KS. It can be seen that this energy is greater than the energy of a single-phase solution throughout this area. This means that according to the principle of minimum energy, it is necessary to apply energy from outside for the system disintegration. Wherein, having a spherical shape, the particles of the solid phase reach the maximum possible size without a tendency to further growth (figure 3).

It follows from this dependence (8) that the system is prone to decomposition into two phases through the entire section between the minima of the Gibbs energy the dependence on the composition. This is proved mathematically in (1), that is, the system is in a metastable state between the energy extremes. We quantify the law (1) for polyorthosilicic acid solution in 2-butanol (figure 4).

Figure 3. Decomposition within the binodal dome.

Figure 4. The first derivative of the Gibbs energy (8) for the polymer solution.

It can be seen from figure 4 that the system tends to nucleophilic decomposition at room temperatures. This is confirmed by experimental data (figure 5).

However, the KL segment is partially characterized by a nucleophilic decomposition (figure 2). Let us consider the system above the inflection point \( M \). Suppose that the solution has the composition \( Q \). Then it can decompose into two solutions, \( R \) and \( L \). In this case, the energy of mechanical mixture is less than the energy of a single-phase solution.
Figure 5. Morphostructure of the film surfaces obtained using various solvents: SiO$_2$ – ethanol system (a); SiO$_2$ – 1-butanol system (b); SiO$_2$ – 2-butanol system (c).

Figure 6. Labyrinthine structures in spinodal decomposition.

Figure 7. The first derivative of the Gibbs energy (8) for the polymer solution.

Figure 8. Spinodal decomposition obtained by polymerization (a), and thermal cooling (b).

Wherein, the system stratifies almost instantly without any external energy consumption. This process is called spinodal decomposition, and it is characterized by the appearance of labyrinthine structures...
It follows that the region of spinodal decomposition is localized between the inflection points on the system energy, which corresponds to (2). Let us consider this ratio for the SiO$_2$ – 2-butanol system (figure 7).

This dependence shows that it is possible to carry out spinodal decomposition of a polymer solution by thermal cooling, or by chemical cooling (polymerization with a decrease in configurational entropy, or rapid solvent evaporation) of the system. The methods can be implemented in practice (figure 8).

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