Prediction of phase equilibria in the W–Si system in the generalized lattice model

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Abstract. The present work is devoted to the phase diagrams calculation of the W–Si system within the framework of the generalized lattice model taking account of volume effects. The theoretically calculated phase diagram is compared with the corresponding experimental diagrams.

1. Introduction
Investigation of the thermodynamic properties and phase equilibria in the W–Si system is of great importance for microelectronics. For example, the compound WSi₂ used in the creation of Schottky barriers, heterostructures, rectifying and ohmic contacts in VLSI. At high temperature heat treatment of contact in W–Si the effect of gettering of defects and impurities was observed [1, 2]. In this connection an important problem is to study the composition of the coexisting phases in the binary system W–Si in a wide range of temperatures and concentrations. The aim of this work is a theoretical calculation of the phase diagram of the W–Si system within the generalized lattice model [3].

2. Model
The phase diagram of the binary system W–Si refers to the phase diagram of the eutectic type with several intermediate phases of constant and variable composition. The phase diagram of the eutectic type with intermediate phase of variable composition is schematically presented in Figure 1.

It is easy to see that the left and right parts of the initial phase diagram are similar to a conventional phase diagram of the eutectic type. The fundamental difference between both parts of the phase diagram in Figure 1 and the phase diagram of the eutectic type is that the mole fractions \( x \) of the \( B \) component (reckoned along the concentration axis) vary in the range \( 0 \leq x \leq n/(m+n) \) for the left subsystem \( A–A_mB_n \) and in the range \( n/(m+n) \leq x \leq 1 \) for the right subsystem \( A_mB_n–B \). As a consequence, the lengths of the segments that correspond in the concentration axis to the left and right parts of the diagram are not equal to unity, whereas the length of the concentration axis in any phase diagram should be equal to unity. These differences do not permit one to directly use the well-developed methods for calculating phase diagrams in the case of simulation of the components of phase diagrams for systems with intermediate phases. The method of calculation of phase diagrams of such type has been proposed in paper...
The method is based on the nonlinear transformations of the concentration axes and makes it possible to correctly reduce the calculation of the phase diagrams with several intermediate phases to a sequence of phase diagrams of individual subsystems. These cases were studied in detail in papers [4,5]. For this reason, we do not write out the explicit expressions for the nonlinear transformations of the concentration axes, which can be found in the papers mentioned above.

According to the basic principles of the generalized lattice model, the chemical potentials of a homogeneous binary solution (per mole of a material) can be represented in the following form [6]

\[
\begin{align*}
\mu_1 &= \mu_{10} + RT \ln x + W \lambda \left( \frac{1-x}{x + \lambda(1-x)} \right)^2, \\
\mu_2 &= \mu_{20} + RT \ln(1-x) + W \left( \frac{x}{x + \lambda(1-x)} \right)^2,
\end{align*}
\]

where \(\mu_{i0}\) is the standard chemical potential of the \(i\)th component, \(R\) is the universal gas constant, \(T\) is the temperature of the system, \(x\) is the mole fraction of the first component, \(W\) is an analog of the energy of mixing in the liquid phase, \(G\) is an analog of the energy of mixing in \(\alpha\) solid solution based on atomic component \(A\) and \(U\) is an analog of the energy of mixing in \(\beta\) intermediate phase based on molecular component \(A_mB_n\). Then relationships (1) determine the chemical potentials
of components in liquid phase. The chemical potentials of components in solid solutions are considered in a similar way.

We can obtain all parameters of general lattice model for binary solutions of the eutectic type taking into account the chemical equilibrium in the three-phase system, i.e., equating the chemical potentials of the components in the solid and liquid phases.

Equations of the chemical equilibrium in the three-phase system form a closed system, whose solution allows us to find the concentration dependences of the liquidus branches, solidus branches and solvus branches and, hence, to construct the phase diagrams of binary system \( A - A_mB_n \) in the framework of the generalized lattice model.

It should be noted that the chemical equilibrium in the subsystem of an \( A_mB_n - B \) binary solution is considered in a similar way.

### 3. Phase diagram calculation

The table presents the calculated parameters of the generalized lattice model for the W–Si binary system.

| \( A-B \) | \( q_1 \) | \( q_2 \) | \( \lambda \) | \( \overline{W}, \text{K} \) | \( \overline{U}, \text{K} \) | \( \overline{G}, \text{K} \) |
|----------|--------|--------|--------|-----------------|-----------------|-----------------|
| \( \text{Si}_2\text{W} - \text{Si}_3\text{W}_5 \) | 25.0   | 5.0    | 0.109  | 3411            | 1654            | -               |
| \( \text{Si}_3\text{W}_5 - \text{W} \) | 2.0    | 25.0   | 2.437  | 10491           | 8303            | -               |

Here \( \overline{W} = W/R, \overline{U} = U/R \), and \( q_i = \Delta H_i/RT_i \), where \( \Delta H_i \) are the latent heats of the liquid–solid transition for the pure components, \( T_i \) stands for the melting temperatures of the pure components. The parameters \( q_i \) were determined with the use of the reference data on the latent heats of the liquid–solid transition.

In addition it should be noted that explicit account of ”volume” effects in the W–Si system with intermediate phases of constant composition (\( \text{Si}_2\text{W} \)) and variable composition (\( \text{Si}_3\text{W}_5 \)) was carried by introducing ”specific” the atomic volumes of W and Si within the generalized lattice model.

The corresponding phase diagram calculated with these parameters are depicted in Figure 2. It should be noted that the results obtained from the theoretical calculations are in agreement with the experimental data available in the literature [7–9].

Thus, comparison with experimental data shows that the theoretical approach can be used to adequately description and prediction of the phase equilibria in the W-Si binary system.
Figure 2. Phase diagram of the W–Si system. Dashed lines are the experimental data taken from [7-9]. Solid lines indicate the results obtained from theoretical calculations.

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