THERMODYNAMIC PROPERTIES OF IRON, ALUMINUM, BORON, AND PHOSPHORUS IN DILUTE SILICON SOLUTIONS BY MOLECULAR INTERACTION VOLUME MODEL

S.-Y. Li a, b, K. Liu a, c, F. Yang b, F.-S. Xi a, b, J.-J. Wu a, b,*, W.-H. Ma a, b, Y. Lei a, b, Y.-J. Wang c, X.-N. Zhang c

a State Key Laboratory of Complex Nonferrous Metal Resources Cleaning Utilization in Yunnan Province, Kunming University of Science and Technology, Kunming, PR China
b Key Laboratory for Nonferrous Vacuum Metallurgy of Yunnan Province, Kunming University of Science and Technology, Kunming, PR China
c HuanOu Semiconductor Material Technology Co., LTD, Tianjin, PR China

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Abstract

The thermodynamic properties of impurity components in silicon solutions play an important role in the chemical removal process to the metallurgical route. In this paper, the component activity coefficients and interaction parameters of dilute silicon solutions were estimated by the molecular interaction volume model (MIVM). The activity coefficients (\( \gamma_i \)) of component i in dilute binary Si-i and ternary Si-i-j solutions at 1687-1873 K were firstly calculated. The concentration dependences of the interaction parameter and activity coefficient were also obtained. The self-interaction parameters (\( \varepsilon_{ii} \)) for Si-i system were obtained as, \( \varepsilon_{Fe} = -2.728 - 362.031 / T \), \( \varepsilon_{Al} = 2.157 - 1876.776 / T \), \( \varepsilon_{B} = -4.842 + 1444.926 / T \) and \( \varepsilon_{P} = -2.543 + 1376.036 / T \). At the same time, the interaction parameters among components B, Al, and Fe in dilute ternary Si-i-j solutions were also derived as\( \varepsilon_{BAl} = -1.2758 - 2946.306 / T \), \( \varepsilon_{BFe} = 0.7467 - 9765.9298 / T \) and \( \varepsilon_{AlFe} = -1.3967 + 3319.6803 / T \). Most important of all, the temperature dependences of the interaction parameters and activity coefficients in dilute Si-i and Si-i-j solutions with a certain i or j concentration were deduced. The results show that the predicted self-interaction parameters of B, Al, Fe, and P in binary silicon solutions reasonably agree with the experimental data. This further shows that MIVM is of reliability and can be expanded to a multi-component dilute silicon solution.

Keywords: Molecular interaction volume model; Activity coefficient; Interaction parameter; Silicon solution

1. Introduction

With the increase of energy consumption in the world, renewable resources become fewer. Solar energy is an important renewable energy source that is considered to be promising in the future. However, the process of producing solar energy materials is complicated, resulting in the high cost of solar cells production [1, 2]. An expensive semiconductor grade silicon (SEG-Si, >99.999999%) yielded from the chemical method is used as a solar cell to convert solar energy to electric power. However, SEG-Si for solar cell supply is restricted and extravagant. We have to develop an innovative process for the production of solar grade silicon (SoG-Si, >99.9999%) with low energy consumption in order to spread solar cell system widely [3].

The typical impurity elements such as boron, phosphorus, aluminum, calcium, and iron play an important role in silicon materials and simultaneously exert a pronounced and negative influence upon the photoelectric properties of SoG-Si [4, 5]. Many researchers focused on impurity removal from silicon solutions using the metallurgical route. The thermodynamic parameters of these impurity components in silicon solutions are crucial to study the reactions between impurity elements and oxidizing mediums. In order to supply help to the removal of impurity elements in MG-Si solution, Miki et al. [6, 7] measured the activity and interaction coefficients of some impurity components in silicon. However, not enough experimental and computational data have been collected and used for the research of impurity removal so far. Therefore, a unique economic and effective method to estimate the thermodynamic parameters of silicon solutions depending on less experimental data by a computational module is required. Safarian et al. [8] calculated the activities of elements such as Al, Ca, and Mg in silicon solutions through a quasi-regular
solution model. There is a good correlation between
the calculated activities and the reported activity data
in the literature. However, the component activity
coefficients of dilute Si-Me solutions were just
calculated at 1687 K (the melting point of silicon) and
the interaction parameters were not calculated and
mentioned. Matsumiya et al. [9] predicted the activity
coefficients and the interaction parameters of the
solute components in infinite dilute Si solutions by the
use of first-principles calculations based on the
density functional theory (DFT). The calculated
activity coefficients and interaction parameters of Al,
Fe, Ti, and Pb in Si solutions are roughly in agreement
with the results of experiments but there are some
quantitative discrepancies from the experimental
results.

Due to the complexity of high-temperature
experiments and the limitations of experimental
accuracy, it is difficult to obtain thermodynamic
data by experimental means under certain
conditions. In addition, the reproducibility of the
measurement results is also poor. The differences
between the results of different researchers are also
very large and even the signs are the opposite. In
addition, there are many binary and ternary alloy
systems, and it is impossible to rely on experiments
to fill this huge data gap. Therefore, many scientific
researchers try to use the thermodynamic model to
predict the activity coefficient of the component.
For example, Wilson [10] proposed Wilson’s
equation in 1964; Lupis et al. [11] proposed a quasino-
usual solution theoretical model in 1967; Zhou
[12] proposed a new generation of geometric
models in 1997. However, these models are only
applicable to a specific system and a specific
concentration range. The MIVM model [13] has a
clear physical basis and can predict the
thermodynamic properties of different types of
universal multi-alloy systems. Moreover, the model
is inclusive and can be reverted to the well-known
Wilson equation, Flory-Huggins equation and
NRTL equation under certain conditions, and the
thermodynamic consistency and diffusion stability
satisfy the Gibbs-Duhem equation. The MIVM that
was invented by Tao [14-16] was derived from the
statistical thermodynamics and was of better
stability and reliability to predict the
thermodynamic parameters of binary and multi-
component alloy solutions. Tao derived a new
expression of the regular partition function of
liquids and their mixtures based on statistical
thermodynamics. The concept and expression of the
local coordination number of liquid mixtures were
proposed, and the molecular interaction volume
model was deduced.

In the present work, the component activity
coefficients and some meaningful interaction
parameters in dilute binary and ternary silicon
solutions at 1687-1873 K have been calculated by the
MIVM. The results will be significant to guide and
optimize the purification techniques of silicon for
metallurgical route. Furthermore, this work supplies
an important method in the theoretical research of
silicon material and many thermodynamic parameters
of silicon solutions will be calculated.

2. Thermodynamic background

According to the definition of molecular
interaction volume model by Tao [10], the molar
excess Gibbs energy $G_m^E$ of mixed solution i-j is
expressed as Eq. (1).

$$
G_m^E = x_i \ln \left( \frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} \right) + x_j \ln \left( \frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) - \frac{x_i x_j Z_{B_{ij}} \ln B_{ij} + Z_{B_{ji}} \ln B_{ji}}{2 (x_i + x_j B_{ij})}
$$

where $x_i$ and $x_j$ are the molar fractions of
components i and j, $V_{mi}$ and $V_{mj}$ the molar volumes, $Z_{B_{ij}}$ and
$Z_{B_{ji}}$ the nearest molecules that construct a
molecular cell or first coordination shell surrounding
a center molecule i and j. $B_{ij}$ and $B_{ji}$ the pair-potential
parameters for the i-j binary system and are defined as
Eq. (2).

$$
B_{ij} = \exp\left[ -\frac{(\varepsilon_{ij} - \varepsilon_{i})}{kT} \right], \quad B_{ji} = \exp\left[ -\frac{(\varepsilon_{ij} - \varepsilon_{j})}{kT} \right]
$$

where $\varepsilon_{ij}$, $\varepsilon_{i}$, and $\varepsilon_{j}$ are the pair-potential energies of
i-j, j-i and i-j, respectively. $\varepsilon_{ij} = \varepsilon_{ji}$, k is the
Boltzmann constant. The expressions of activity
coefficient for component i and component j ($\gamma_i$, $\gamma_j$)
are listed as Eqs. (3) and (4, as well).

$$
\ln \gamma_i = \ln \left( \frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} \right) + x_j \left( \frac{V_{mj} B_{ji}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) - \frac{x_j^2 \left( Z_{B_{ij}} \ln B_{ij} - Z_{B_{ji}} \ln B_{ji} \right)}{2 (x_i + x_j B_{ij})^2 (x_j + x_i B_{ij})^2}
$$

$$
\ln \gamma_j = \ln \left( \frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}} \right) - x_i \left( \frac{V_{mi} B_{ij}}{x_i V_{mi} + x_j V_{mj} B_{ji}} \right) - \frac{x_i^2 \left( Z_{B_{ij}} \ln B_{ij} - Z_{B_{ji}} \ln B_{ji} \right)}{2 (x_i + x_j B_{ij})^2 (x_j + x_i B_{ij})^2}
$$

Expanding Eq. (1) to a multi-component silicon
solution i-j-k, the molar excess Gibbs energy can be expressed as Eq. (5).
In previous work, the binary Si-Al and Si-Fe solutions were used to reliability to predict the activity coefficients of thermodynamics, which is of better stability and respectivity [21-24].

Based on the infinite dilution activity coefficients $\gamma_{i}^\infty$ and $\gamma_{j}^\infty$ of the binary alloy solutions and the values of the related parameters of their pure components in Table 1 [17-19], the required binary parameters $B_{ij}$ and $B_{ji}$ can be obtained by Eqs. (7) and (8), respectively.

\[
\ln \gamma_{i}^\infty = 1 - \ln \left( \frac{V_{ai}B_{ji}}{V_{ai}B_{ij}} \right) - V_{ai}B_{ij}V_{ai} - \frac{1}{2} \left( Z_{i}B_{ji} + Z_{j}B_{ij} \ln B_{ji} \right)
\]

\[
\ln \gamma_{j}^\infty = 1 - \ln \left( \frac{V_{aj}B_{ij}}{V_{aj}B_{ji}} \right) - V_{aj}B_{ij}V_{aj} - \frac{1}{2} \left( Z_{j}B_{ij} + Z_{i}B_{ji} \ln B_{ij} \right)
\]

For the binary system $i$-$j$, the required parameters $B_{ij}$ and $B_{ji}$ at other temperature can be obtained by the Newton-Raphson methodology [13].

Based on the infinite dilution activity coefficients $\gamma_{i}^\infty$ and $\gamma_{j}^\infty$ of the binary alloy solutions and the values of the related parameters of their pure components in Table 1 [17-19], the required binary parameters $B_{ij}$ and $B_{ji}$ can be obtained by Eqs. (7) and (8) and the Newton-Raphson methodology [13]. The coordination number $Z$ of liquid components was available in document [20].

Meanwhile, $B_{ij}$ and $B_{ji}$ at other temperature can be obtained by Eq. (2), in which the pair-potential energy interaction parameters $-(\varepsilon_{ij} - \varepsilon_{ii})/k$ and $-(\varepsilon_{ij} - \varepsilon_{jj})/k$ is assumed to be independent of temperature when the values of $B_{ij}$ and $B_{ji}$ at a given temperature are known. Substituting the parameters $B_{ij}$ and $B_{ji}$ into Eqs. (2) and (3), the component activities of binary Si-Al, Si-Fe and Si-P solutions can be obtained. The required binary parameters $B_{ij}$ and $B_{ji}$ and the infinite dilution activity coefficients of the binary alloy solutions are shown in Table 2, respectively [21-24].

### 3. Results and discussion

The MIVM was derived from the statistical thermodynamics, which is of better stability and reliability to predict the activity coefficients of binary, ternary, and even multi-component alloy solutions at the whole composition range. In our previous work, the binary Si-Al and Si-Fe solutions were selected as examples for verifying effectiveness of MIVM at the whole composition range [25, 26]. Then, the binary Si-B and Si-P solutions could also be worked out. The calculations were employed at the same temperature as experiments for the binary Si-B, Si-Al, Si-Fe and Si-P systems by Eqs. (2-4). The activity values calculated by the MIVM model were compared with the experimental values reported in the literature [23] as shown in Fig. 1. It was found that the activities of components Si, P, Fe in the binary Si-P and Si-Fe solutions calculated by MIVM were completely in accord with the determined experimental results at the whole composition range of solutions. In spite of some differences in a high P concentration range, they were still accordant in a low P concentration range for the Si-P solution. Considering all these, it was confirmed that the prediction to the component activities in binary Si-Fe and Si-P solutions by MIVM were basically reasonable and reliable. At the same time, this model was also the base of the component interaction parameters in the solutions.

![Figure 1. Calculated activities of related binary solutions by MIVM (lines) and by experimental data (points) (a) Si-Fe at 1873 K; (b) Si-P at 1700 K](image_url)
It is too rough to get the activities of components Fe and P in binary solutions at the whole composition range. The mass concentration (w_i, ppmw) of impurity component i in MG-Si is usually very low. The activities of these components in dilute silicon solutions with a mass concentration range of 1-2000 ppmw were calculated by MIVM and shown in Fig. 2. It was found that the activity of component i with the same mass concentration in the dilute binary silicon solution had the difference of one or several orders of magnitude. The Wagner’s equation \[ 27 \] for the component interaction parameter in solution is frequently used to represent the thermodynamic parameters of dilute solutions, particularly for the iron-based alloys. It is often used to calculate the component activity coefficients in at finite solutes using the first or the second order interaction parameters. In this paper, the second and the higher-order interaction parameters are neglected. The Wagner’s equation for dilute binary solution can be defined as Eq. (9).

\[
\ln \gamma_i = \ln \gamma_i^{\infty} + x_i \epsilon_i
\]

The concentration (x_i) dependence of component activity coefficients (\( \gamma_i \)) at 1873 K was estimated and the relation between \( \ln \gamma_i \) and x_i are shown in Fig. 3.

The effectiveness of MIVM has been verified in Ref. [13-16] and the predicted activity coefficients are in good agreement with both the experimental results and the calculated ones by the Wagner’s equation. Therefore, the interaction parameters can be indirectly acquired by Eq. (9) based on the calculated results of MIVM. Then, the self-interaction parameters can be estimated by the logarithm fitting of the activity coefficient as a function of solute concentrations.
Fig. 4(b). However, there is a large deviation between the calculated and the reported values of $e_i^P$ and the slope, respectively, determined by Tang in Fig. 4(a). The predicted value of $e_i^P$ is between the experimental values of Tang, Shimpo and Chen in Fig. 4(d). The self-interaction coefficient of $P$ obtained indirectly by the MIVM model deviates from the results obtained by Shimpo [30] and Chen [29], but the results are within the same order of magnitude. This may be the poor agreement between the activity data of Si-P binary system calculated using the MIVM model and the experimental data reported in the literature, resulting in the self-interaction coefficient of $P$ under low $P$ concentrations having some deviation from other researchers’ results. There is a certain deviation from the results of others. This result is inconsistent with the sign of that of Dalaker [28]. The reason may be that the method to obtain the self-interaction coefficient of $P$ by FACT thermodynamic calculation software was not accurate enough. It was confirmed that a linear functional relationship between self-interaction parameter ($e_i^P$) and $1/T$ was obeyed by the fitting of results and Eqs. (11) - (14) can be gotten.

$$e_i^P = A + B/T$$  \hspace{1cm} (10)

where $A$ and $B$ are constant. Using the least-squares method and taking $e_i^P$ and $1/T$ as the ordinate and the abscissa, $A$ and $B$ can be derived from Y axis and the slope, respectively.

The temperature dependences of self-interaction parameter ($e_i^P$) and activity coefficient ($\gamma_i$) with a component $i$ mass concentration of 50 ppmw at 1693-1873 K are shown in Fig. 4, which displays a reasonable agreement with the results by literatures [6, 7, 9, 22, 28-30]. The self-interaction coefficients of boron calculated using MIVM agree with those determined by Tang in Fig. 4(a). $e_i^B$ shows a good agreement with the results by Matsumiya and Tao in Fig. 4(b). However, there is a large deviation between this study and Miki et al. [6]. The main reason is that the experimental method they used for Si-Al system was at a high Al concentration. There is a good correlation between the calculated $e_i^P$ and the reported data by Miki and Tao in Fig. 4(c). However, there is a large deviation from the results of the first-principles calculation method based on density functional theory by Matsumiya [9], which may be caused by the limitations of the density functional theory. The predicted value of $e_i^P$ is between the experimental values of Tang, Shimpo and Chen in Fig. 4(d). The self-interaction coefficient of $P$ obtained indirectly by the MIVM model deviates from the results obtained by Shimpo [30] and Chen [29], but the results are within the same order of magnitude. This may be the poor agreement between the activity data of Si-P binary system calculated using the MIVM model and the experimental data reported in the literature, resulting in the self-interaction coefficient of $P$ under low $P$ concentrations having some deviation from other researchers’ results. There is a certain deviation from the results of others. This result is inconsistent with the sign of that of Dalaker [28]. The reason may be that the method to obtain the self-interaction coefficient of $P$ by FACT thermodynamic calculation software was not accurate enough. It was confirmed that a linear functional relationship between self-interaction parameter ($e_i^P$) and $1/T$ was obeyed by the fitting of results and Eqs. (11) - (14) can be gotten.

$$\ln \gamma_i = \ln \gamma_i^0 + x_i e_i^P + x_i e_i^P'$$ \hspace{1cm} (15)

Then, a linear functional relation between logarithm of activity coefficient ($\ln \gamma_i$) and concentration ($x_i$) can be gotten as Eq. (16).

$$\ln \gamma_i - x_i e_i^P = \ln \gamma_i^0 + x_i e_i^P'$$ \hspace{1cm} (16)

The concentration ($x_i$) dependence of component activity coefficients ($\gamma_i$) at 1873K was estimated and the relation between $\ln \gamma_i - x_i e_i^P$ and $x_i$ are shown in Fig. 5. For the dilute ternary Si-B-Fe, Si-B-Al, and Si-Al-Fe solutions, the temperature dependences of the interaction parameter ($e_i^P$) and $\ln \gamma_i - x_i e_i^P$ at 1693-1873 K are shown in Fig. 6. With the increase of temperature, the interaction parameters $e_i^P$ of the ternary dilute Si-B-Fe and Si-B-Al solutions also

\[ e_i^B = -2.728 - 362.031 / T \]  \hspace{1cm} (11)

\[ e_i^P = 2.157 - 1876.776 / T \]  \hspace{1cm} (12)

\[ e_i^{P'} = -4.842 + 14445.926 / T \]  \hspace{1cm} (13)

\[ e_i^P = -2.543 + 13767.036 / T \]  \hspace{1cm} (14)

Although there are no related reports to the interaction parameter ($e_i^P$) for the dilute ternary silicon solution, similarly with the binary solution, the Wagner’s equation for the dilute ternary solution can be defined as Eq. (15).
Figure 4. Temperature dependences of the self-interaction parameter ($\gamma_i^*$) and the activity coefficient ($\gamma_i$) with the component $i$ mass concentration of 50 ppmw at 1693-1873 K (a) Si-B solution; (b) Si-Al solution; (c) Si-Fe solution; (d) Si-P solution

Figure 5. Activity coefficient of component $i$ with different $j$ concentration of in ternary Si-$i$-$j$ solutions at 1873 K

Figure 6. Temperature dependences of interaction parameter ($\gamma_{ij}^*$) and $\ln\gamma_{ij} = x_{ij}^e$ in dilute ternary Si-$i$-$j$ solution with a component $j$ concentration of 1500 ppmw (a) Si-B-Fe solution; (b) Si-B-Al solution; (c) Si-Al-Fe solution
increase. And it is the opposite to $e^{i}_{i,j}$ in the Si-Al-Fe solutions. It was confirmed that a good linear functional relationship between interaction parameter ($e^{i}_{i,j}$) and $1/T$ was obeyed by the fitting of results and Eqs. (17) - (19) can be gotten.

\begin{align*}
    e^{i}_{i} &= -1.2758 - 2946.306 / T \\  
    e^{i}_{j} &= 0.7467 - 9765.9298 / T \\  
    e^{i}_{i,j} &= -1.39677 + 3319.6803 / T
\end{align*}

4. Conclusions

The reliability of prediction by MIVM depends on the data of the activities or the infinite dilute activity coefficient in binary silicon solutions. In this paper, the activity coefficients and self-interaction parameters of B, Al, Fe, and P in dilute binary Si-B, Si-Al, Si-Fe, and Si-P solutions were calculated and then contrasted with the results in the existing literature. They are consistent with the results in the literature. It was proved that the prediction of the component activity coefficients and the interaction parameters of silicon solutions by MIVM was credible. By comparison, the predicted results showed good agreement with the ones in the literatures. The model calculation was also applied to the ternary silicon solutions. The activity coefficients of components B, Al, and Fe in dilute ternary Si-B-Fe, Si-B-Al, and Si-Al-Fe solutions and the corresponding interaction parameters among B, Al, and Fe were obtained. The concentration dependences of the interaction parameter and the activity coefficient of dilute binary Si-i and ternary Si-i-j solutions were derived. The temperature dependences of interaction and the activity coefficient parameter were deduced and obtained by a linear fitting.

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References

TERMODINAMIČKE OSOBINE ŽELEZA, ALUMIJUMA, BORA I FOSFORA U RAZREDENIM RASTVORIMA SILICIJUMA PO MODELU JAČINE MOLEKULARNE INTERAKCIJE

S.-Y. Li a, b, K. Liu a, c, F. Yang b, F.-S. Xi a, b, J.-J. Wu a, b,*, W.-H. Ma a, b, Y. Lei a, b, Y.-J. Wang c, X.-N. Zhang c

a Glavna državna laboratorija za čisto iskorišćavanje resursa kompleksnih obojenih metala u provinciji Junan, Univerzitet za nauku i tehnologiju u Kunmingu, Kunming, NR Kina
b Glavna laboratorija za vakuumsku metalurgiju obojenih metala u provinciji Junan, Univerzitet za nauku i tehnologiju u Kunmingu, Kunming, NR Kina
c HuanOu kompanija za tehnologiju poluprovodnih materijala, LTD, Tiandzin, NR Kina

Apstrakt

Termodinamičke osobine primesa u rastvoru silicijuma imaju važnu ulogu u procesu hemijskog uklanjanja metalaškim putem. U ovom radu su procenjeni koeficijenti aktivnosti komponente i parametri interakcije razređenog rastvora silicijuma modelom jačine molekularne interakcije (MIVM). Prvo su izračunati koeficijenti aktivnosti ($\gamma$) komponente i u razređenom dvojnom Si-i i trojnom Si-i-j rastvoru na temperaturi od 1687-1873 K. Takođe je dobijena koncentracijska zavisnost interakcionih parametara i koeficijenata aktivnosti. Parametri samo-interakcije ($\epsilon$) za Si-i sistem dobijeni su kao $\epsilon_{Si} = -2.728 - 362.031 / T$, $\epsilon_{Si} = 2.157 - 1876.776 / T$, $\epsilon_{Si} = -4.842 + 14445.926 / T$ i $\epsilon_{Si} = -2.543 + 13767.036 / T$. U isto vreme, izvedeni su interakcioni parametri među komponentama B, Al i Fe u razređenom trojnom Si-i-j rastvoru kao $\epsilon_{B} = -1.2758 - 2946.306 / T$, $\epsilon_{Al} = 0.7467 - 9765.9298 / T$ i $\epsilon_{Fe} = -1.39677 + 3319.6803 / T$. Najvažnije od svega je da su utvrđene temperaturne zavisnosti interakcionih parametara i koeficijenata aktivnosti u razređenim Si-i i Si-i-j rastvorima sa određenom i ili j koncentracijom. Rezultati pokazuju da su predviđeni samo-interakcijski parametri B, Al, Fe i P u dvojnim rastvorima silicijuma u skladu sa eksperimentalnim podacima. Ovo dalje pokazuje da je MIVM pouzdan i da se može proširiti na višekomponentne razređene rastvore silicijuma.

Ključne reči: Model jačine molekularne interakcije; Koeficijent aktivnosti; Interakcioni parameter; Rastvori silicijuma.