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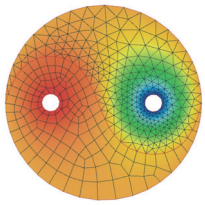

THERMODYNAMIC COMPUTATIONS OF THE INTERACTION COEFFICIENTS BETWEEN BORON AND PHOSPHORUS AND COMMON IMPURITY ELEMENTS IN LIQUID SILICON

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Abstract

Using the thermodynamic software FACT, and the SINTEF database for high purity silicon, the interaction coefficients between the doping elements boron and phosphorus and a range of impurity elements (Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, Sn, Ti, V, Zn, Zr) have been calculated in liquid silicon in the temperature range 1420-1620°C. The calculations predict significant interactions between boron and phosphorus and all the evaluated elements, except between phosphorus and nitrogen, where no significant interaction was found.

Key words: thermodynamics, interaction coefficients, solar grade, silicon

1. INTRODUCTION

In order for the photovoltaic contribution to the global energy consumption to increase, an increased cost-competitiveness versus other energy sources is necessary. Silicon is the material of choice for photovoltaic cells, accounting for some 90% (del Cañizo et al., 2009) of the market. The material cost of high purity silicon is a significant contribution to the cost of such cells. The silicon contribution to the total cell cost depend on source and cell design, but estimates of 14% and >30% are listed here as examples (del Cañizo et al., 2009; Shon-Roy and Wiesnoski, 2010). Thus, one way of increasing the cost-competitiveness of photovoltaic energy will be to lower the production cost of high purity silicon, and the last few years have seen a flutter of activity within alternative methods of refining.

Two of the most critical elements to control in any refinement process are boron and phosphorus. These common doping elements are obviously electrically active, and they are difficult to remove with directional solidification because of their high segregation coefficients (P = 0.35, B = 0.8 (Huff et al, 1971)). Therefore, other methods of refining such as slag treatment, vacuum refining or novel techniques must be employed to reduce boron and phosphorus contents to acceptable levels.

In perfecting current refining methods, as well as in the development of new and improved refining techniques, a good theoretical description of the thermodynamics of the system is a necessary tool.

As the starting material in all silicon refining processes contain high levels of several impurities in addition to boron and phosphorus, the interactions between B and P and these elements will influence the activities of the doping elements, which in turn will affect the stability and ease of removal of B and P. Knowledge of these interactions will also be necessary to perform good quantitative analysis of novel refining techniques.

In 2009, SINTEF published a self-consistent thermodynamic database for solar grade silicon (SoG-Si) for the FACT^{TM} software. It was based on

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a thorough survey of various thermodynamic data in various systems [Tang et al., 2009].

In the current work, the SINTEF SoG-Si database is used to calculate, between 1420 and 1620 °C, the interaction coefficient between B and P in liquid silicon, and of both elements with {Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, Sn, Ti, V, Zn, Zr}.

2. THEORY AND METHOD

2.1. Self interactions, P-X and B-X interactions

The activity (a) of a solute α in a solvent is given by its activity coefficient (γ):

$$a_\alpha = \gamma_\alpha X_\alpha \tag{1}$$

where X_α is the mole fraction of solute α. If a second element β is present in the solution, then the activity coefficient of α can be described in terms of interaction coefficients:

$$\ln(\gamma_A) = \varepsilon_\alpha^0 + \varepsilon_\alpha^\alpha X_\alpha + \varepsilon_\alpha^\beta X_\beta + higher\ order\ terms \tag{2}$$

Here, ε_α^0 gives the limit of the activity coefficient of α at infinite dilution, $\varepsilon_\alpha^\alpha$ is the self-interaction parameter and ε_α^β is the first order interaction parameter between elements α and β. The higher order terms, if included, would represent interactions between several atoms each of α and β simultaneously. In the current work, calculations are performed at high enough dilution (<100 ppma for all non-Si elements) so that it is assumed that all higher order terms are ignored.

Before calculating the interaction parameters between boron and phosphorous and other elements in liquid silicon, it was necessary to determine ε_α^0 and $\varepsilon_\alpha^\alpha$ for boron and phosphorous: ε_B^0, ε_P^0, ε_B^B, ε_P^P.

In order to calculate ε_B^0 and ε_B^B, FACT computations were performed on an otherwise pure silicon melt with various amounts of boron using the SINTEF solar grade silicon database (Tang et al., 2009). The temperature was varied from 1420 to 1620 °C in steps of 10 °C and the boron content was varied between 1 and 100 ppma in steps of 1 ppma for a total of 2100 calculations. At each temperature and boron concentration, the activity and mole fraction of boron was computed, yielding the activity coefficient of boron, $\gamma_B = a_B/X_B$.

At each temperature, ε_B^0 and ε_B^B was estimated by fitting the logarithm of the activity coefficient as a function of boron content:

$$\ln(\gamma_B) = \varepsilon_B^0 + \varepsilon_B^B X_B \tag{3}$$

This yielded 21 pairs of values for each of (T, ε_B^0) and (T, ε_B^B). Using the temperature dependency $\varepsilon = \alpha + \beta/T$, the full temperature dependencies of ε_B^0 and ε_B^B could be derived.

To calculate ε_P^0 and ε_P^P a similar procedure was used, where 2100 computations were performed on the pure Si-P-system with temperature varying from 1420 to 1620 °C in steps of 10 °C and the phosphorous content varying between 1 and 100 ppma in steps of 1 ppma. The derivation of $\varepsilon_P^0(T)$ and $\varepsilon_P^P(T)$ from the calculated data was identical to the method for boron. Figure 1 shows the two step method for ε_B^0 and ε_B^B.

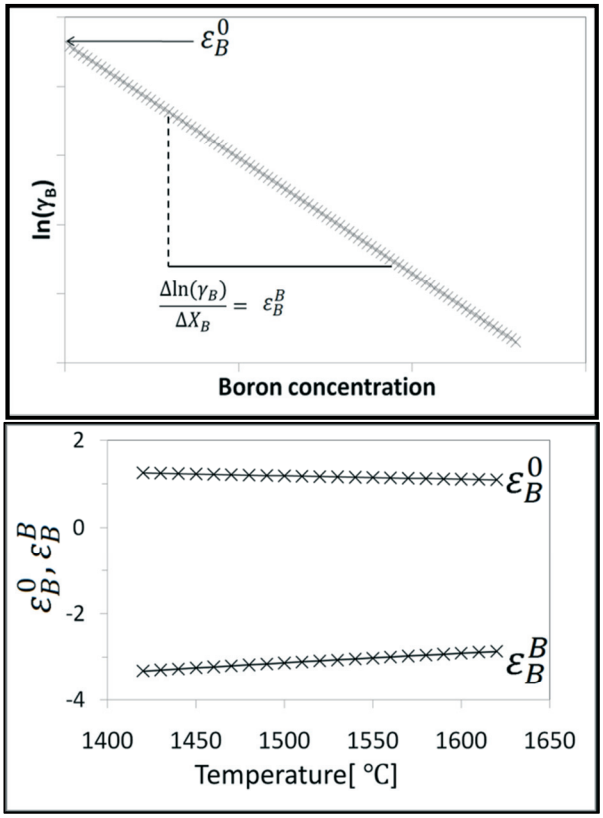


Fig. 1. *Illustration of the two-step method for calculating ε_B^0 (T) and ε_B^B (T). The left hand figure illustrates finding ε_B^0 and ε_B^B at a temperature T as the y-axis intersection and slope of the plot of ln (γ_B) as a function of boron concentration. The right hand side illustrates how the temperature dependencies $\varepsilon=\alpha+\beta/T$ are derived from the resulting pairs of values (ε,T).*

When calculating the interactions between boron and other elements, FACT computations were performed on the Si-B-X system for each element. The temperature was varied between 1420 and 1620 °C in steps of 10 °C, the boron content was varied be-

tween 10 and 100 ppma in steps of 10 ppma and the content of X was varied from 1 to 100 ppma in steps of 1 ppma for a total of 21000 computations. At each point (T, X_B,X_X) the activity and mole fraction of boron was computed as before, and in addition the activity and mole fraction of the element X. At each temperature the interaction coefficient ε_B^X was calculated by fitting $\ln(\gamma_B)$ versus X_B and X_X:

$$\ln(\gamma_B) = \varepsilon_B^0(T) + \varepsilon_B^B(T)X_B + \varepsilon_B^X X_X \qquad (4)$$

using the expressions for ε_B^0 and ε_B^B as found before. The temperature dependence was then found by fitting ε_B^X=α+β/T to the 21 ε_B^X values found at different temperatures.

The process was repeated for all elements {Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, Sn, Ti, V, Zn, Zr} and then the same was done for phosphorous to calculate ε_P^X=α+β/T for all elements {Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, Sn, Ti, V, Zn, Zr}.

2.2. P-B interaction

From the theory of interaction coefficients reciprocal interaction coefficients are identical, that is:

$$\varepsilon_B^P = \varepsilon_P^B \qquad (5)$$

Thus, for the calculation of the ε_P^B and ε_B^P, the fitting of the data was done simultaneously. FACT computations were performed on the otherwise pure Si-P-B system with the temperature varying from 1420 to 1620 °C in steps of 10 °C and the boron and phosphorous contents both varying from 1 to 100 ppma for a total of 210000 computations. At each temperature the coefficient ε_B^P was calculated that gave the best fit for

$$\ln(\gamma_B) + \ln(\gamma_P) = \varepsilon_B^0(T) + \varepsilon_B^B(T)X_B + \varepsilon_P^0(T) + \varepsilon_P^P(T)X_P + \varepsilon_B^P(X_B + X_P) \qquad (6)$$

The temperature dependency was then found, as before, by fitting the 21 ε_B^P values to $\varepsilon_B^P = \alpha + \beta/T$.

3. RESULTS

The limit of the activity coefficient of boron in liquid silicon at infinite dilution was determined as

$$\varepsilon_B^0 = -0.25 + 2444/T \qquad (7)$$

The boron-boron self-interaction coefficient was determined as:

$$\varepsilon_B^B = 0.99 - 7301/T \qquad (8)$$

The limit of the activity coefficient of phosphorus in liquid silicon at infinite dilution was determined as:

$$\varepsilon_P^0 = 13.65 - 23439/T \qquad (9)$$

The phosphorus-phosphorus self-interaction coefficient was determined as:

$$\varepsilon_P^P = -27.35 + 46947/T \qquad (10)$$

The phosphorus-boron interaction coefficient was determined as:

$$\varepsilon_P^B = \varepsilon_B^P = -21.79 + 35549/T \qquad (11)$$

Table 1. *Interaction parameters between boron and phosphorus and the elements X={Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, P, Sn, Ti, V, Zn, Zr} for temperatures between 1420-1620 °C, concentrations of P/B in the range of 10-100 ppma and concentrations of X in the range 1-100 ppma.*

X	ε_B^X		ε_P^X	
	±α	±β (·10³)	±α	±β (·10³)
Al	-6.36	8.34	-9.67	16.86
C	-3.76	4.77	-12.9	22.5
Ca	-24.8	40.9	-22.6	38.4
Cr	-12.9	25.2	-5.91	14.2
Cu	-18.1	32.2	-6.45	12.9
Fe	-33.1	46.1	-24.6	32.4
Mg	5.78	-5.63	1.61	3.29
Mn	-10.9	23.1	-2.78	9.98
Mo	-6.79	21.3	17.8	-21.3
N	-3.73	5.51	(-0.001)	(-0.002)
Na	-5.92	16.9	-10.7	26.9
Ni	-40.7	78.9	-31.1	63.1
O	-12.1	45.1	-16.6	54.4
Sn	-32.03	49.4	1.77	-9.57
Ti	-12.5	14.8	-7.16	6.79
V	-18.4	27.5	-11.8	17.2
Zn	-17.5	29	-5.16	8.42
Zr	-30.1	64.3	-7.33	25.1

The interaction parameters between boron and phosphorus and the elements X={Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, P, Sn, Ti, V, Zn, Zr} are listed in table 1. All results from the current work are valid in the temperature range 1420-1620 °C and impurity concentrations in the range 1-100 ppma.

A positive interaction between P (B) and an element X means that P (B) becomes more unstable in

the liquid silicon system if X is present, and thus that it becomes easier to remove P (B). Conversely, a negative interaction means that it is harder to remove P (B) from a silicon melt in which element X is present.

4. ERROR-ESTIMATES

The residual error when fitting using the sum of least squares methods has an expectance value equal to the variance of the modelled system. Thus for the fitting of an interaction coefficient, the variance can be approximated by:

$$s^2 = \sum_T \sum_{X_B} \left(\ln(\gamma_B(T, X_B)) - (\varepsilon_B^0(T) + \varepsilon_B^B(T) X_B + \varepsilon_B^X(T) X_X) \right)^2 \quad (12)$$

When fitting two parameters α and β, 95% confidence intervals around the estimates $\hat{\alpha}$ and $\hat{\beta}$ can be defined by:

$$\hat{\alpha} \pm t_{2.5\%}(\nu) \cdot (s^2 c_{11})^{1/2} \quad (13)$$

$$\hat{\beta} \pm t_{2.5\%}(\nu) \cdot (s^2 c_{22})^{1/2} \quad (14)$$

Table 2. *Error estimates in interaction parameters.*

X	Error in: ε_B^X		Error in: ε_P^X	
	±α	±β	±α	±β
ε^0	0.045 %	0.008 %	0.0001 %	0.000 1%
B	0.012 %	0.003 %	0.003 %	0.003 %
Al	0.010 %	0.012 %	0.003 %	0.003 %
C	0.016 %	0.022 %	0.002 %	0.002 %
Ca	0.002 %	0.003 %	0.001 %	0.001 %
Cr	0.005 %	0.004 %	0.005 %	0.003 %
Cu	0.003 %	0.003 %	0.004 %	0.004 %
Fe	0.002 %	0.002 %	0.001 %	0.002 %
Mg	0.011 %	0.018 %	0.018 %	0.015 %
Mn	0.006 %	0.005 %	0.010 %	0.005 %
Mo	0.009 %	0.005 %	0.074 %	0.121 %
N	0.016 %	0.019 %	827 %	769 %
Na	0.011 %	0.006 %	0.003 %	0.002 %
Ni	0.002 %	0.001 %	0.001 %	0.001 %
O	0.005 %	0.002 %	0.002 %	0.001 %
P	0.003 %	0.003 %	0.000 %	0.000 %
Sn	0.002 %	0.002 %	0.016 %	0.005 %
Ti	0.005 %	0.007 %	0.004 %	0.007 %
V	0.003 %	0.004 %	0.002 %	0.003 %
Zn	0.003 %	0.004 %	0.006 %	0.006 %
Zr	0.002 %	0.002 %	0.004 %	0.002 %

Here, $t_{2.5\%}(\nu)$ is the 2.5% upper percentage point of the Student-t distribution with ν degrees of freedom. c_{11} and c_{22} are the diagonal terms of the matrix $(\mathbf{Z}^T\mathbf{Z})^{-1}$ constructed from the matrix $\mathbf{Z}$ defined by the matrix equation:

$$\boldsymbol{\varepsilon} = \boldsymbol{Z} \begin{bmatrix} \hat{\alpha} \\ \hat{\beta} \end{bmatrix} \quad (15)$$

The calculated error-estimates are tabulated in table 2. As can be seen, the data fits very well, with typical error estimates being on the order of some hundredths or even thousandths of one per cent.

It must be noted that the error-estimates calculated by these formulas in the current work only give the mathematical error-estimates based on how well the calculated activity coefficients fit the theoretical expression. It does not take into account any uncertainty inherent in the calculations themselves, which depend on the quality of the solar grade silicon database, in turn dependent on the literature data.

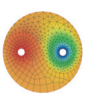
The exception to the good data fit is the phosphorus-nitrogen interaction parameter, given in table 1 as $\varepsilon_P^N = -0.001 + 0.02/T$. The uncertainties here are several times greater than the estimated parameters α and β, and thus the result is not statistically significant. The numerical values are still included here for completeness, but the conclusion is that there is no interaction between phosphorus and nitrogen in liquid silicon.

5. CONCLUSION

The interaction parameters between boron and phosphorus and a range of impurity elements (Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, Sn, Ti, V, Zn, Zr) in liquid silicon have been calculated in the temperature range 1420-1620°C using the FACT software and the SINTEF database for high purity silicon. There are significant interactions predicted between boron and phosphorus and all the evaluated elements, except between phosphorus and nitrogen, where no significant interaction was found. Except for the P – N-case, the results show very low error estimates, indicative of the self-consistency of the database.

The results indicate that the activity of B and P are dependent on other impurities present, and that the stability and ease of removal of these elements will depend on the total composition of the starting material for any refining process.

The results and conclusions are valid for dilute (<100 ppma) binary solutions in the investigated temperature range, and are furthermore dependent



on the literature data that forms the basis for the high purity silicon.

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TERMODYNAMICZNE OBLICZENIA WSPÓŁCZYNNIKÓW ODDZIAŁYWANIA POMIĘDZY BOREM I FOSFOREM ORAZ TYPOWYMI PIERWIASTKAMI STANOWIĄCYMI ZANIECZYSZCZENIE W CIEKŁYM KRZEMIE

Streszczenie

W pracy wykorzystano oprogramowanie termodynamiczne FACT i bazę danych SINTEF dla krzemu o wysokiej czystości do oceny oddziaływania pomiędzy zagęszczającymi pierwiastkami borem i fosforem oraz typowymi pierwiastkami (Al, C, Ca, Cr, Cu, Fe, Mg, Mn, Mo, N, Na, Ni, O, Sn, Ti, V, Zr) stanowiącymi zanieczyszczenie w ciekłym krzemie w zakresie temperatur 1420-1620^{o}C. Wykonane obliczenia wykazały znaczne oddziaływania boru i fosforu z wszystkimi wymienionymi pierwiastkami, z wyjątkiem oddziaływania pomiędzy fosforem i azotem, którego nie zaobserwowano.

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