Theoretical Estimation of the Solubility of Oxygen in Silicon Melt

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ABSTRACT

The solubility of oxygen in silicon melt has been calculated by applying the scaled particle theory of the Percus-Yevick equation for the liquid state. The calculated value is found to agree semi-quantitatively well with experimental data for oxygen solubility in silicon melt, when considering a crude but useful approximation in which an solute oxygen atom and the surrounding silicon atoms in the nearest neighbor shell are assigned as mixed hard sphere solvent atoms.

1. INTRODUCTION

A large amount of silicon single crystals are produced for semiconducting device materials by the Czochralski (CZ) method. When silica crucibles are usually employed in the CZ process for containing the melt, the oxygen that enters the melt from the crucible is rather inevitable and partitioned between the crystal and the melt during crystal growth /1/. The incorporation of oxygen in CZ grown silicon crystals has been the subject of numerous investigations. It is well known that oxygen in small concentrations in the crystal have some beneficial effects such as improvement in mechanical strength of the wafer and intrinsic gettering. On the other hand, higher concentration oxygen causes bulk defects in the wafer mainly due to the oxide precipitation /2,3/. Thus, the oxygen solubility in silicon melt is a key parameter for the growth of silicon single crystals by the CZ process.

There are several experimental reports on the solubility of oxygen in silicon melt, though the temperature dependence of the solubility shows some scatter /4-7/. On the other hand, theoretical interpretation of gas solubility in melts is still limited because of uncertainties regarding molecular and atomic structures of liquid metals. Emi and Pehlke /8/ propose an expression of the solubility of gases in liquid Fe, Co and Ni within the framework of the scaled particle theory which is equivalent to a hard sphere version of the Percus-Yevick equation for the liquid state. The usefulness of this approach has been demonstrated by showing the solubility of hydrogen, nitrogen and carbon in liquid iron, cobalt and nickel to be consistent with experimental observations /8,9/. This prompts us to use the scaled particle theory for discussing the solubility of oxygen in silicon melt in which solute-solute interaction is not so appreciable.

The purpose of this work is to estimate the solubility of oxygen in the silicon melt by applying the scaled particle theory.

2. THEORY

The theoretical expression of the solubility of gases in liquid metals has already been described in detail by Emi and Pehlke /8/. Therefore, only some essential points and additional details, which are necessary for the present work, are given below.

The partition function of an oxygen molecule q_{O_2} may be expressed:

$$q_{O_2} = \frac{(4\pi m_O \mathrm{k}T)^{3/2} V}{\mathrm{h}^3} \frac{8\pi^2 I\,\mathrm{k}T}{\mathrm{h}^2} \left[1 - \exp(-\frac{\mathrm{h}\nu}{\mathrm{k}T})\right]^{-1} W_e \frac{\varepsilon^2}{\gamma} \tag{1}$$

where m_O is the mass of an oxygen atom, k is the Boltzmann's constant, h is the Planck's constant, T is absolute temperature, I and ν are the moment of inertia of rotation and the frequency of vibration of an oxygen molecule, respectively. W_e is the degeneracy of the electronic ground state, ε is the spin degeneracy of oxygen nuclei, and γ is the symmetry factor. Then, the chemical potential of an isolated oxygen atom in gas phase can be given in the following equation:

$$\mu_O^g = \frac{1}{2}\mu_{O_2}^g + \frac{\chi_d}{2kT}$$

$$= \frac{1}{2}\left(\frac{\partial}{\partial N}\left(-kT\ln\left[\frac{q_{O_2}^N}{N!}\right]\right)\right)_{T,V} + \frac{\chi_d}{2kT}$$

$$= kT\ln\left[\left(\frac{4\pi m_O kT}{h^2}\right)^{3/2}\frac{8\pi^2 I\,kT}{h^2}W_e\frac{\varepsilon^2}{\gamma}\right]^{-\frac{1}{2}}\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right]^{\frac{1}{2}}$$

$$+\frac{1}{2}kT\ln\left(\frac{p}{kT}\right)+\frac{\chi_d}{2kT} \qquad (2)$$

where p is the pressure of the melt and χ_d is the dissociation energy of O-O bond which is introduced to adjust the difference in the energy standard state for O_2 and O.

The introduction of oxygen atom in the melt can be considered equivalent to the following two steps, along the way similar to the method first mentioned by Emi and Pehlke /8/.

i) to create a cavity in the melt of a size suitable to accommodate the sphere
ii) to put into the cavity a sphere which interacts with the melt.

When denoting the reversible work required for step i) and ii) to be g_c and g_i, the chemical potential of oxygen in the melt (μ_O^l) is given by

$$\mu_O^l = g_c + g_i - kT\ln\frac{(2\pi m_O kT)^{3/2}}{h^3} + kT\ln\frac{x}{v_M}$$

$$\frac{x}{v_M} \approx \frac{N}{V_M} = \frac{[\%O]N_A d_m}{100M_O} \qquad (3)$$

where x is the molar fraction of the solute, v_M and V_M are the partial molecular volume and volume of the melt, respectively, N_A is Avogadro's number, d_m is the density of the melt, and M_O is the atomic weight of the solute. Reiss *et al.* /10/ derived an approximate expression for g_c by extending the scaled particle theory as applied to the statistical mechanical theory of the hard sphere model. The term of g_c is given by the sum of the volume work expended in creating the cavity of volume $(4/3)\pi r^3$ and the surface work expended against the interfacial tension between the fluid and a perfect hard wall; that is,

$$g_c = \left(\frac{4}{3}\pi r^3\right)p + 4\pi r^2\sigma_0\left[1-\left(\frac{2\delta}{r}\right)\right] \qquad (4)$$

where σ_0 is the surface tension and δ is a factor for converting from surface tension to interfacial tension. It is worth mentioning /10/ that the introduction of a hard sphere of diameter a_S as into a fluid of hard spheres of diameter a_M is considered equivalent to the introduction of a cavity of the radius which is given by $r=1/2(a_S+a_M)$. Then, after statistical considerations,

$$g_c = K_0 + K_1 r + K_2 r^2 + K_3 r^3 \qquad (5)$$

$$K_0 = kT\left(-\ln(1-y)+\frac{9}{2}\left[\frac{y}{1-y}\right]^2\right)-\frac{\pi p a_M^3}{6} \qquad (6)$$

$$K_1 = -\frac{kT}{a_M}\left(6\left[\frac{y}{1-y}\right]+18\left[\frac{y}{1-y}\right]^2\right)+\pi p a_M^2 \qquad (7)$$

$$K_2 = \frac{kT}{a_M^2}\left(12\left[\frac{y}{1-y}\right]+18\left[\frac{y}{1-y}\right]^2\right)-2\pi p a_M \qquad (8)$$

$$K_3 = \frac{4}{3}\pi p \qquad (9)$$

$$y = \frac{\pi a_M^3 \rho}{6} \qquad (10)$$

where y is the packing fraction and ρ is the number density of the atoms. The g_i term in eq. (3) may be dropped out, because this term arises when a hypothetical oxygen sphere appears to be a non-rigid, or soft potential is added to the hard sphere potential.

For solution equilibria of oxygen, one has $\mu_O^l = \mu_O^g$. Then, the expression for the solubility of oxygen in Sieverts' constant form is derived from equation (2) and (3):

$$\ln K = \ln\left[\frac{[\%\mathrm{O}]}{p_{\mathrm{O}_2}^{1/2}}\right] = \frac{1}{2}\ln\left[\frac{2(\pi m_{\mathrm{O}})^{3/2}\mathrm{k}^{1/2}}{3\mathrm{h}^3}\right] + \frac{1}{2}\ln\left[\frac{\mathrm{h}^2}{8\pi^2 I\,\mathrm{k}}\right] + \frac{1}{2}\ln\left[1-\exp\left(-\frac{\mathrm{h}\upsilon}{\mathrm{k}T}\right)\right] + \frac{\chi_\mathrm{d}}{2\mathrm{k}T} - \frac{1}{4}\ln T - \ln\frac{\mathrm{N_A} d_\mathrm{m}}{100 M_\mathrm{O}} - \frac{g_\mathrm{c}}{\mathrm{k}T} \qquad (11)$$

When the values of *r* and *y* are given, this equation enables us to provide a way to estimate the solubility of oxygen in silicon melt.

3. RESULTS AND DISCUSSIONS

It has been established that oxygen atoms incorporated into silicon dominantly occupy interstitial sites with average position midway between two neighboring silicon atoms, on the basis of the infrared absorption analysis for the crystalline case. Two neighboring silicon atoms give up their covalent bond and engage with an interstitial oxygen atom instead, forming an isosceles triangle with Si, O, Si at the corners /11/. The non-linear Si-O-Si bridge has six equivalent positions in crystal and the transition between those positions occurs frequently because the transition does not involve the breaking of chemical bond /12/. According to these results, the following model description for "introduction of cavity" in the melt could be applied.

It is assumed that the affinity of oxygen for silicon might be retained even in the liquid state and then the free rotation of a pair of oxygen-silicon is likely to prevent the penetration of surrounding silicon atoms into a sphere by taking the time average with sufficiently long intervals. In this sense, a simple sum of the solute atom diameter and solvent atom radius would be made to be the radius $1/2a_\mathrm{S}$ of solute-solvent pair sphere. This model is schematically illustrated in Fig. 1. Here, it should be stressed that the concept of the pair and sphere is considered on the basis of time average, and does not imply the existence of a separate phase and a solute atom would be moving around a partner solvent atom with changing the partner from time to time.

The numerical values of the physical properties appearing in eq. (11) for estimating the oxygen solubility in silicon melt are summarized in Table 1. Since the hard sphere diameter of metallic melts is considered to be an effective one and includes the electron gas, which incompletely screens the ionic charge, a unique method for determining the diameter

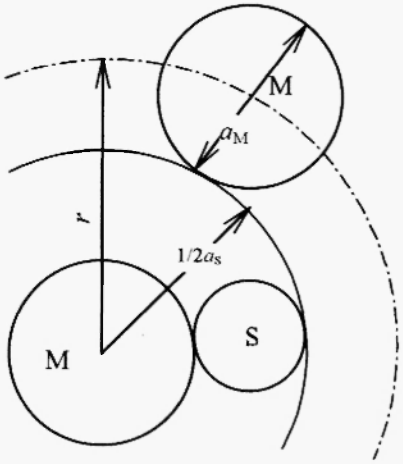

Fig. 1: The radius of the cavity (*r*) assigned to a solute atom of oxygen, S, dissolved in a liquid metal. (M: silicon atom)

Table 1

Numerical values used for estimating the oxygen solubility in silicon melt at 1690 K.

a_O	0.122 nm	χ_d	493.917 kJ
a_M	0.235 nm	d_m	2.51 Mg/m^3
I	19.34×10^{-40} g.cm^2	ρ	5.37×10^{22} m^{-3}
ν	4.709×10^{13} s^{-1}		

has not been established yet. Thus, in the present case, the nearest neighbor distance between Si atoms (0.235 nm) calculated from the crystal structure was chosen for the diameter of silicon a_M. The hard sphere diameter of oxygen in liquid silicon is 0.122 nm taken from the previous work /13/, based on the results of diffraction experiments in both crystalline and glassy states of the corresponding alloy systems. The oxygen solubility value calculated from eq. (11) is 1.9×10^{18} /cm^3 at 1690 K. We must note here that there are several experimental data of oxygen solubility in silicon melt /4-7/ available for comparison. Although the deviation among these experimental data become significant at higher temperatures, it can be rather noticed that all data at the temperature close to the melting point are given in the narrow range from 1×10^{18} to 3×10^{18} /cm^3. These values are likely to be consistent with the result obtained in this work.

On the other hand, the change in oxygen solubility with temperature is not obtained at the present time by a realistic way, because the oxygen solubility in eq. (11) is very sensitive to the value of y, and temperature dependence of y for silicon melt has not been reported yet in the sufficiently wide temperature range. By taking a different point of view, however, it is possible to obtain fundamentals for the variation in packing fraction of silicon melt by using eq. (11) when the oxygen solubility in silicon melt is given. In order to estimate the temperature dependence of y, the experimental solubility data by Huang *et al.* /6/ was chosen as an example. For this calculation, the hard sphere diameter of oxygen was assumed to remain constant with temperature. The temperature dependence of the melt density, d_m, was also considered. Figure 2 shows the resultant y value plotted as a function of temperature by closed circles, together with the corresponding hard sphere diameter of a_M. It is rather stressed here that the value of y at 1730 K is found to be 0.363 which is not far from the value estimated from the experimental structural data of silicon melt /14/. The temperature dependence of the packing fraction may be approximated by the exponential function of $y(T)$ =

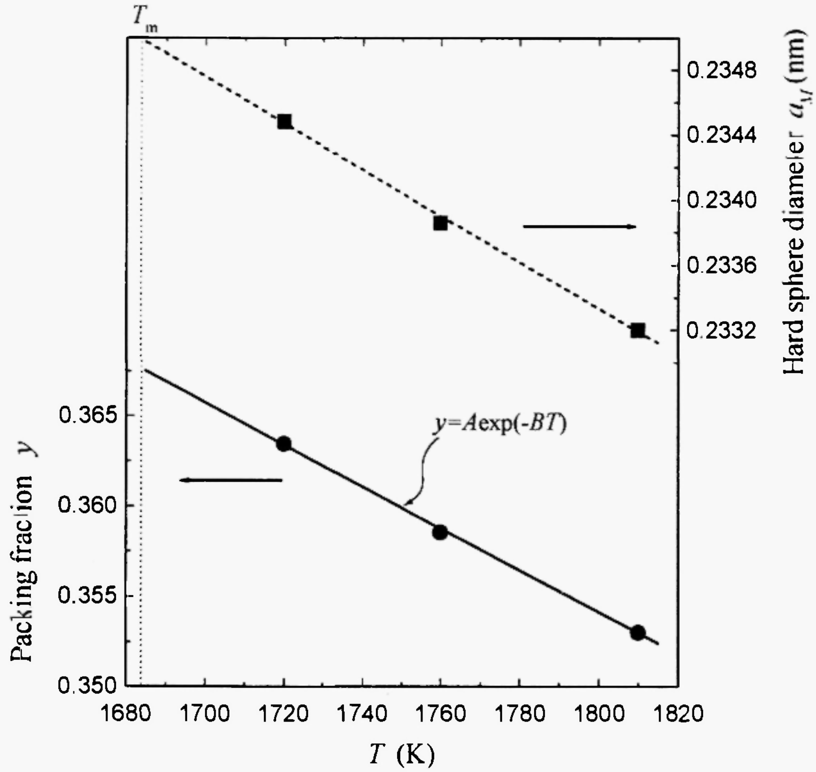

Fig. 2: Temperature dependence of packing fraction y (closed circles) estimated from the oxygen solubility data /11/ by using eq. (11), together with the corresponding hard sphere diameter of a_M (closed squares). The solid line denotes a fitted exponential function of y=Aexp(-BT) and broken line is a corresponding value of a_M.

$A\exp(-BT)$ /14/. Applying this equation to the present case, the parameters A and B were estimated by the least-squares fitting method, and resultant values of A and B are 0.63 and 3.2×10^{-4}, respectively. These values are comparable with those of other liquid metals /14/. However, the following results should be mentioned. The oxygen solubility data of Huang *et al.* /6/ show no significant temperature dependence, similar to the results reported by Ekhult and Carberg /4/. On the other hand, Hirata and Hoshikawa /5/ and Seidl and Muller /7/ indicate a positive temperature coefficient of the oxygen solubility in silicon melt. These previous contradictory results often are induced from confusion when optimizing the CZ process for the silicon crystal growth. For this reason, before the full potential of the present results can be assessed, the temperature dependence of the packing fraction of silicon melt should be experimentally determined, so that the behavior of oxygen solubility could be theoretically predicted more precisely.

4. CONCLUDING REMARKS

The solubility of oxygen in silicon melt was theoretically estimated within the framework of the scaled particle theory first proposed by Emi and Pehlke for the hydrogen solubility in liquid Fe. The present approach is found quite useful by making qualitative prediction possible with respect to the solubility of oxygen in silicon melt, although further experimental determination of the temperature dependence of packing fraction is essentially required. Nevertheless, the present authors conclude that the present theoretical approach works rather well and it would be interesting to extend the idea presently employed to the subject of oxygen incorporation in the CZ process for silicon crystal, so that the validity may be tested in wider base.

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