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Thermodynamics of Phosphorus Removal from Silicon in Solvent Refining of Silicon

Abstract: Refining of silicon for solar applications using metallurgical approaches has attracted a considerable attention in the recent years. The present study involves employing solvent refining as a purification technique in which silicon recrystallization takes place from an iron-silicon alloy melt. It is believed that iron will perform as the impurity “getter” and purified silicon crystals grow from the alloy melt, while the impurities are segregated to the liquid alloy. The focus of this article is on removal of phosphorus, as a critical impurity in solar silicon. In order to assess the feasibility and efficiency of phosphorus removal through solvent refining, the distribution of phosphorus between solid Si and Fe-Si melt at 1483–1583 K (1210–1310 °C) was measured. Interaction parameter between phosphorus and iron was calculated by varying the concentration of phosphorus at each temperature.

Keywords: silicon, thermodynamics, solvent refining, impurity

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1 Introduction

Silicon is the base material for semiconductor devices, and also the most widely used material for photovoltaic (PV) arrays. It accounts for over 90 percent of today’s PV materials [1–3].

Producing silicon with acceptable purity level for solar applications through a cost efficient process is a major challenge in solar silicon industry. Silicon solar cells can play a significant role in answering the world’s need for energy if cost reductions can be achieved through manufacturing process. Considerable effort has been made to replace the energy intensive, complex vapor-phase purification by a simpler and less costly process. Producing low-cost solar grade silicon by refining metallurgical grade silicon is one of the approaches that have attracted wide research interests. Since metallurgical processes are selective in removing impurities, a combination of various purification techniques can be applied to decrease the impurity level in silicon. Each refining step is responsible for lowering specific impurities due to different thermodynamic characteristics of impurities.

Phosphorus is one of the critical impurities in solar grade silicon that significantly influences the efficiency of PV cell. Consequently it is crucial to control the concentration of phosphorus in solar grade silicon. The segregation coefficient of phosphorus in silicon is 0.35 [4] which is significantly larger than that of most other impurity elements. Therefore phosphorus is one of the problematic elements to remove in directional solidification refining processes. The current study focuses on solvent refining as a purification technique to remove phosphorus. In principle, the method is similar to the crystal growth techniques such as Zone Refining and Czochralski that reject the impurities in Si to the liquid front, during the solidification process. In the solvent refining method, this effect is enhanced by alloying silicon with a “getter” metal that acts as the trapper of the impurities. It is believed that under controlled solidification, purified silicon crystals will grow from the alloy melt, while phosphorus is preferentially segregated to the liquid alloy. Extensive studies by Morita’s research group have shown that it is possible to enhance impurity removal from silicon by solvent refining technique using aluminum as the getter element [5–9].

In a recent study on purification of metallurgical grade silicon by a combination of solvent refining and heavy media separation, iron has been successfully employed as the alloying element [10–12]. The work involved non-equilibrium solidification of Fe-Si alloys followed by separation and analysis of the Si product. In order to assess the feasibility and efficiency of phosphorus removal through solvent refining, it is critical to establish the thermodynamics of impurity distribution between growing Si crystals and the liquid phase. This study was undertaken to evaluate the segregation coefficient of phosphorus between Si and Si-Fe melt, aiming to establish the
fundamentals of the process. Furthermore, the interaction parameter between iron and phosphorus was evaluated to determine the affinity of iron for phosphorus.

2 Experimental procedure

The first step of the experimental process is melting a mixture of silicon, iron, and phosphorus to prepare the alloy with the desired composition. As the presence of elements other than Fe, Si, and P can influence the thermodynamic properties of phosphorus, it is critical to avoid the introduction of other impurities from the possible sources. Electrolytic iron and high purity silicon with +99.9985% metal were used as the starting materials. Quartz crucibles are considered suitable to avoid contamination from the crucible.

As the Fe-Si phase diagram, Figure 1, depicts any Fe-Si alloy should contain more than 58.2 mass% silicon in order to form silicon crystals during equilibrium solidification above the eutectic temperature. Considering the minimum required silicon content, the solvent refining process includes melting and controlled solidification of a Si-Fe-P alloy (~80 mass% Si–~20 mass% Fe). The mixtures of silicon, iron, and phosphorus powders were heated up to 1873 K in a vertical tube furnace. The crucibles were kept at 1873 K for 4 hours and then slowly cooled down to 1583 K at the rate of 0.5 K/min. The crucible was kept at 1583 K for 1 hour and finally quenched in water. Different quenching temperatures (1533 and 1483 K) were also examined to investigate the effect of temperature on phosphorus removal.

The solidified alloy was crushed and ground to 53 μm (270 Mesh). The next stage involved separation of silicon phase and alloy particles by leaching in a HF solution. Leaching solution contained 10 Vol.% HF, 20 Vol.% acetic acid and 70 Vol.% deionized water. Si-Fe alloy dissolves in HF while silicon particles remain intact. After two steps of leaching followed by filtration, Si product was digested in a mixture of 10 Vol.% HF, 40 Vol.% HNO₃, and 50 Vol.% deionized water for chemical analysis.

ICP-AES was used for measuring the concentration of phosphorus and iron in the solidified silicon. The concentration of phosphorus in the entire alloy was measured with a similar technique.

3 Results and discussion

As mentioned earlier, thermodynamic behavior of silicon impurities determines the efficiency of impurity removal in solidification refining techniques. To examine the possibility of phosphorus removal from silicon, the distribution coefficient of phosphorus between solid silicon and the alloy matrix, as well as the interaction parameter between P and Fe were evaluated.

3.1 Chemical analysis

The concentration of phosphorus in the entire sample (Si+ Fe–Si) and in the silicon phase with corresponding quenching temperature is presented in Table I. Using these two measured concentrations, the concentration of

![Fig. 1: Fe-Si phase diagram [13].](image-url)
phosphorus in iron-silicon alloy melt is calculated based on mass balance.

### 3.2 Distribution coefficient

The distribution coefficient of phosphorus between solid silicon and iron-silicon melt is essentially similar to phosphorus segregation coefficient, but at a temperature different from the melting point of silicon:

\[
K_p = \frac{C_{P \text{ in solid Si}}}{C_{P \text{ in Fe-Si melt}}} \quad (1)
\]

Figure 2 shows the $K_p$ values decrease with temperature, implying better purification when the alloy is quenched from higher temperature. The distribution coefficient becomes smaller than 0.35 above 1285 °C. In other words solvent refining is more effective than directional solidification above 1285 °C. However, this also indicates lower Si yield for a given alloy mass. Table I shows that the distribution coefficient is not dependent on the phosphorus content of the Si. It implies linear dependence of liquidus and solidus temperatures on phosphorus content in this ternary system. The linear behavior is expected due to a small variation in the P concentration in Si and Fe-Si.

### 3.3 Phosphorus removal and silicon yield

The extent of phosphorus removal from silicon at each temperature is calculated from its distribution coefficient based on the following equation

\[
\% \text{Removal} = 100 \left(1 - \frac{K_p}{1 + K_p}\right) \quad (2)
\]

The variation of silicon yield and P removal percentage with temperature are presented in Figure 3. As seen, higher silicon purity is accompanied by a decreased Si yield.

### 3.4 Interaction parameter between phosphorus and iron

From fundamental point of view, it is important to determine the relative affinity of Si and Fe towards phosphorus,
as the solubility of P in Si is affected by the presence of Fe. This may best be represented by the interaction parameter of Fe on P, $\varepsilon_{PFe\text{ in solid } Si}^P$, that is deduced as following.

Due to the very small variation in the phosphorus content of Fe-Si melt, the activity of Fe in the alloy melt is considered to be constant at each temperature. According to Equation 3, the activity of Fe in solid Si is also constant.

$$\frac{\Delta G_m^{\text{ fus}}}{RT} + \ln a_{Fe\text{ in Fe-Si melt}} = \ln a_{Fe\text{ in solid Si}} + \ln X_{Fe\text{ in solid Si}} = C(\text{ const.})$$

(3)

The activity coefficient of iron in solid silicon can be presented as Equation 4.

$$\ln \gamma_{Fe\text{ in solid Si}} = \ln \gamma_{Fe\text{ in solid Si}}^\circ + \varepsilon_{Fe\text{ in solid Si} P\text{ in solid Si}}^P X_{P\text{ in solid Si}}$$

(4)

where $\gamma_{Fe\text{ in solid Si}}^\circ$ is the activity coefficient of iron at its infinite dilution relative to pure solid iron. Considering the small content of iron in solid silicon, self interaction parameter can be neglected and Equation 5 can be obtained by substituting $\ln \gamma_{Fe\text{ in solid Si}}^\circ$ from Equation 4 into Equation 3.

$$\ln X_{Fe\text{ in solid Si}} = -\varepsilon_{Fe\text{ in solid Si} P\text{ in solid Si}}^P X_{P\text{ in solid Si}} - \ln \gamma_{Fe\text{ in solid Si}}^\circ + C$$

(5)

$\varepsilon_{Fe\text{ in solid Si} P\text{ in solid Si}}^P$ can be determined from the slope of the linear plot of $\ln X_{Fe\text{ in solid Si}}$ vs. $X_{P\text{ in solid Si}}$, as depicted in Figure 4. The negative values of the slopes of the lines, i.e. negative interaction coefficients, suggests a strong affinity between the two elements which is favorable for solvent refining with iron.

The interaction parameter between iron and phosphorus becomes more negative by increasing temperature, indicating a stronger affinity between the two (while in Si) at higher temperatures. Consequently, higher temperatures are favorable for phosphorus removal from silicon. This trend can be explained, noting the relative stability of iron and silicon phosphides. Table II includes the Gibbs free energies of all iron phosphides and silicon phosphate as well as the difference between them at various temperatures. It can be seen that the difference between Gibbs free energies of all iron phosphides and silicon phosphate increase with temperature. In other words, as the temperature increases, the iron–phosphorus compounds become more stable than silicon phosphate, thus higher affinity between Fe–P compared to Si–P. The larger the difference the higher the affinity of iron for P compared to Si. It should be noted that by increasing temperature, the affinity of both iron and silicon for phosphorus decreases, but the iron affinity for phosphorus decreases less than the affinity of silicon for phosphorus.

4 Conclusion

Greater P removal can be achieved when Si is grown from Fe–Si melt at higher temperature because distribution coefficient of phosphorus between solid silicon and the iron-silicon melt decreases with temperature. About 80% phosphorus removal was obtained at 1583 K. Smaller distribution coefficient was achieved at the expense of lower
silicon yield. Large negative values were obtained for interaction parameter between phosphorus and iron in solid silicon at different temperatures. Negative values of interaction parameter indicate large affinity of iron for phosphorus in silicon.

Interaction parameter between phosphorus and iron becomes more negative as the temperature increases, pointing to more favorable thermodynamic conditions for P removal.

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References


Table II: The Gibbs free energy of iron and silicon phosphides and their difference at various temperatures

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