



Impurity segregation in electrochemical processes and its application to electrorefining of ultrapure silicon

Meng Tao*

School of Electrical, Computer and Energy Engineering, Laboratory for Terawatt Photovoltaics, Arizona State University, Tempe, AZ 85287-5706, USA

ARTICLE INFO

Article history:

Received 2 August 2012

Received in revised form 30 October 2012

Accepted 30 October 2012

Available online 23 November 2012

Keywords:

Impurity segregation

Electrorefining

Ultrapure materials

Solar-grade silicon

ABSTRACT

A theory for impurity segregation in electrochemical processes is formulated based on the Nernst equation, which forms the theoretical foundation for electrorefining. It is found that the current two-electrode configuration, while being widely used to purify metals, is incapable of producing ultrahigh purity. A three-electrode configuration is required, in which the potential applied to the anode or the cathode with respect to the reference electrode is the key to produce ultrapure materials. The theory is applied to electrorefining of metallurgical-grade silicon to produce solar-grade silicon. It is suggested that two-step electrorefining is required to remove all the impurities, in which the anode and cathode potentials are controlled in separate steps. The precise anode and cathode potentials for each step are determined from the impurity concentrations in metallurgical-grade silicon and the target impurity concentrations for solar-grade silicon. It is also found that low process temperatures promote effective electrorefining.

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1. Introduction

The high energy input for fabricating wafer-Si solar cells at $\sim 4 \text{ kWh/W}_p$ [1,2] presents two bottlenecks to their terawatt-scale deployment. If wafer-Si cells were produced at $1 \text{ TW}_p/\text{yr}$, the amount of electricity required would equal to $\sim 20\%$ of the 2007 global electricity production [1], a factor that is not in today's demand numbers. On the other hand, industrial electricity costs $\sim \$0.11/\text{kWh}$ in 2008 [3], which translates into $\sim \$0.44/\text{W}_p$ in electricity cost alone for wafer-Si cells. The most energy-intensive step in the fabrication of wafer-Si cells is the Siemens process, which reduces trichlorosilane to polycrystalline Si, with an energy tag of $\sim 200 \text{ kWh/kg}$ [4]. Electrorefining of Si in a molten salt was proposed as an alternative to the Siemens process [5], with an estimated energy input of $\sim 16 \text{ kWh/kg}$ [6] and an experimental value of $\sim 2 \text{ kWh/kg}$ for the electrolysis only [7]. The first attempt to electrorefine Si employed a metallurgical-grade Si (MG-Si) anode [5]. The potential applied between anode and cathode was $0.03\text{--}0.3 \text{ V}$, temperature $\sim 1000^\circ\text{C}$, and the purity of the resultant Si 99.99%. A molten Si cathode was proposed to increase the growth rate of Si [8], although the purity of Si was only 99.97% from 99.5% pure quartz. A solid anode of Si–Cu alloy was reported [9], with process temperature reduced to 750°C , leading to sub-ppm impurity concentrations except P which was 3 ppm. After a long dormant period of ~ 30 years [10], there is a renewed interest in electrorefining for

solar-grade Si (SG-Si) [7,11–13], due to the rapid growth of the solar cell industry in recent years.

As pointed out by Elwell et al. [6], all the experiments discussed above were carried out without a satisfactory theory for electrorefining. Empirical electrorefining has been successful in producing metals up to $\sim 99.99\%$ pure, which is sufficient for most applications of metals, e.g. Al and Cu. However, electrorefining has not produced ultrapure materials such as solar-grade Si, with required purity above 99.9999% [7]. Here we formulate a theory for impurity segregation in electrochemical processes based the Nernst equation, which establishes the theoretical foundation for electrorefining. The theory points to a clear pathway to ultrapure materials by electrorefining. As an example, the theory is applied to analyze electrorefining of MG-Si to produce low-cost energy-efficient SG-Si.

2. Theory

A representative molten salt process for electrorefining of Si is shown in Fig. 1. The anode can be MG-Si or Si–Cu alloy, molten or solid, from which Si is electrolytically dissolved into the molten salt:



An impurity in Si can also be electrolytically dissolved into the molten salt, depending on the applied potential:



* Corresponding author. Tel.: +1 480 965 9845.

E-mail address: meng.tao@asu.edu

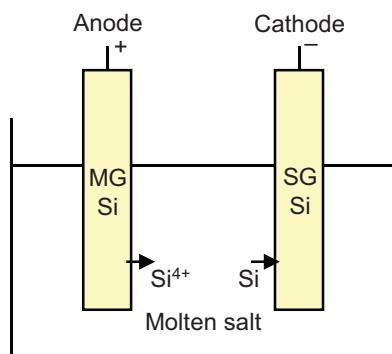


Fig. 1. A representative electrorefining process for Si. The anode can be either impure Si or impure Si alloyed with Cu, where Si is electrolytically dissolved into the molten salt. The cathode can be either pure Si or metallic. The Si deposited on the cathode is purer than the Si on the anode.

where M stands for an impurity and z is the oxidation state of the impurity. On the cathode, Si deposits:



Depending on the applied potential, an impurity can also deposit on the cathode:



The cathode can be molten or solid. Two segregation coefficients can be defined. One is between anode and molten salt, and the other is between cathode and molten salt:

$$k_{\text{anode}} = \frac{C_{\text{anode}}}{C_{\text{ms}}} \quad \text{and} \quad k_{\text{cathode}} = \frac{C_{\text{cathode}}}{C_{\text{ms}}} \quad (1)$$

where C_{anode} , C_{ms} , and C_{cathode} are the impurity concentrations in the anode, molten salt, and cathode, respectively.

The general form of the Nernst equation for a half-cell is:

$$E_{\text{red}} = E_{\text{red}}^o - \frac{kT}{ze} \ln \frac{a_{\text{red}}}{a_{\text{ox}}} \quad (2)$$

where E_{red} is the applied reduction potential, E_{red}^o the standard reduction potential for the impurity, k the Boltzmann constant, T the temperature, e the electron charge, and a_{red} and a_{ox} the chemical activities of the reductant and oxidant of the impurity. For low impurity concentrations, the activities can be replaced by concentrations of the reductant and oxidant C_{red} and C_{ox} :

$$E_{\text{red}} = E_{\text{red}}^o - \frac{kT}{ze} \ln \frac{C_{\text{red}}}{C_{\text{ox}}} \quad (3)$$

According to reactions (R2) and (R4), the reductant is in either the anode or the cathode, and the oxidant is always in the molten salt. Therefore, C_{ox} can be replaced by C_{ms} , and C_{red} can be replaced by either C_{anode} or C_{cathode} :

$$E_{\text{anode}} = E_{\text{red}}^o - \frac{kT}{ze} \ln \frac{C_{\text{anode}}}{C_{\text{ms}}} \quad \text{and} \quad E_{\text{cathode}} = E_{\text{red}}^o - \frac{kT}{ze} \ln \frac{C_{\text{cathode}}}{C_{\text{ms}}} \quad (4)$$

With Eq. (1), Eq. (4) can be rewritten as:

$$E_{\text{red}} = E_{\text{red}}^o - \frac{kT}{ze} \ln k_o \quad (5)$$

where k_o is the segregation coefficient for either anode or cathode, and E_{red} the reduction potential applied to either anode or cathode. After rearrangement, Eq. (5) becomes:

$$E_{\text{red}} - E_{\text{red}}^o = -\frac{kT}{ze} \ln k_o \quad (6)$$

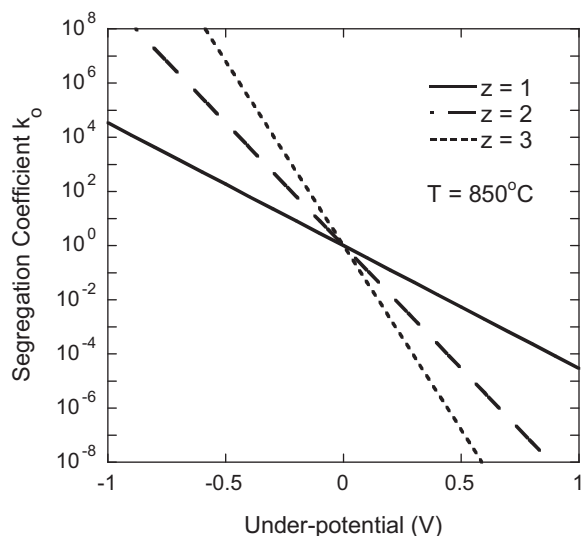


Fig. 2. Segregation coefficient vs. under-potential at 850 °C. The segregation coefficient can be smaller or larger than unity depending on whether an under- or over-potential is applied. It can be very small or very large, when the under- or over-potential increases. Segregation is also more prominent for higher oxidation states.

where $E_{\text{red}} - E_{\text{red}}^o$ is the driving force for impurity segregation. Notice that a negative $E_{\text{red}} - E_{\text{red}}^o$ represents an over-potential for reduction and a positive $E_{\text{red}} - E_{\text{red}}^o$ is an under-potential for reduction.

3. Discussion

Eq. (6) forms the basis for impurity segregation in electrochemical processes. It states that the segregation coefficient is controlled by the applied potential, and it can be larger or smaller than unity depending on whether an over-potential or under-potential is applied. It is reminded that for electrorefining, the segregation coefficient for the anode needs to be large to keep impurities in the anode, and it needs to be small for the cathode to keep impurities in the molten salt, according to Eq. (1). The segregation coefficient can also be far from unity if the under- or over-potential increases. Fig. 2 plots segregation coefficient at 850 °C as a function of under-potential for different oxidation states. The y axis is logarithmic. The segregation coefficient exceeds 10^4 at under-potential 1 V (or 10^{-4} at -1 V) for all the oxidation states considered, and reaches 10^{14} at under-potential 1 V (or 10^{-14} at -1 V) for $z=3$. These values are much larger (or smaller) than those found in float-zone or Czochralski growth [14], i.e. electrorefining should be much more effective in purification than those methods.

Fig. 2 also reveals that impurity segregation is much more prominent for higher oxidation states. At under-potential 0.5 V, the segregation coefficient is 5.4×10^{-3} , 2.9×10^{-5} , 1.6×10^{-7} for $z=1, 2, 3$, respectively. This can be a useful tool for mechanistic studies of impurity behavior in electrochemical processes, i.e. the oxidation state of an impurity is revealed in a semi-logarithmic plot of segregation coefficient vs. applied potential. If $z=1$, the slope is -10.31 V^{-1} at 850 °C according to Eq. (6). If $z=2$, the slope is -20.63 V^{-1} at the same temperature. For $z=3$, the slope is -30.94 V^{-1} . The slope increases in an increment of 10.31 V^{-1} at 850 °C, which should be easily distinguishable in the experiment.

The effect of temperature on segregation coefficient is plotted in Fig. 3 between 700 °C (973 K) and 1000 °C (1273 K), where high temperatures push the segregation coefficient toward unity.

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