Experimental and Molecular Simulation Studies of Silicon Production in a Microwave Furnace

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Introduction

Silicon as a raw material for solar cells is industrially produced in an electric arc furnaces by carbothermal reduction of SiO_2 according to the simplified reaction equation

$$SiO_2 + 2C \rightarrow Si + 2CO.$$

However, the underlying reaction mechanism is still subject of discussions, as it involves a complex system of reactions between solid, liquid and gaseous compounds and by-products such as SiC and SiO.

Due to the complex reaction system of silicon production, it is believed that the heating of a mixture of silica and carbon in the ratio 1:2 in a laboratory furnace will either result in the production of SiC or SiO, but not in silicon metal [1,2]. Contrary to these observations, we present an approach for silicon production in a laboratory microwave furnace leading to silicon metal [3]. A new promising approach to get insight into the complex reaction mechanisms are MD simulation studies using the reactive force field ReaxFF [4, 5]. We here also present studies on its capability to describe the SiO_2-C reaction system.

Experimental Setup

We developed a special designed microwave furnace with a microwave power up to 6 kW and a high-temperature resistant cavity. Experiments can be carried out under vacuum and inert-gas atmosphere, while cavity's pressure, incoming and absorbed microwave power, flow of inert-gas, and temperature (by IR thermometer and thermocouples) can be measured. Since the absorbed microwave power depends on the electric field strength, much effort was put into the cavity's design. Therefore, we used simulation techniques [6] to model the electric field, and simulations results were found to be in good agreement with experiments.

Experimental Results

With carbon being a very good microwave absorbent we started measuring its heating rates at different microwave powers. Results indicate heating rates of the core of more than 500 K/min with a microwave power of 900 W as shown in figure 1. As the thermocouple wires affect the microwave field, measurements were taken after turning off the microwave power. Due to this, cooling of the sample has to be taken into account. Thus, the temperature drop of the surface was observed by the IR during the time we needed to obtain the value from the thermocouple. We then assumed that the cooling in the core of the sample and at the surface is the same.

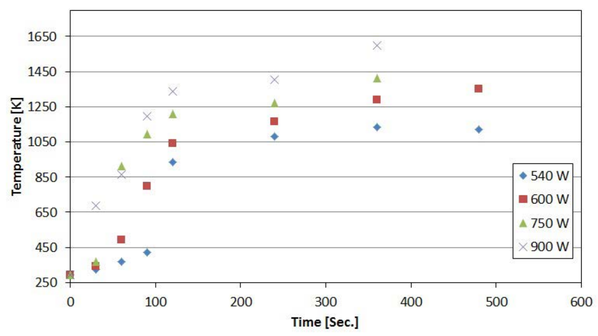

Figure 1: Experimental results of heating pure char-coal.

The reaction mixture of silica and char-coal in a ratio 1:2 is heated with a constant surface heating rate of 50 K/min until a surface temperature of 1,273 K (1,000 °C) is reached. For this heating profile, the surface temperature is measured with the IR thermometer and compared to the reaction temperatures in the sample, measured with thermocouple by the same procedure as described above. As seen from figure 2, the reaction temperature after 15 min is estimated to be below 2,000 K (1,727 °C). The product is analysed by energy dispersive x-ray spectroscopy (EDX), which confirms that metallic silicon is produced in the microwave furnace (see also figure 2).

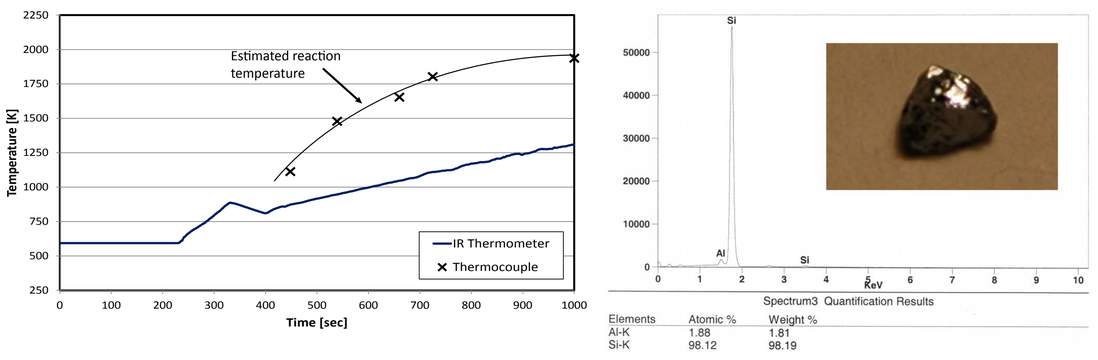

Figure 2: Surface and reaction temperature in the mixture (left) and EDX of the product (right).

Simulations of Pure Materials in the System SiO_2-C

We examined the ability of the reactive force field ReaxFF by van Duin et al. [5] to reproduce properties of pure compounds in the reaction system SiO_2-C, i.e. SiO_2, SiC, silicon and carbon, and the gaseous compounds CO, CO_2, O_2 and SiO [7]. For all solid compounds the simulated structural parameters are in good agreement with literature values.

As SiO is stated to be one of the most important intermediates in silicon production, we also tested the ability of the ReaxFF model to reproduce the formation of gasous SiO [8]. As shown by figure 3, gasous SiO molecules were formed in the simulation at temperature between 1,000 and 1,500 K, which ist in good agreement with experiment.

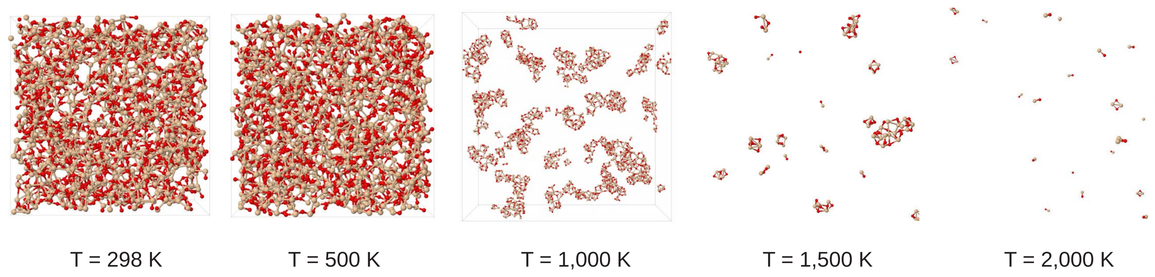

Figure 3: Simulation results for heating of solid SiO up to 2,000 K.

To analyse the influence of surface defects on the chemical reaction, we are currently analysing surface structures of SiO_2 polymorphs at different temperatures. Figure 4 shows the surface structures of low-quartz resulting from heating up to 2,300 K .

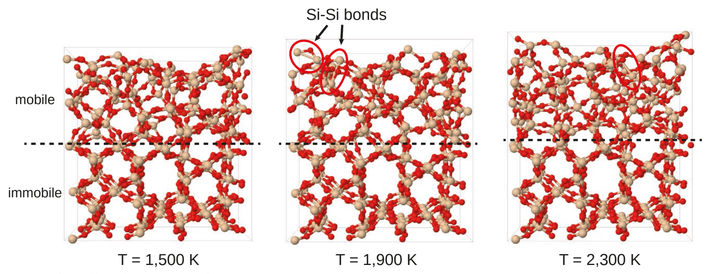

Figure 4: Simulation results for heating low-quartz to temperatures up to 2,300 K.

With increasing temperatures silicon gets over-coordinated, which leads to a weakening of the Si-O bond by increasing its length. This results in additional Si-Si bonds (e.g. the ones marked in figure 4) as well as additional Si-O bonds.

Chemical Reactions

To identify reactive sites on SiO_2 surfaces, we added carbon atoms in a simulation box above a defective SiO_2 surface and followed their reaction paths. Figure 5 shows different reaction steps during the reaction of a carbon atom with the SiO_2 surface, where carbon forms gaseous CO in contact with the SiO_2 surface.

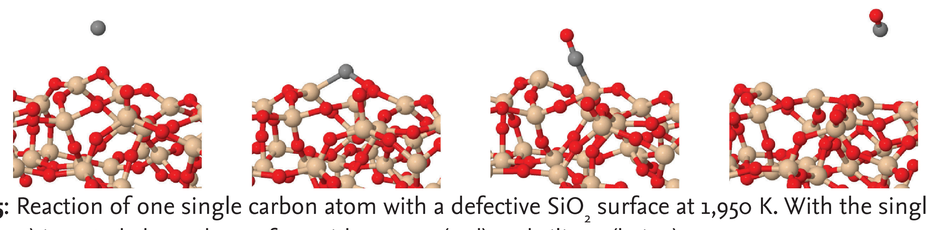

Figure 5: Reaction of one single carbon atom with a defective SiO_2 surface at 1,950 K. With the single carbon atom (grey) inserted above the surface with oxygen (red) and silicon (beige).

Conclusions

Although the new process still requires fundamental investigation, we have shown the ability of producing silicon metal in a microwave furnace, which is a promising approach to increase both the energy efficiency of silicon production and the silicon quality. MD-simulation results suggest, that the ReaxFF is well suited for simulation studies on the SiO_2-C reaction system to get insight into the reaction mechanisms of silicon production.

Acknowledgment

This work is supported by Deutsche Bundesstiftung Umwelt (AZ 28408).

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