Abstract #2038, 224th ECS Meeting, © 2013 The Electrochemical Society

Three-Electrode Electrorefining for Ultrapure Solar-Grade Si

Xiaofei Han, Bin Zhou and Meng Tao
School of Electrical, Computer and Energy Engineering,
Arizona State University, Tempe, AZ 85287-5706, USA

The current industrial processes, the Siemens and fluidized-bed processes, to produce ultrapure polycrystalline Si employ $SiHCl_3$ for purification by distillation, with extreme high energy cost up to ~200kWh/kg [1]. Electrorefining was proposed as a much more energy-efficient alternative to ultrapure Si [2]. After almost 50 years and at least a dozen studies worldwide, electrorefining has yet to achieve the purity required for solar-grade Si, which is >99.9999%. The overwhelming majority of these studies employed a 2-electrode electrochemical cell to purify Si. We recently pointed out that the thermodynamics of the 2-electrode cell prevents any purification and a 3-electrode cell is required to achieve a ultrahigh purity [3].

In this paper, we report our preliminary experimental results on Si electrorefining using a 3-electrode high-temperature and high-vacuum electrochemical cell. The applied voltage, type of salt and deposition temperature were studied for their effect on impurity concentrations in the deposited Si. Cyclic voltammetry measurement was performed to determine the applied voltage. The electrode weight difference before and after electrorefining was measured by a high-resolution electronic balance. Secondary ion mass spectroscopy was carried out to determine impurity concentrations in the deposited Si on the cathode.

Figure 1 shows the cyclic voltammetry of our Si electrorefining bath. Si is oxidized to Si^{4+} ions when a positive voltage is applied on it. Si^{4+} or more complex Si ions in the molten salt are reduced on the cathode where a negative voltage is applied. Figure 2 shows the impurity concentrations in a Si film deposited on the counter electrode when 0.9 V is applied on the working electrode. Figure 3 shows the impurity concentrations in a Si film deposited on the working electrode when –0.8 V is applied on it. Clearly the applied voltage has a critical effect on impurity concentration, and a positive voltage on the working electrode significantly reduces concentrations of all impurities. Controlling the applied voltage on the working electrode can only be achieved in a 3-electrode cell. Contamination also plays a critical role in the final impurity concentration (data not shown). The weight difference between working electrode and counter electrode is small (data not shown), indicating a likely reversible reaction for Si in electrorefining.

Acknowledgments:
This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-09ER46597.

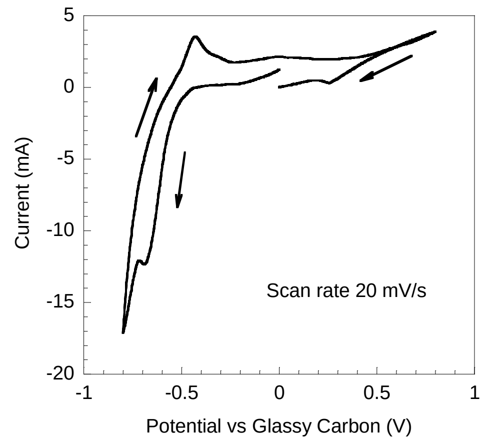

Figure 1. Cyclic voltammetry in a LiCl molten salt with Si electrodes.

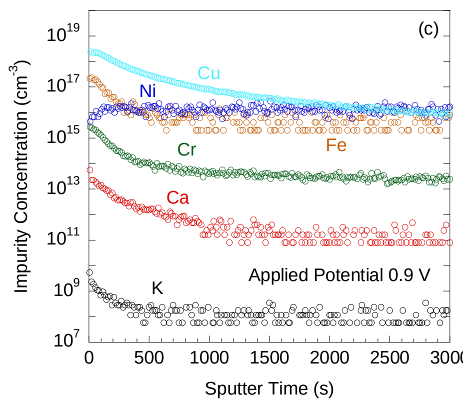

Figure 2. Impurity concentrations in deposited Si by SIMS at applied voltage of 0.9 V on working electrode.

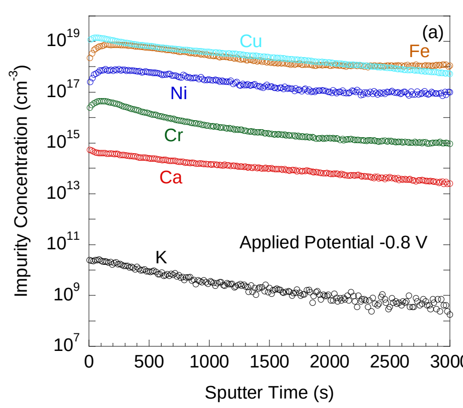

Figure 3. Impurity concentrations in deposited Si by SIMS at applied voltage of –0.8 V on working electrode.

References

[1] C.S. Tao, J. Jiang and M. Tao, “Natural resource limitations to terawatt-scale solar cells”, Solar Energy Materials and Solar Cells 95, 3176 (2011)

[2] R. Monnier and J.C. Giacometti, “Research on the electrolytic refining of silicon”, Helvetica Chimica Acta 47, 345 (1964)

[3] M. Tao, “Impurity segregation in electrochemical processes and its application to electrorefining of ultrapure silicon,” Electrochimica Acta 89, 688 (2013)