Direct Carbothermic Silica Reduction from Purified Silica to Solar-Grade Silicon

Kenji Itaka[1]*, Takuya Ogasawara[1], Abderahmane Boucetta[1], Rabie Benioub[1], Masatomo Sumiya[2], Takuya Hashimoto[3], Hideomi Koinuma[4], Yasubumi Furuya[1]

[1] North Japan Research Institute for Sustainable Energy, Hirosaki University, 2-1-3, Matsubara, Aomori, 030-0813, Japan.

[2] Widegap Materials group, National Institute for Materials Science, Tsukuba, 305-0044,Japan.

[3] College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajousi, Setagaya-ku, Tokyo 156-8550, Japan.

[4] Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, 277-8568,Japan.

*E-mail: itaka@cc.hirosaki-u.ac.jp

Abstract. The shortage of silicon for solar cells has much attract in research and development of the low cost mass production process of solar grade Silicon (SOG-Si). The key of the strategy to silicon for solar cells in long terms is the efficiency in reduction. We developed a new concept reduction furnace using the combinatorial method in order to investigate the metallurgical process for silicon reduction. The production of reduced Si shows purity with less 2ppm level.

1. Introduction

Two peculiar features of deserts, which are powerful solar radiation and non-use vast area, represent the treasury of solar energy that is one of candidates for the next generation sustainable energy from Nature[1, 2]. In viewpoint of reserves of natural resources, the material selection for solar cells which covers the vast deserts is only the silicon, which exists generally in large quantities as oxides in the desert as element on the earth. The Siemens method, which has been a silicon reduction process used for many years, is suitable for the integrated semiconductor industry which needs ultra-high purity grade. However, the cost of this process is too high due to low yield in the reaction process of chloride gas. The purity level of silicon for the solar cells is required to be 6N (99.9999%) with respect to the impurities of boron
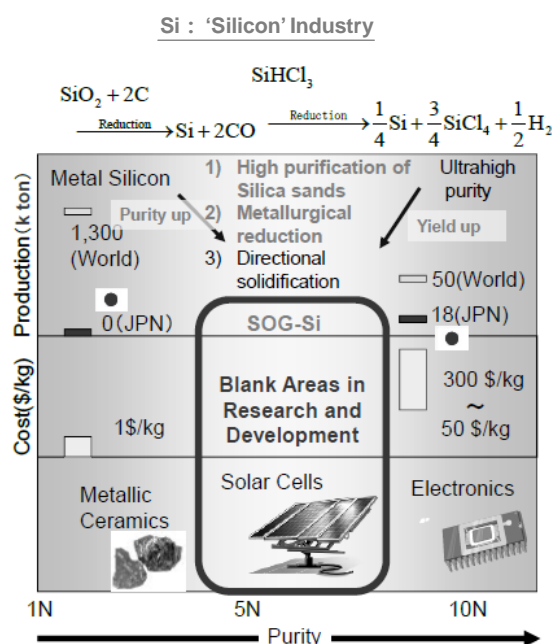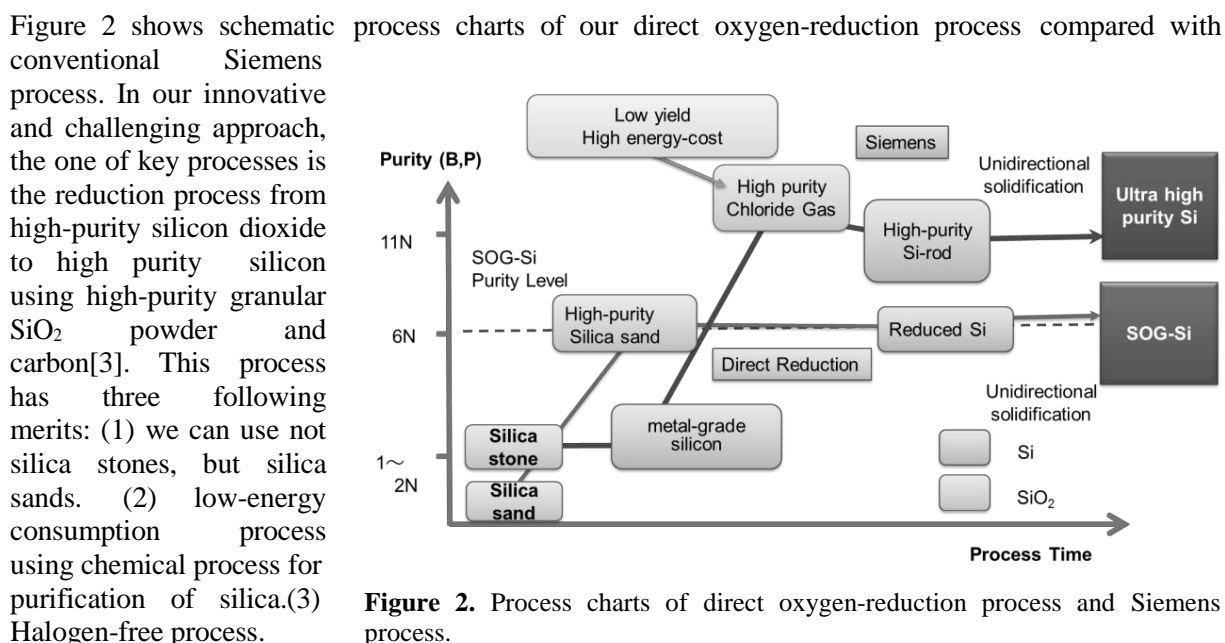

Figure 1. Strategy to 'Silicon' business industry.

and phosphorus. This purity grade is much higher than that of metal silicon (~2N), and much lower than that of semiconductor silicon (~11N) as shown in Figure 1. The shortage of silicon for solar cells has much attract in research and development of the low cost mass production process of SOG-Si. There are two strategic paths to the process of 6N-graded silicon, that is, solar-grade silicon (SOG-Si): One is the way to improve the process of metal silicon in purity using high-purity silicon dioxides. The other is the way to improve the yield of the process of the silicon for electronics.

Figure 2 shows schematic process charts of our direct oxygen-reduction process compared with conventional Siemens process. In our innovative and challenging approach, the one of key processes is the reduction process from high-purity silicon dioxide to high purity silicon using high-purity granular SiO_2 powder and carbon[3]. This process has three following merits: (1) we can use not silica stones, but silica sands. (2) low-energy consumption process using chemical process for purification of silica.(3) Halogen-free process.

Figure 2. Process charts of direct oxygen-reduction process and Siemens process.

2. Thermodynamics in Direct Reduction of Silica

Reduction and synthesis processes of oxides can be roughly estimated with the Ellingham Diagram, which is temperature dependence of chemical potential of oxygen molecules. Figure 3 shows the Ellingham Diagrams of Silicon, Iron, Titanium and Aluminium, which are calculated using thermodynamic database MALT2[4]. Red lines indicate the chemical potential of oxygen molecules in hydrogen reduction and carbon-carbon monoxide reduction processes. The line of the hydrogen reduction crosses only the Iron curve, while the line of the carbon hydrogen reduction crosses the silicon curve. This indicates that the reduction of silicon from silica cannot be performed by normal hydrogen gas. The reduction of silicon has similarities to that of titanium oxides and aluminium oxides.

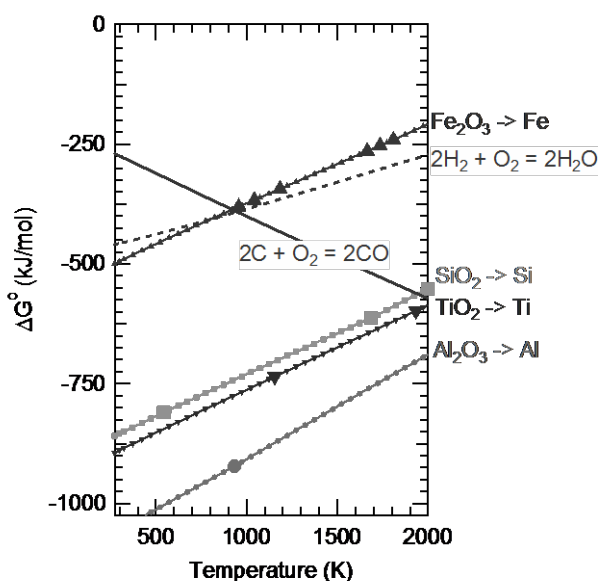In the case of use of carbon for the reduction, however, this reduction reaction consists of a

Figure 3. Ellingham Diagrams of Silicon, Iron, Titanium and Aluminum.

lot of complicated reaction paths as shown in Figure 4. For the optimization of not only the main process but also sub process, the control of many parameters such as reaction temperature, partial pressure and composition is required.

First, SiO$_2$ reacted to carbon above 1300°C generates SiO gas, which is volatile under conventional condition. Then, the following reactions will proceed.
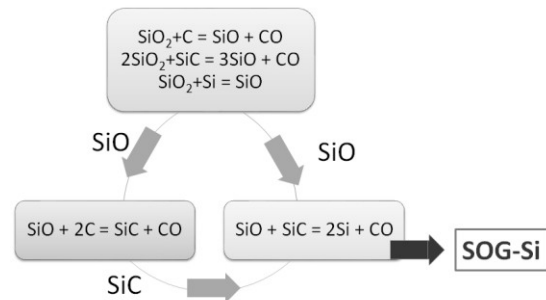

Figure 4. Reaction process paths from SiO$_2$ to Si.

$$Si[sl] + SiO_2[sl] = 2SiO[g] \tag{1}$$

$$SiO[g] + SiC[s] = 2Si[sl] + CO[g] \tag{2}$$

$$SiO[g] + C[s] = Si[sl] + CO[g] \tag{3}$$

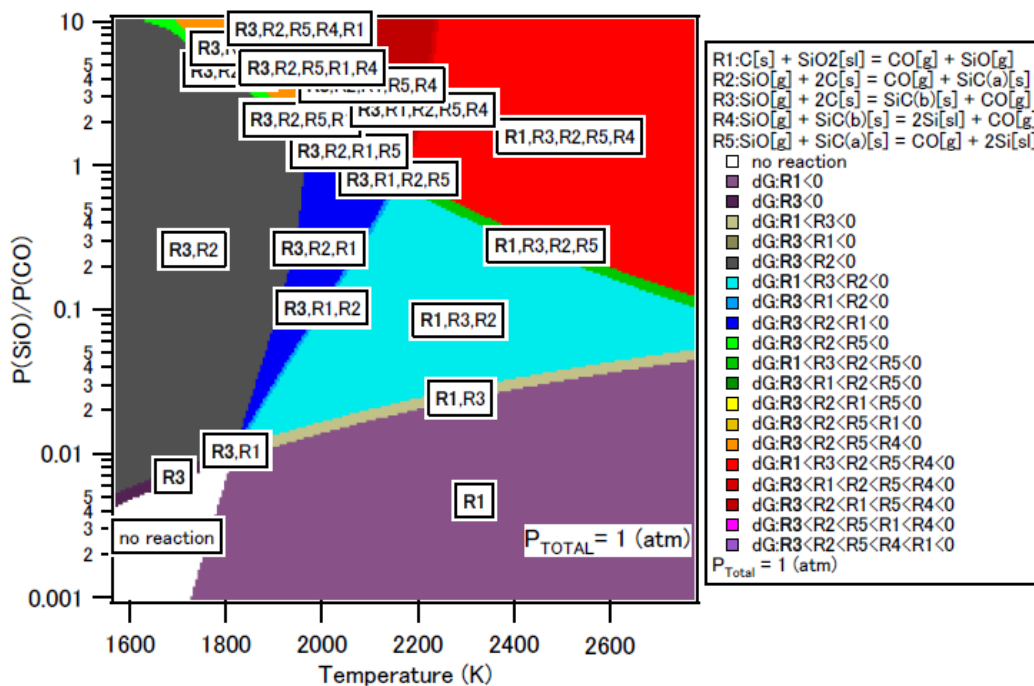$$SiO[g] + 2C[s] = SiC[s] + CO[g] \tag{4}$$

Figure 5. (online color) Phase diagrams of the silica reduction processes. Each bold annotation indicates the preferential reaction in the phase.

Figure 5 shows phase diagrams of the silica reduction processes (a) with carbon and (b) without carbon (only with silicon carbides) calculated using thermodynamic database MALT2[4]. The reaction with the formation of the final product silicon is only R2. What should be noted is that there is no phase with the preferential reaction (2) in Fig. 5 (a). After exhausting carbon, the phase diagram Fig. 5(a) migrates to the phase diagram Fig.5 (b). On the phase diagram Fig. 5(b), the R2 reaction becomes dominant in the region of high SiO partial pressure based on carbon monoxides partial pressure.

3. Combinatorial Silica Reduction Furnace

This reduction reaction consists of a lot of complicated reaction paths as shown in Fig. 4. For the optimization of not only the main process but also sub process, the control of many parameters such as reaction temperature, partial pressure and composition is required. Combinatorial technology is widely applicable to a variety of materials and processes. Ever since the proposal of combinatorial solid state nano science and technology, several automated parallel synthesis
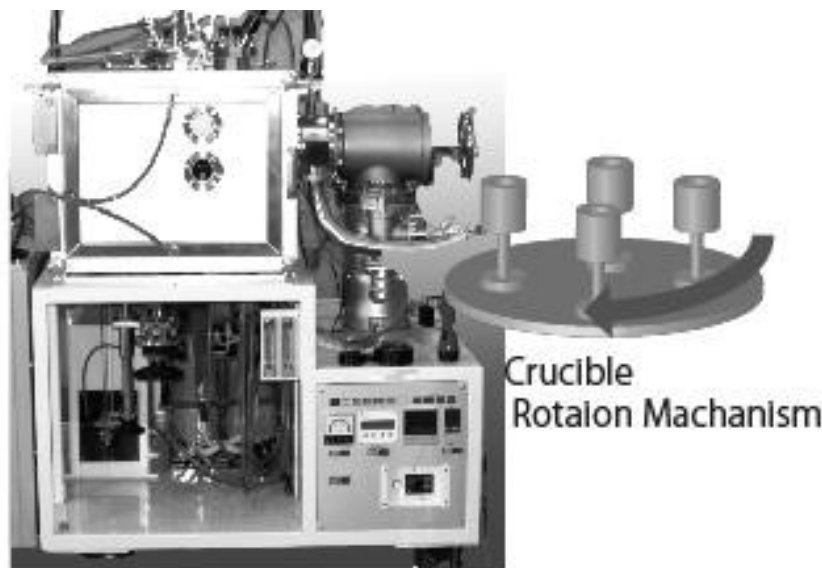

Figure 6. Photo image of combinatorial reduction furnace system.

systems for high-throughput screening of new functional materials have been developed[5], and the combinatorial autoclave reactor was developed to investigate optimum reaction conditions efficiently for alternating CO_2 copolymerization with epoxide[6]. Thus, the combinatorial methods are powerful tools to optimize a complicated chemical reaction. We developed a new concept reduction furnace using the combinatorial method in order to investigate the metallurgical process for silicon reduction as shown in Figure 6.

Our system can run four processes with starting compositions and process temperatures by only one setup. Normally, vacuum evacuation of the chamber takes 2-3 hours using the diffusion pump. In this system, the waste time for vacuum evacuation for each crucible can be saved. In addition, the systematic data can be obtained under similar background condition because of less perturbation. The combination method is useful in systematic screening in these parameters in the optimization. Our developed silica reduction furnace system will serve as a powerful tool for the investigation and optimization in the silica reduction process.

Figure 7 shows the image of the obtained Silicon (weight ~5g) using our furnace. The heating time was 30 min. The impurities level of this sample were 1.1~1.4 ppm for boron and 1.1~2.6 ppm for phosphor.

4. Conclusion

We developed a new concept reduction furnace using the combinatorial method in order to investigate the metallurgical process for silicon reduction. Our system can

Figure 7. Photo of the obtained Silicon. The impurities level of this sample were 1.1~1.4 ppm for boron and 1.1~2.6 ppm for phosphor.

run four processes with starting compositions and process temperatures by only one setup. The combination method is useful in systematic screening in these parameters in the optimization. Our developed silica reduction system will serve as a powerful tool for the investigation and optimization

in the silica reduction process. We obtained reduced Si with a purity with less 2 ppm level by new direct carbothermic reduction process. The addition of SiC raw materials accelerates the production of silicon.

Acknowledgments

5. REFERENCES

[1]   Komoto K, Ito M, Van Der Vleuten P, Faiman D and Kurokawa K eds 2009 *Energy from the Desert, Very Large Scale Photovoltaic Systems: Socio-economic, Financial, Technical and Environmental Aspects*: Earthscan Pubns Ltd; Volume Three)

[2]   Kurokawa K ed 2006 *Energy from the Desert: Practical Proposals for Very Large Scale Photovoltaic Systems*: Routledge)

[3]   Sakaguchi Y, Ishizaki M, Kawahara T, Fukai M, Yoshiyagawa M and Aratani F 1992 Production of High-Purity Silicon by Carbothermic Reduction of Silica Using Ac-Arc Furnace with Heated Shaft *Isij International* **32** 643-9

[4]   Yokokawa H, Yamauchi S and Matsumoto T 1994 Thermodynamic Database Malt2 and Its Applications to High-Temperature Materials Chemistry *Thermochimica Acta* **245** 45-55

[5]   Koinuma H, Itaka K, Matsumoto Y, Yoshida Y, Aikawa S and Takeuchi K 2010 Vacuum and Pressured Combinatorial Processings for Exploration of Environmental Catalysts *Topics in Catalysis* **53** 35-9

[6]   Koinuma H and Takeuchi I 2004 Combinatorial solid-state chemistry of inorganic materials *Nature Materials* **3** 429-38