Si Production by Direct Electrolytic Reduction of Solid SiO_2 in Molten $CaCl_2$

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1. Introduction

Recently, we found that solid SiO_2 can be electrochemically reduced to Si in molten $CaCl_2$ at 1123 K [1-3]. Although solid SiO_2 is a good insulator, we have succeeded in causing the electrochemical reaction by using the "SiO_2 contacting electrode", in which a Mo wire directly contacts with SiO_2. The reaction is written as

$$SiO_2 + 4e^- \text{ (through conductor)} = Si + 2O^{2-} \quad (1)$$

This method might lead to a new process of inexpensive solar grade Si production and a new Si chip technology. We have proposed a novel concept of an electrode reaction, in which electrons are supplied not through the original oxide but through the produced Si columns [1]. We have also studied the dependence of electrolysis potential on the reaction [2] and revealed the Si formation mechanism [3]. In the present study, produced Si was characterized with regard to size and crystal face of Si columns, and purity.

2. Experimental

300 g of $CaCl_2$ was contained in a glassy carbon crucible. All the experiments were performed under a dry Ar atmosphere kept at 1123 K. SiO_2 contacting electrode was prepared by winding a Mo wire (0.2 mm, 99.95 %, Nilaco Corp.) as a current lead, about ten turns around a quartz glass plate (15 x 5 x 1 mm, total metal impurities < 1 ppm; NP grade, Tosoh Quartz Corp.). The counter electrode was a graphite rod. The reference electrode was an Ag^+/Ag electrode. All potentials are given with reference to a Ca^{2+}/Ca electrode potential.

3. Results and discussion

In our previous study, it has been confirmed by XRD, SEM and EDS that SiO_2 is reduced to Si at 0.70-1.25 V (vs. Ca^{2+}/Ca) and the formed Si makes alloy with Ca at 0.35 V [2]. Produced Si is crystalline although the original SiO_2 is amorphous.

To observe the morphology of the crystalline Si, the cross-section of the samples was observed by SEM; the samples were prepared by potentiostatic electrolysis at various potentials between 0.70 V and 1.20 V for 1 hour. It was confirmed that the produced Si was columnar at all potentials. The size of the column was larger at more negative potential and was larger inside of the plate; the diameter was 0.5-5 μm and the length was 3-40 μm. The impurity of the Si was quantified by EDS. It was confirmed that the impurity level except oxygen was less than the detection limit of EDS (0.1 at%). Further observation of the produced Si was conducted by FE-SEM. Figure 1 shows the SEM image of the Si columns. It was confirmed that the column had a hexagonal shape and a stacking structure.

To investigate the crystallographic condition, TEM and ED measurements were conducted to the Si column. As shown in Fig. 2, the Si column was proved to be composed of a single crystal, having many {111} twin planes perpendicular to the column axis. The single crystal hexagonal Si column was found out to be produced by an in-situ thermal annealing of amorphous Si formed by removing oxygen from Si-O-Si bond of SiO_2.

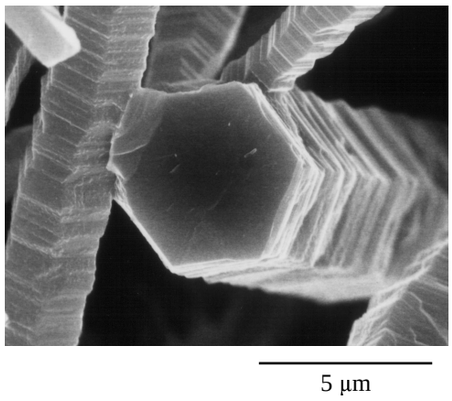

Fig. 1 FE-SEM image of the Si columns obtained by potentiostatic electrolysis at 1.10 V for 1 hour in molten $CaCl_2$ at 1123 K.

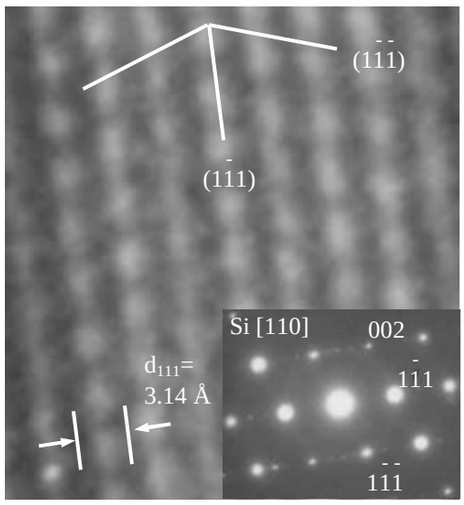

Fig. 2 High resolution TEM image and ED pattern of the cross-section along the axis of the Si column obtained by potentiostatic electrolysis at 1.10 V for 1 hour at 1123 K.

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Reference

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