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Effect of electrolysis potential on reduction of solid silicon dioxide in molten $CaCl_2$

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Abstract

Electrochemical reduction of solid SiO_2 by using a contacting electrode method was investigated in molten $CaCl_2$ at 1123 K. The samples were prepared by potentiostatic electrolysis at 0.35–1.30 V (vs. Ca^{2+}/Ca) for 1 h. From the results of XRD, SEM and EPMA, it was confirmed that SiO_2 was electrochemically reduced to Si at 1.25 V or more negative potential, which agreed with the thermodynamic calculation. The current–time curves during electrolysis and the cross-sectional SEM measurements of the samples clearly showed that reduction rate is higher at more negative potential. In addition, Si–Ca alloy formation was confirmed at 0.35 V.

Keywords: A. Oxides; C. Electron microscopy; C. X-ray diffraction; D. Phase transitions

1. Introduction

Silicon is one of the most important technical materials due to the eminent and ever increasing importance of electronics in technology and everyday life. Moreover, clean electricity produced by Si solar cells is highly expected as new energy that can substitute for fossil energy in the future. Since the demands for high purity Si, especially for solar grade Si, are steadily increasing, the development of inexpensive production method of high purity Si has significant meaning. By the conventional carbothermal reduction of SiO_2 [1], the produced Si inevitably includes impurities such as SiC. Therefore, the produced Si is needed to be purified by distillation after gasification to silane gases (SiH_4, $SiHCl_3$, etc.). Since the purification procedure spends much energy and cost, it has been strongly required to develop a new production process of high purity, especially solar grade, Si without distillation.

Recently, we found that solid SiO_2 can be reduced electrochemically in molten $CaCl_2$ at 1123 K [2]. Although solid SiO_2 is a good insulator (the specific electric resistance is in the range of 10^8–10^9 Ω cm at 1123 K) [3], we have succeeded in taking place the electrochemical reaction by using the 'SiO_2 contacting electrode', in which a Mo wire directly contacts with SiO_2. In the previous study, a high purity quartz plate (15 mm × 5 mm × 1 mm, total metal impurities <1 ppm) was successfully reduced to Si with a considerably high rate. The reduction mechanism was explained as follows [2]. When the electrode potential of the Mo wire is more negative than the reduction potential of SiO_2, the corresponding oxygen fugacity at the electrode becomes low enough to reduce SiO_2. Here, the relation between the electrode potential, E, and the oxygen fugacity, f_{O_2}, is expressed as

$$E = E^0 + \frac{RT}{2F}\ln(f_{O_2}^{1/2}/a_{O^{2-}}) \qquad (1)$$

where E^0 is the standard potential, F is the Faraday constant and $a_{O^{2-}}$ is the activity of O^{2-} ion in molten salt. Then, the oxygen in the SiO_2 near the three-phase interface between Mo wire, SiO_2 and molten salt moves to the interface due to difference in oxygen chemical potential. The electron-transfer occurs at the Mo wire in the interface. Since the resistivity of pure Si is considerably low at the experimental temperature (about 2×10^{-2} Ω cm at 1123 K [4]), the formed Si can serve as a new conducting medium. As the results, new three-phase interfaces are formed

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and the reduction proceeds continuously toward bulk SiO_2. The total reaction is written as

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

This novel method might open up a new route for the high purity Si production. When only oxygen can be removed from high purity SiO_2, Si with similar purity is produced. This method is especially promising for economical production of solar grade Si, since SiO_2 of solar grade purity is inexpensive [5]. In order to assess the possibility of this method, it is important to investigate the reduction rate and the existence of side reactions. The reduction rate should be closely related to f_{O_2} at the three-phase interface, which is controlled by E, as seen from the Eq. (1). For instance, assuming the initial concentration level of O^{2-} ion in the melt to be 0.01 mol% and using the reported $\Delta G_f^0(CaO(1))$ and $\Delta G_f^0(SiO_2(s))$ [6], reduction of SiO_2 is expected to occur at more negative than 1.21 V (vs. Ca^{2+}/Ca). Furthermore, it was confirmed that Si–Ca alloy was formed at negative potential region as a side reaction [2]. In the present study, therefore, potential dependences of the reaction and the reduction rate of solid SiO_2 in molten $CaCl_2$ at 1123 K were investigated in detail.

2. Experimental

Three hundred grams of $CaCl_2$ (reagent grade, Wako Pure Chemical Co., Ltd) was contained in a glassy carbon crucible (10 cm depth, 9 cm inner diameter and 0.2 cm wall thickness, Tokai Carbon Co., Ltd) and was kept under vacuum at 473 K for 72 h and at 773 K for 24 h to remove water. All the experiments were performed under a dry Ar atmosphere in a sealed stainless steel holder kept at 1123 K.

A SiO_2 contacting electrode shown in Fig. 1 was prepared by equally winding a Mo wire (ϕ 0.2 mm, 99.95%, Nilaco Corp.) as a current lead, about ten times around a quartz glass plate (15 mm × 5 mm × 1 mm, total metal impurities <1 ppm; NP grade, Tosoh Quartz Corp.). The counter electrode was a graphite rod (5 mm × 5 mm × 20 mm, Tokai Carbon Co., Ltd). The reference electrode was an Ag^+/Ag electrode, which was prepared by immersion of an Ag wire (ϕ 1.0 mm, 99.99%, Nilaco Corp.) in molten $CaCl_2$ containing 2 mol% AgCl (99.5%, Wako Pure Chemical Co., Ltd) set in a porous mullite tube (ϕ 6.0 mm, $3Al_2O_3\cdot 2SiO_2$, HB grade, Nikkato Corp.). The potential of this electrode was calibrated with a reference to that of a Ca^{2+}/Ca electrode prepared by electrodepositing Ca metal on a Mo wire. All potentials in this report are given with a reference to this Ca^{2+}/Ca electrode potential.

Samples were analyzed by XRD (Multiflex 2kW, Rigaku Corp., Cu Kα line, 1.5418 Å) and observed by SEM (S-2600H, Hitachi) after removing a Mo wire and washing in distilled water. The compositions of the samples were analyzed by EPMA (E-MAX ENERGY EX-200, Horiba Corp.).

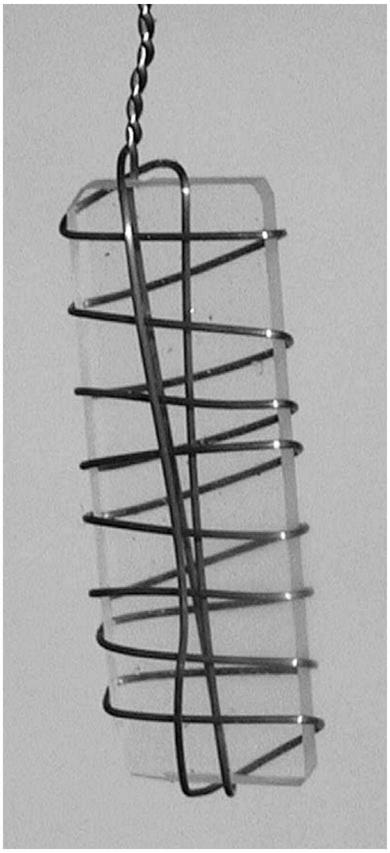

Fig. 1. Photograph of a SiO_2 contacting electrode.

3. Results and discussion

3.1. Current–time curves

In our previous study [2], the cyclic voltammogram for a SiO_2 contacting electrode suggested that the electrochemical reduction of SiO_2 occurs at more negative potential than approximately 1.3 V (vs. Ca^{2+}/Ca), and the reduction to Si was confirmed at 1.1 V or more negative potential by XRD, SEM and EPMA. In the present study, to investigate the reduction between 1.1 and 1.3 V, potentiostatic electrolysis was conducted at (a) 1.30, (b) 1.25, (c) 1.20, and (d) 1.10 V for 1 h. Since the reduction rate was considerably higher at more negative potentials [2], potentiostatic electrolysis was also carried out at (e) 1.00 and (f) 0.70 V. Moreover, electrolysis was also conducted at (g) 0.35 V, at which Si–Ca alloy formation has been confirmed [2], to further investigate the alloy formation reaction.

Fig. 2 shows current–time curves during the electrolysis, where the cathodic current values are directly correspond to the reduction rates. At 1.30 V, only residual current was

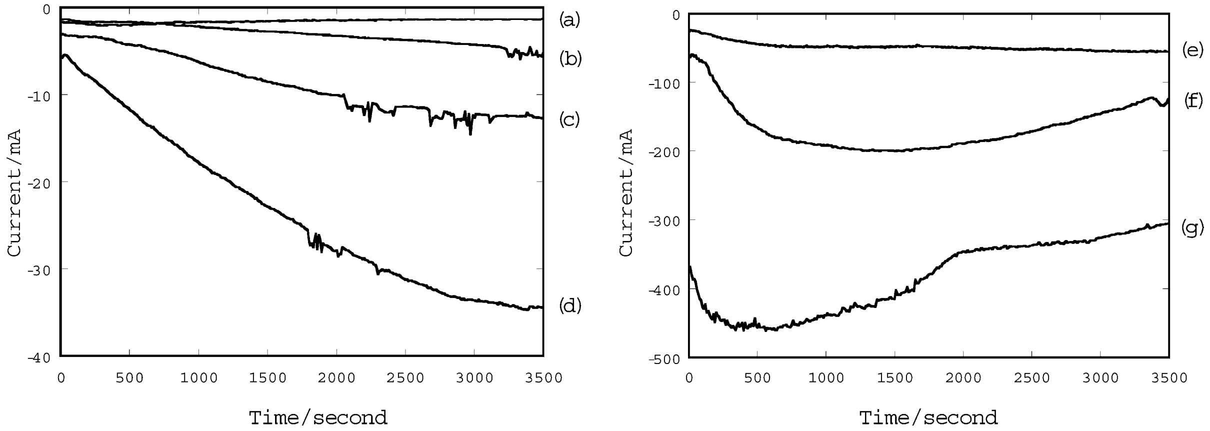

Fig. 2. Current–time curves during the potentiostatic electrolysis of SiO_2 contacting electrodes at (a) 1.30, (b) 1.25, (c) 1.20, (d) 1.10, (e) 1.00, (f) 0.70 and (g) 0.35 V in molten $CaCl_2$ at 1123 K.

observed, suggesting that no reduction occurred. At all other potentials (0.35–1.25 V), cathodic currents were observed and were obviously larger at more negative potentials. For 1.25, 1.20, 1.10 and 1.00 V, cathodic current increased with the electrolysis time, indicating an enlargement of the reaction interface. For 0.70 and 0.35 V, the currents increased in the beginning but decreased afterwards. This behavior is explained as follows: the current increases as long as the reaction interface enlarges, however, after the whole surface is reduced to Si, the reduction rate becomes low because the reaction proceeds only the inner direction.

3.2. Sample analysis

Fig. 3 shows the appearances of the samples after electrolysis. In the case of 1.30 V, no change was observed. For the samples at 1.00–1.25 V, original transparency apparently changed to dark brown or black. Area of the color change clearly increased as the electrolysis potential became negative. For the samples at 0.70 and 0.35 V, the reaction proceeded considerably inside and the samples became highly brittle.

Fig. 4 shows the XRD patterns of the samples. The samples at 0.70–1.20 V were all identified as Si. In the case of 0.35 V, the sample was identified as CaSi and $CaSi_2$. Considering that the Si–Ca alloy formation was not completed for 1 h, it is thought that CaSi exist at the surface and $CaSi_2$ exists inside of the sample. As expected from appearance in Fig. 3, no peak was observed for the samples at 1.25 and 1.30 V. To further analyze of the latter two samples, SEM measurements were performed at the contacting point of the Mo wire. As shown in Fig. 5, the trace of reduction was found for the sample at 1.25 V. EPMA analysis at the reaction zone also showed that Si was the only detected element. It was thus confirmed that SiO_2 is reduced to Si at 1.25 V or more negative potential.

These results almost agree with the thermodynamic consideration in the introduction section that reduction of SiO_2 is expected to occur at more negative than 1.21 V. The slight difference may be explained by the difference in the initial concentration level of O^{2-} ion and/or the smaller activity coefficient of O^{2-} ion than unity.

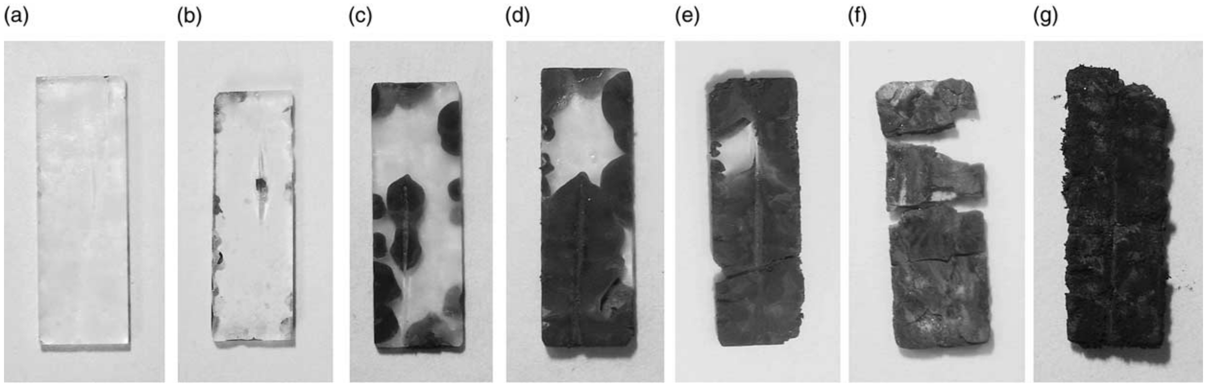

Fig. 3. Photographs of the samples obtained by potentiostatic electrolysis at (a) 1.30, (b) 1.25, (c) 1.20, (d) 1.10, (e) 1.00, (f) 0.70 and (g) 0.35 V for 1 h in molten $CaCl_2$ at 1123 K.

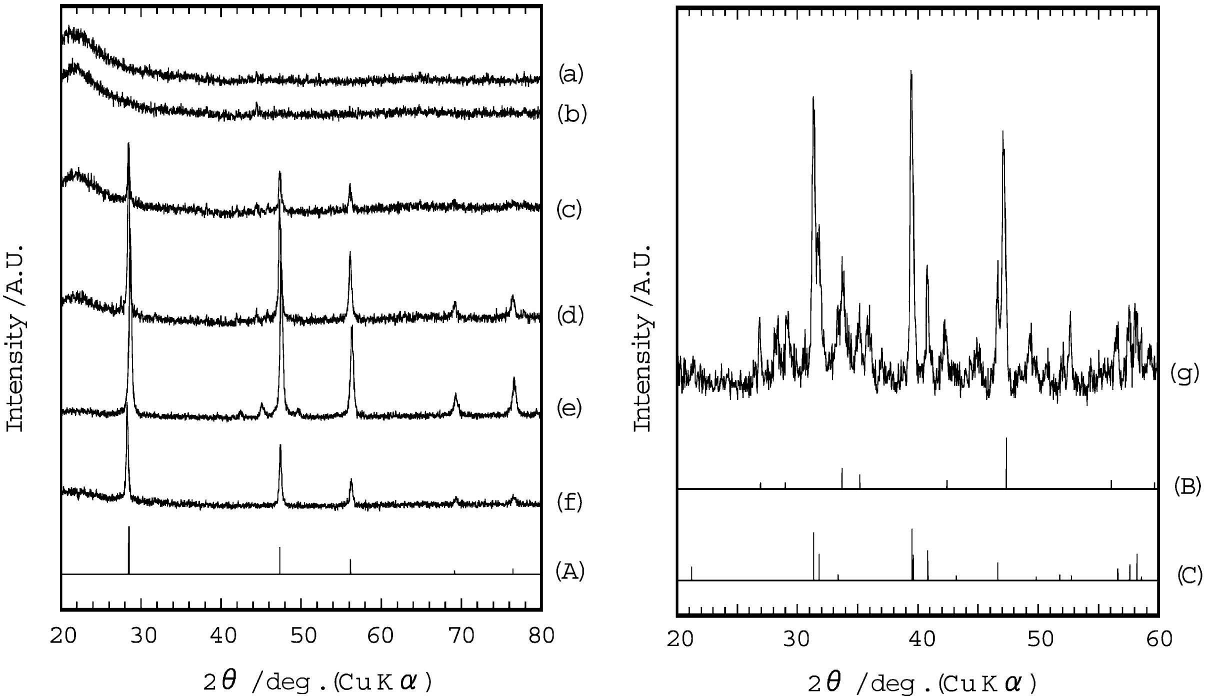

Fig. 4. XRD patterns of the samples obtained by potentiostatic electrolysis at (a) 1.30, (b) 1.25, (c) 1.20, (d) 1.10, (e) 1.00, (f) 0.70 and (g) 0.35 V for 1 h in molten $CaCl_2$ at 1123 K, and XRD patterns of (A) Si (JCPDS no. 27-1402), (B) $CaSi_2$ (JCPDS no. 01-1276) and (C) CaSi (JCPDS no. 26-0324).

3.3. Reduction rate

To clarify the effect of electrolysis potential on reduction rate, cross-sections of the samples were observed by SEM. As shown in Fig. 6, the reduced Si layers were porous for all cases. For the samples at 1.10 and 1.20 V, the observed layer was near the contacting point of Mo wire. The mechanism of porous formation has already been described in our previous paper [2]. The reduced layer apparently became thicker as the electrolysis potential being more negative. These results prove that the reduction rate is higher at more negative potential in both surface and inner directions. This is explained by that the fugacity of oxygen at the three-phase interface is controlled by the electrode potential as seen from Eq. (1); $f_{O_2}=8.3\times10^{-34}$ atm at 1.20 V and $f_{O_2}=8.4\times10^{-43}$ atm at 0.70 V, assuming $a_{O^{2-}}=10^{-4}$ (anion fraction). Since the difference of oxygen chemical potential between the three-phase interface and the bulk SiO_2 is larger at more negative potential, reduction rate becomes higher at more negative potential. The observed reduction rate, e.g., approximately 200 μm for 1 h at 1.00 V, seems to be sufficiently high for such a preliminary construction of the SiO_2 contacting electrode, consisting of a dense quartz plate and a simple Mo wire. If powdery or porous SiO_2 are contacted with a fine wire mesh, the reduction rate will become high enough for a practical application. Moreover, current efficiency was calculated as 90% for the reduction at 1.00 V, estimating the amount of Si and SiO_2 from the cross-sectional SEM measurement. This result also indicates the potential availability of the new reduction method from a viewpoint of energy efficiency. Concerning the impurities in the produced Si, it has been

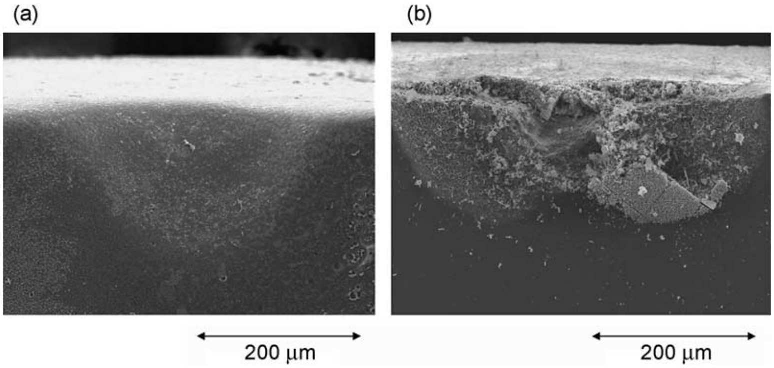

Fig. 5. SEM images of the contacting zone of the samples obtained by potentiostatic electrolysis at (a) 1.30 and (b) 1.25 V for 1 h in molten $CaCl_2$ at 1123 K.

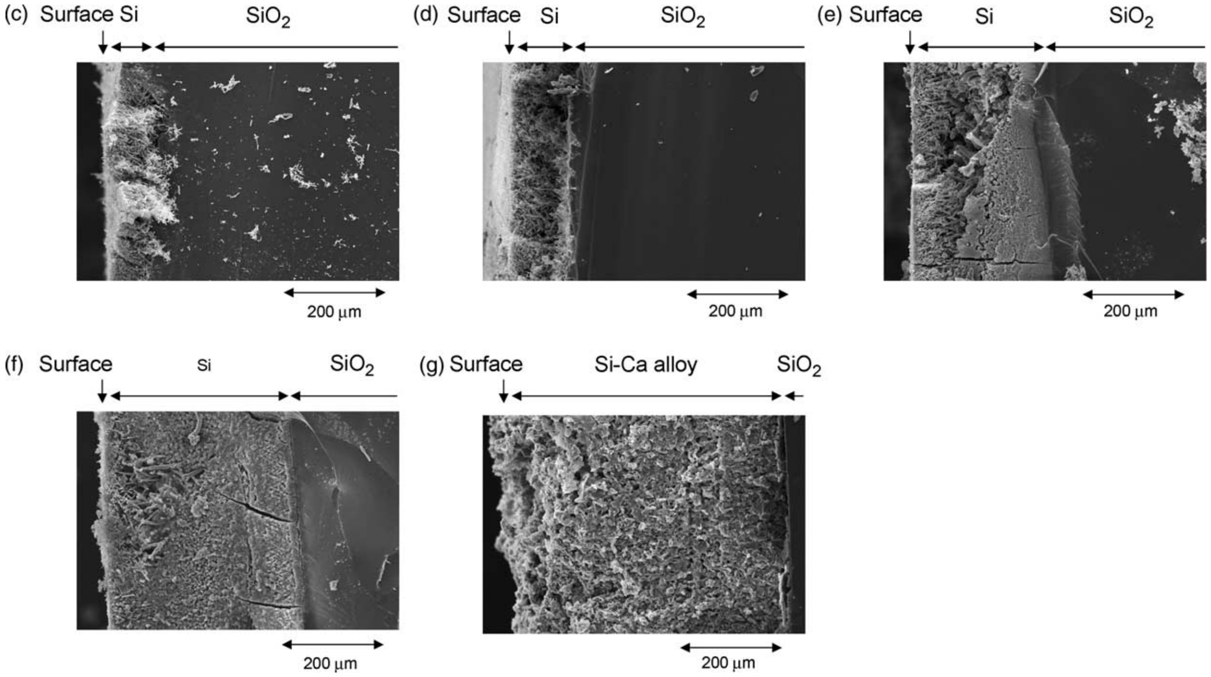

Fig. 6. Cross-sectional SEM images of the samples obtained by potentiostatic electrolysis at (c) 1.20, (d) 1.10, (e) 1.00, (f) 0.70 and (g) 0.35 V for 1 h in molten $CaCl_2$ at 1123 K.

confirmed that the impurities other than oxygen was below detection limit of EPMA. To discuss the impurity level of solar grade Si, further microanalysis by emission spectrography is being conducted.

4. Conclusion

The effect of electrode potential on reduction of solid SiO_2 has been investigated in molten $CaCl_2$ at 1123 K. SiO_2 is reduced to Si between 0.70 (vs. Ca^{2+}/Ca) and 1.25 V, while CaSi and $CaSi_2$ are formed at 0.35 V. The reduction rate of SiO_2 is higher at more negative potential. The reduction rate, approximately 200 μm for 1 h at 1.00 V, in spite of using a dense quartz plate. The impurities other than oxygen for the produced Si are below the detection limit of EPMA.

Acknowledgements

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