Melting Structure of Silicon Dioxide in Molten Salts

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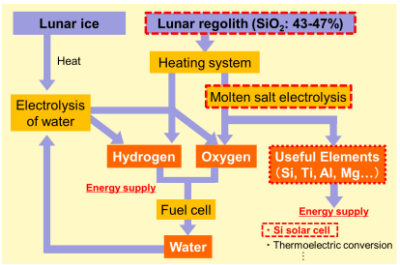
Introduction

In-situ Resource Utilization (ISRU) on the moon



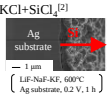
We have focused on fabrication of Si film from SiO_2 (lunar regolith) by molten salt electrolysis

✔ Fluoride melts have advantage for Si deposition

Previous study: $CaCl_2$+bulk solid SiO_2[1], KF-KCl+$SiCl_4$[2]

- Si source : SiO_2
- Lower temp.

■ Fluoride melts[3]
- ● High solubility of SiO_2
- ● Low temp.: 500℃ ～ 600℃



[1] T. Nohira, K. Yasuda, Y. Ito, *Nat. Mater*, 2 (2003).
[2] K. Yasuda, K. Maeda, R. Hagiwara, T. Homma, T. Nohira, *J. Electrochem. Soc.*, 164 (2017).
[3] Y. Sakanaka, T. Goto, *Electrochim. Acta*, 64 (2015).

✔ **Electrodeposition of Si film under microgravity**

- The influence of natural convection is very small.
  → **transportation phenomena of Si ions is affected by melting structure**
- Thickness and current efficiency of electrodeposited Si is dependent on melt composition.

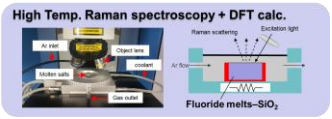
Only few studies on high-temp. melt structure

Objective

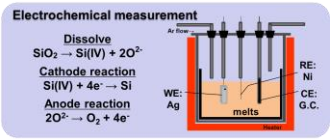
Clarification of melting structure of SiO_2 in fluoride melts → Effects on Si electrodeposition process

Experimental

✔ Si ion structure :Raman analysis



✔ Si deposition :Electrochemistry

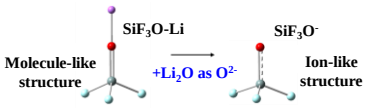


Conclusions

✓ We investigated melting structures of fluoride melts adding SiO_2 by high temp. Raman analysis and DFT calculations.

✓ **Melting structure of Si ion**
- **Molecule-like and ion-like structures of Si ion were identified.**
- **The formation of ion-like structure was promoted by addition of Li_2O**

; Suggesting good effect of O^{2-} on Si deposition



✓ **Si electrodeposition**:
- **Solubility of SiO_2 was increased by O^{2-}.**

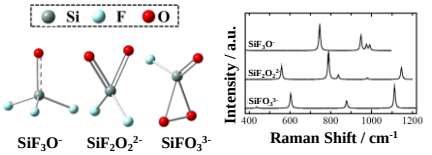
→ Reduction current of Si ion was increased.
→ Thickness of Si films was increased.
- **Effect of O^{2-} on current efficiency :13.3→50.8%**

✓ **Future work** should integrate high-temp. Raman technique with the Si electrodeposition and investigate effects of microgravity.

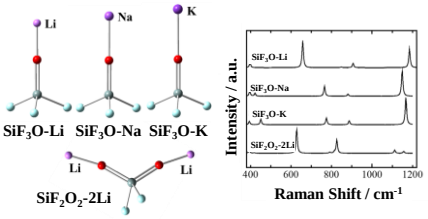
Melting structure of SiO_2 in fluoride melts

1. Optimized Si ion structure by DFT calculation

Ion-like structure



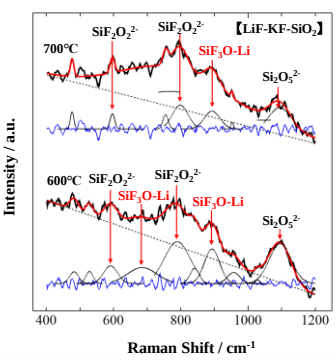
Molecule-like structure



● Condition: DFT with the B3LYP / 6-311+G(d)

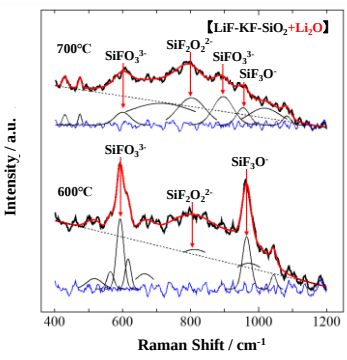
2. Comparison with High-Temp. Raman analysis → Ion-like Si structure was only observed by adding O^{2-} in melts

Fluoride melt + SiO_2



+ 5.0mol% Li_2O

Fluoride melt + SiO_2 + Li_2O



The noticeable difference:

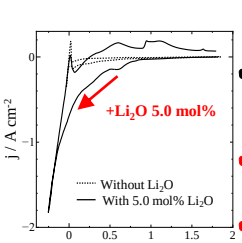
Molecule-like structure (SiF_3O-Li) was observed. $\xrightarrow{+O^{2-}\text{ ion}}$ **Only ion-like structure.**

; Suggesting good effect of O^{2-} ion on Si electrodeposition

Effects of O^{2-} ion on Si electrodeposition

3. Increasing of O^{2-} in melt → Increasing of reduction current of Si ion

Cyclic voltammetry



LiF-NaF-KF-SiO_2, 600℃, 100 mV s^{-1}

✔ Adding Li_2O
- Broad current transition
- Increasing of current

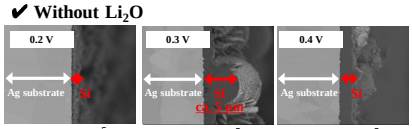
✔ Various coordination structure of Si ion :$SiFO_3^{2-}$, $SiF_2O_2^{2-}$, SiF_3O^-

✔ Increasing of SiO_2 solubility

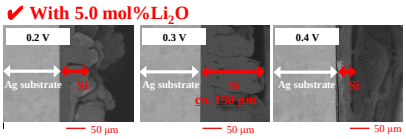
4. Increasing of O^{2-} in melt → Increasing of thickness of electrodeposited Si film

Cross-sectional SEM image

✔ Without Li_2O



✔ With 5.0 mol%Li_2O

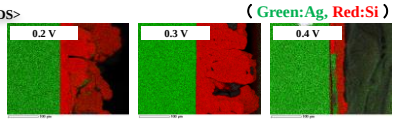


● Potentiostatic electrolysis at 1 h

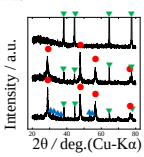
5. Electrodeposited samples →Polycrystalline Si film

EDS & XRD for electrodeposited Si

<EDS> (Green:Ag, Red:Si)



<XRD>



0.3 V: Si
0.2 V: Si, K-Si

Current efficiency: 13.3 → 50.8% (at 0.3 V)