資源エネルギーその場利用を指向した溶融塩技術
---Si 電析技術

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Molten Salt Electrolysis for in-situ Resources Utilization
---Electrodeposition of Si---

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Abstract

Potentiostatic electrodeposition of Si film on Ag substrate is engaged in molten fluoride electrolyte (LiF-KF-NaF+SiO_2) at 600°C. The addition of Li_2O into the melt enhanced 30 times faster deposition rate. High temperature Raman spectroscopy may suggest that the higher concentration of Si precursor complex results in these experimental results.

Introduction

A series of ISRU work was reported since 1988 in 5th Space Environmental Utilization Symp. organized by Science Council of Japan and ISAS[1, 2] as well as JAXA Space Energy Symp[3]. Our temporal goal is to provide O_2 gas generation on inert anode and light metal electrodeposition onto cathode in high temperature molten oxide. It is mandatory to provide or accumulate thermodynamic and electrochemical properties of molten oxide by utilizing JAXA's ELF facility installed on ISS. Preliminary Experiments on Mineral Processing and Molten Salt Electrolysis with Regolith Simulant with various elements had been engaged in Kyoto, MIT(inert anode[4-7]) and Doshisha University. Especially, oxygen gas evolution on a kind of inert anode and metal electrodeposition on cathode were intensively observed. However, it was noticed that more fundamental research toward sustainable ISRU project should be necessary to examine the interfacial phenomena between electrode and molten salt with simplified composition. Now that, we focused on the electrodeposition mechanism of Si in molten fluoride at quite lower temperature than the case of molten oxide. Si dense film is electrodeposited at 10 times higher rate in molten fluoride salt with addition of Li_2O. A high temperature Raman spectroscopy is applied to study such a fast rate electrodeposition behavior.

Experiment

Experimental setup on molten salt electrolysis was described in our previous reports [8-10]. High temperature Raman spectroscopy experiment set up is illustrated in Figure 1. High temperature electrolytic cell is designed to combine a confocal scanning laser microscope. Each Si precursor complex ion is identified with DFT computation and reported data [11,12].

Results & Discussion

Cross sectional images of potentiostatic electrodeposited film over 3600 seconds on Ag substrate are illustrated in Fig 2. The effects of electrode potential and the addition of Li_2O are examined. Si layers with thicknesses of a few micrometers were obtained in the cases without Li_2O, whereas the thicknesses of Si layers increased from tens to hundreds of micrometers with Li_2O, especially at 0.2 and 0.3 V. It is noteworthy to mention the 30 times faster deposition rate. XRD analysis showed that the peaks attributed to polycrystalline Si were found in the samples with electrolytic potentials at 0.2 and 0.3 V. The K-Si alloy was also detected in the sample at 0.2 V. The reason should be understood why Li_2O addition into molten fluoride salt introduces such a drastic deposition rate. High temperature Raman spectroscopy experiment is designed in Doshisha University. Raman spectrum shows primarily the existence of $Si_2O_5^{2-}$ ion in LiF-KF+SiO_2 and LiF-NaF-KF+SiO_2 melts. When 3.0 mol% Li_2O is dissolved into these melts, SiO_4^{4-}, $Si_2O_7^{6-}$, SiO_3^{2-} and SiO_3F^{3-} are identified besides $Si_2O_5^{2-}$ ion is demonstrated in Fig. 3. This indicates that the O^{2-} ions could cleave the Si-O-Si bonds of SiO_2 or silicate ions, such as $Si_2O_5^{2-}$; consequently, the formation of silicon oxyfluoride species such as tetrahedron SiO_3F^{3-} was promoted. Thus, the higher concentration of Si precursors at the Ag substrate may results in such a higher deposition rate. DFT calculation is now engaged in order to further understand the electrodeposition mechanism.

Summary

This study investigated silicon electrodeposition mechanism on cathode in molten fluoride melts as one of the ISRU work. High temperature Raman spectroscopic data revealed that melt structure is a key factor for fabricating high-quality Si layers. Further tailoring toward flat surface and higher purification of electrodeposits should be required from the viewpoint of rational or sustainable design for self-propagating Si PV power generation system around a lunar base. Mineral processing of lunar regolith for separation engineering is another target. The measurements on thermodynamic and electrochemical properties of molten oxide droplet with ISS ELF combining with high temperature Raman spectroscopy technique as well as the molten salt structure analysis in the synchrotron radiation facility must be challenged.

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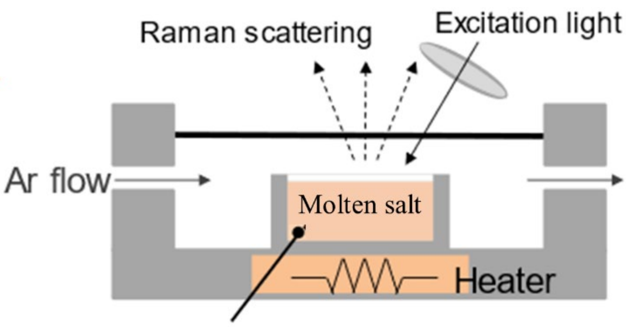

Molten salt	LiF-NaF-KF/ LiF-KF
Si source	SiO_2 (5.0 mol%)
O^{2-} source	Li_2O (3.0 mol%)
temperature	600°C

Fig. 1. Schematic image of the apparatus of the high temperature Raman spectroscopy.

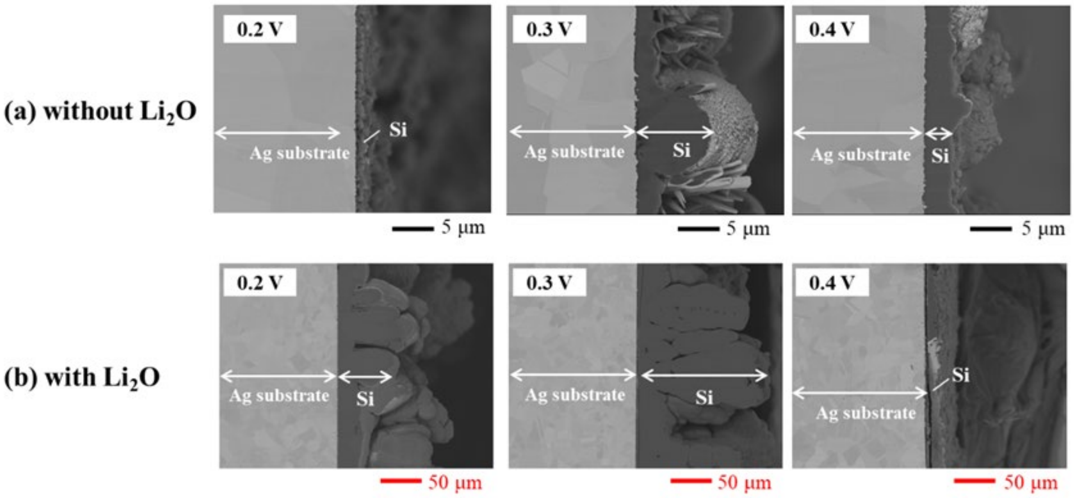

Fig. 2. Cross sectional SEM images of samples after potentiostatic electrolysis at 0.2, 0.3, and 0.4 V for 3600 s in molten LiF-NaF-KF containing 0.5 mol% SiO_2 (a) without and (b) with 5.0 mol% Li_2O at 873 K.

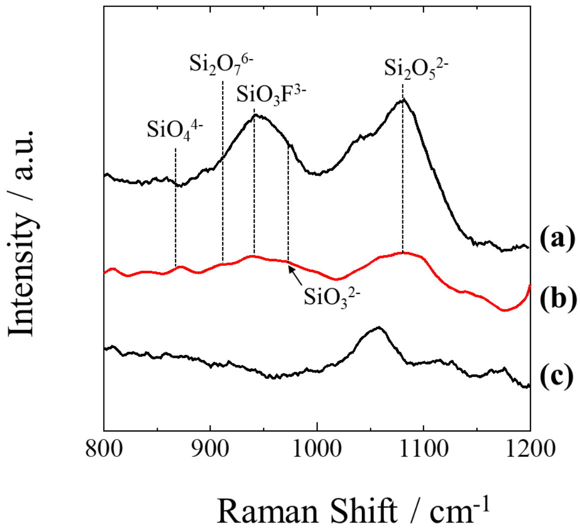

Fig. 3. Raman spectra of molten (a) LiF-KF-SiO_2-Li_2O, (b) LiF-NaF-KF-SiO_2-Li_2O, and (c) LiF-KF-Li_2O at 873 K.