

Broad Band Energy Science Research Section

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1. Introduction

In recent years, renewable energy is attracting a great deal of attention as a means of achieving a sustainable society. Solar cells are one of the promising renewable energies. Thus, the annual installation of PV cells exceeded 117 GW year⁻¹ in 2019 [1]. Nowadays, crystalline Si solar cells account for 96.5% of total solar cell production due to its high efficiency and durability, with demand continuing to increase in 2020. However, the major disadvantages of the conventional Si substrate manufacturing method are the low productivity of the Siemens process and the considerable kerf loss in the Si slicing process. As the demand for crystalline Si solar cells continues to grow, there is a strong need to develop alternative manufacturing methods for Si solar cells.

In this research section, as the one of the new manufacturing methods for Si solar cells, electrodeposition process was developed.

2. Development of Si Plating Processes Using Molten Salt Electrolytes: Direct Plating of n- and p-type Si

Plating n-type and p-type Si directly on the substrates is one of the most promising methods for manufacturing solar cells with fewer steps. We have already proposed new electrodeposition process of Si utilizing KF–KCl as an electrolyte and SiCl₄ as a Si ion source [1]. We also reported electrodeposition of dense Si films with smooth surface in KF–KCl at 923–1073 K [2–5]. In this fiscal year, we investigated the semiconductor characteristics of Si films electrodeposited in KF–KCl–K₂SiF₆ and KF–KCl–K₂SiF₆–KBF₄ at 1023 K. Also, we measured the solar cell characteristics of p–n junction Si films formed by two-step electrodeposition.

Fig. 1 shows photoresponses during the linear sweep voltammetry of Si films electrodeposited in KF–KCl–K₂SiF₆, where the light was chopped at a frequency of 1 Hz. For Si films electrodeposited at lower current densities, anodic currents change with the light chopping, indicating that the obtained Si films are n-type semiconductors. Fig. 2 shows photoresponses of Si films electrodeposited in KF–KCl–K₂SiF₆–KBF₄. When the added amount of KBF₄ was 2 and 5 mol ppm, cathodic currents change with the light chopping. This indicates that the addition of boron, an acceptor element, causes the deposited

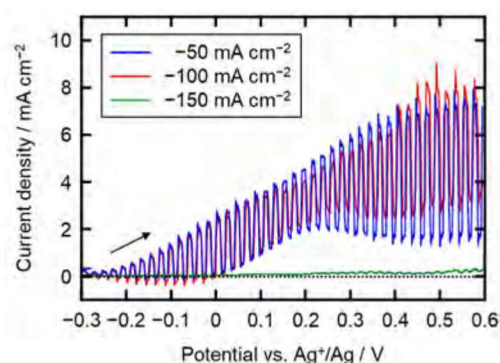


Fig. 1. Linear sweep voltammograms in acetonitrile containing 0.1 M TBAPF₆ and 0.05 M Fc at 298 K. Working electrodes were the Si films obtained by galvanostatic electrolysis of graphite plates at cathodic current densities of 50–150 mA cm⁻² (charge density: -90 C cm⁻²) in molten KF–KCl–K₂SiF₆ (KF:KCl = 60:40 mol%, K₂SiF₆: 3.5 mol%) at 1023 K. Xe light was chopped at a frequency of 1 Hz by a chopper. Scan rate: 10 mV s⁻¹.

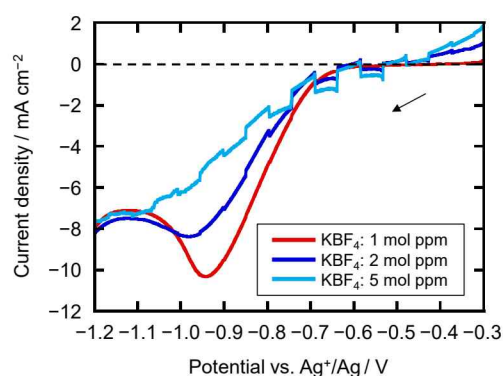


Fig. 2. Linear sweep voltammograms of Si films obtained by galvanostatic electrolysis at -100 mA cm⁻² in molten KF–KCl–K₂SiF₆–KBF₄ (KF:KCl = 60:40 mol%, K₂SiF₆: 3.5 mol%, KBF₄: 1, 2, 5 ppm) at 1023 K. Xe light was chopped at a frequency of 1 Hz by a chopper. Scan rate: 50 mV s⁻¹.

Si films to become p-type.

Next, we conducted two steps electrodeposition; n-type Si was electrodeposited on graphite substrates in $\text{KF-KCl-K}_2\text{SiF}_6$, and then p-type Si was deposited in $\text{KF-KCl-K}_2\text{SiF}_6\text{-KBF}_4$ (5 mol ppm). The characteristics of the solar cells was evaluated by the current-voltage curve as shown in Fig. 3. Power generation was confirmed and $j_{\text{sc}} = 5.8 \times 10^{-3} \text{ mA cm}^{-2}$ and $V_{\text{oc}} = 0.38 \text{ mV}$. These values were much smaller than the desired value, which might be caused by impurities in Si films and failure to accurately define the area of light exposure. Therefore, both the electrodeposition method and the measurement method need to be improved.

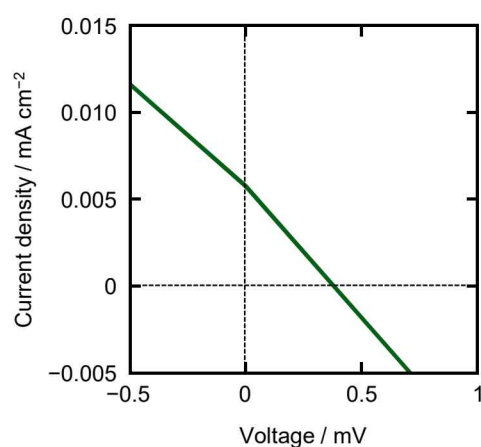


Fig. 3. Current-voltage characteristics of the p-n junction Si film on graphite plate under 1 sun, AM 1.5G illumination.

3. Development of Si Plating Processes Using Molten Salt Electrolytes: Deposition of Large Grain Si Utilizing Zn Liquid Electrode

We have investigated the Si electrodeposition in KF-KCl molten salt and confirmed that p-n junction Si films can be formed directly by electrodeposition. However, one of the issues was that the small crystal grains resulted in a large number of Si boundaries, which reduced the efficiency of solar cells. When Si was electrodeposited on solid substrates, the grain size was 50 nm at 923 K and 20 μm at 1073 K [5]. On the other hands, Maldonado *et al.* obtained crystalline Si by using a liquid metal electrode even at 373 K, where crystalline Si cannot be deposited on solid substrates [6]. They called this method “electrochemical liquid-liquid-solid (ec-LLS) process”. With this background, we conceived the idea of applying the ec-LLS process to Si electrolysis at high temperatures to obtain large Si grains. In this fiscal year, fundamental study was conducted to verify the principle of ec-LLS process in high-temperature molten salt.

Fig. 4(a) shows a photo of the obtained Zn ingot after potentiostatic electrolysis at 0.75 V vs. K^+/K for 48 hours in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K. Si was present on the surface of the Zn ingot facing the BN crucible, not in the molten salt. This indicates that Si precipitation occurred inside the Zn electrode. The precipitation mechanism is thought to be as follows:

- (1) Si(IV) ions are reduced on the surface of the Zn electrode to form a liquid Si-Zn alloy.
- (2) Alloyed Si diffuses into the interior of the Zn electrode.
- (3) Saturated Si precipitates as solid Si.

As shown in Fig. 4(b), grain size of the obtained Si was more than 1 mm, confirming that Si grows at high speed by the ec-LLS process.

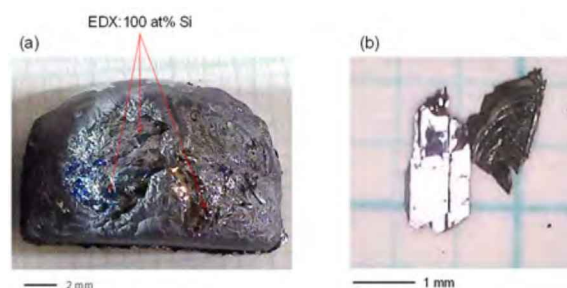


Fig. 4. (a) A photo of the sample obtained by potentiostatic electrolysis at 0.75 V for 48 hours in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K. (b) A photo of a separated large Si after HCl treatment.

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