Electrodeposition of Crystalline Si Films in KF–KCl Melts Using $SiCl_4$ Gas as a Si Source

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Abstract

With the aim of developing a new production process of crystalline Si films, the electrodeposition of Si has been investigated in a water-soluble KF–KCl molten salt containing K_2SiF_6 at 923 K and 1073 K. Cyclic voltammetry and galvanostatic electrolysis confirm that electrodeposition of crystalline Si on a silver substrate occurs at more negative potential than 0.8 V (vs. K^+/K). The crystallite size of the deposited Si significantly increases when the experiment temperature is raised from 923 K to 1023 K. The electrodeposition of Si in the KF–KCl salt after the introduction of $SiCl_4$ was also confirmed.

Introduction

In the current industrial production process of crystalline Si solar cells, ingots of solar-grade Si (SOG-Si) are first prepared and then they are sliced into wafers by diamond wire saws. This process has several problems such as the large kerf loss and the complex process of cell production. If high-quality crystalline Si films are prepared directly on desired substrates at a low cost, a new production process of crystalline Si solar cells will be realized. For this purpose, electrodeposition in high temperature molten salts has been investigated especially in 1970s and 1980s [1–4]. The most studied molten salts for electrodeposition of silicon to date are LiF–KF and LiF–NaF–KF systems containing K_2SiF_6. For instance, Cohen successfully obtained both epitaxial and polycrystalline films of compact, coherent and well-adherent silicon from LiF–KF containing K_2SiF_6 at 1023 K [2]. However, a major problem in the previous works was the removal of the adhered salt on the deposited silicon, because the solubility of LiF to water is very low. Another inherent problem was non-availability of high purity and low cost silicon sources having solar grade purity. The preparation of K_2SiF_6 and Si rod of solar grade purity at a low cost is difficult.

From this background, we proposed a new electrodeposition process of crystalline silicon, as shown in Fig. 1 [5–8]. Here, molten KF–KCl is used as an electrolyte and $SiCl_4$ as a silicon source. We especially selected the molten KF–KCl because both KF and KCl are highly soluble to water. Thus, the adhered salt is easily removed by a simple water washing. Moreover, high purity $SiCl_4$, which is commercially available at a low cost, is able to be used as a silicon source. When gaseous $SiCl_4$ is introduced into the molten KF–KCl, the following reaction occurs:

$$SiCl_4 + 6F^- \rightarrow SiF_6^{2-} + 4Cl^- \quad (1)$$

Thus, when the concentration of F^- ion is adjusted beforehand, the resultant molten salt after the introduction of $SiCl_4$ gas is the same as the molten KF–KCl containing K_2SiF_6. Another advantage of the use of KF–KCl molten salt is the removal of chlorine from the melts by Cl_2 gas evolution on the carbon anode, which realizes the constant composition of molten salt as well as the reuse of recovered Cl_2 for the production of $SiCl_4$.

In the present study, we first explored the electrochemical behavior of Si ions by cyclic voltammetry at 923 K and 1073 K. Then, we examined the effect of the experiment temperature, elevating from 923 K to 1023 K, on the crystallinity of Si films. Finally, electrodeposition of Si from a molten KF–KCl salt after the introduction of $SiCl_4$ was studied.

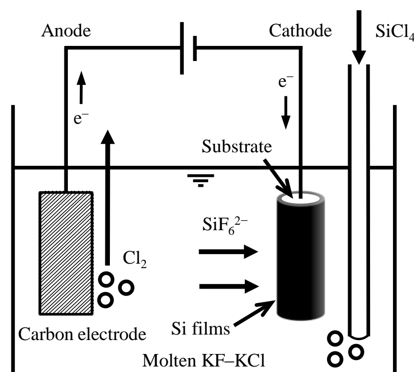

Figure 1. A schematic illustration for the principle of electroplating process of Si in KF–KCl molten salt [5–8].

Experimental

The electrodeposition was conducted in a dry Ar atmosphere at 923 K and 1023 K. Reagent-grade KF and KCl were mixed to a eutectic composition (KF:KCl = 45:55 mol%, melting point = 878 K) and loaded in a graphite crucible. The crucible was placed at the bottom of a stainless steel vessel in an air-tight Kanthal container and dried under vacuum at 673 K for 24 h. A wire or flag of Ag was used as the working electrode and a glassy carbon rod as the counter electrode. A Pt wire was employed as the quasi-reference electrode. The potential was calibrated and given with reference to K^+/K electrode potential. In some experiments, gaseous $SiCl_4$ was

supplied to the melt at 1023 K by a vapor transport method from liquid $SiCl_4$ maintained at 293 K [8]. The electrodeposited samples were washed in hot distilled water at 333 K for 24 h to remove the adhered salt on the deposit. The samples were analyzed by scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and X-ray diffraction (XRD).

Results and Discussion

Cyclic voltammetry

Fig. 2 shows the cyclic voltammograms for a Ag flag electrode in molten KF–KCl–K_2SiF_6 (0.10 mol%) at 923 K and 1073 K. In the scan to the negative direction, cathodic current attributed to an electrodeposition of Si from Si(IV) ions is observed from 0.8 V (vs. K^+/K) at the both temperatures. After switching the scan direction to positive, anodic current for the dissolution of the deposited Si appears. The value of the cathodic current peak is around 70 and 100 mA cm^{-2} at 923 and 1073 K, respectively. The increased current indicates the faster diffusion of Si(IV) ions at 1073 K.

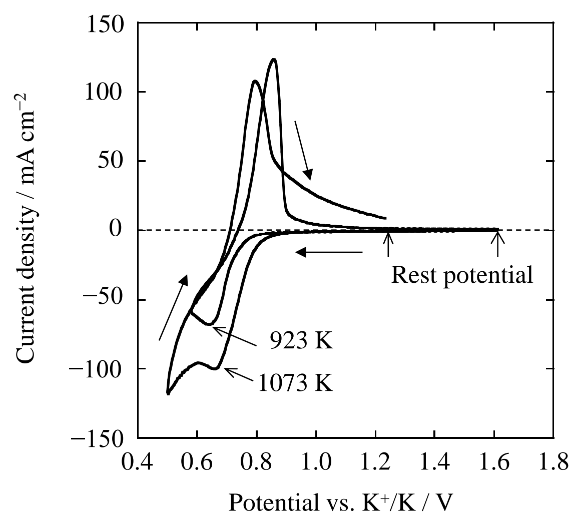

Figure 2 Cyclic voltammograms for a Ag flag electrode in molten KF–KCl–K_2SiF_6 (0.10 mol%) at 923 K and 1073 K. Scan rate: 0.20 V s^{-1}.

The effect of electrodeposition temperature

Si layer was galvanostatically electrodeposited on a Ag wire electrode at 155 mA cm^{-2} for 30 min in molten KF–KCl–K_2SiF_6 (2.0 mol%) at 923 K and 1073 K. The formation of adherent, compact, and smooth Si layers are confirmed by XRD and cross-sectional SEM. The crystallinity of Si films was analyzed by EBSD. Figure 3 shows a result of EBSD for the Si layer prepared at (a) 923 K and (b) 1073 K. At 923 K, the average crystallite size is below 1 μm. On the other hand, the crystallite size of the columnar Si significantly increases up to ca. 10 μm by raising the deposition temperature to 1023 K.

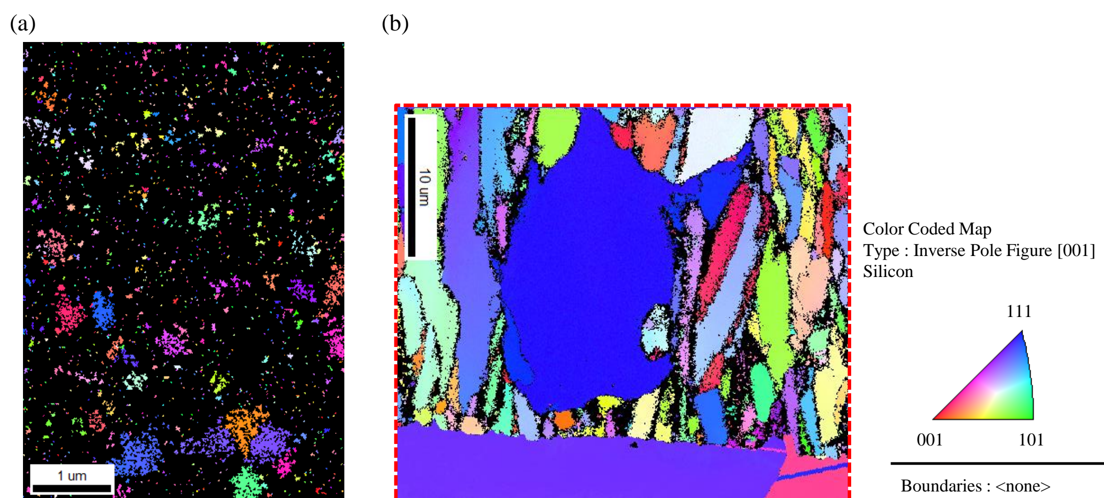

Figure 3 Crystal grain maps from electron back scatter diffraction (EBSD) analysis of the Si deposits. The deposits were obtained by galvanostatic electrolysis of a Ag wire electrode at 155 mA cm^{-2} for 30 min in molten KF–KCl–K_2SiF_6 (2.0 mol%) at (a) 923 K and (b) 1023 K.

Electrodeposition of Si after the injection of $SiCl_4$

Since a dissolution of $SiCl_4$ of 2.30 mol% was confirmed by cyclic voltammetry, the electrodeposition of Si was carried out by galvanostatic electrolysis at –155 mA cm^{-2} for 20 min at 973 K. Figure 4 shows cross-sectional SEM images of the obtained specimen [8]. A compact Si film is observed on a Ag substrate by XRD. This result confirms the feasibility of using $SiCl_4$ gas as a Si source for Si deposition.

The reason for the results that a smooth morphology is only observed near to the substrate and the deposits are granular in the outer layer (Fig. 4(a)) is suggested to be the molar fractions of the F^-

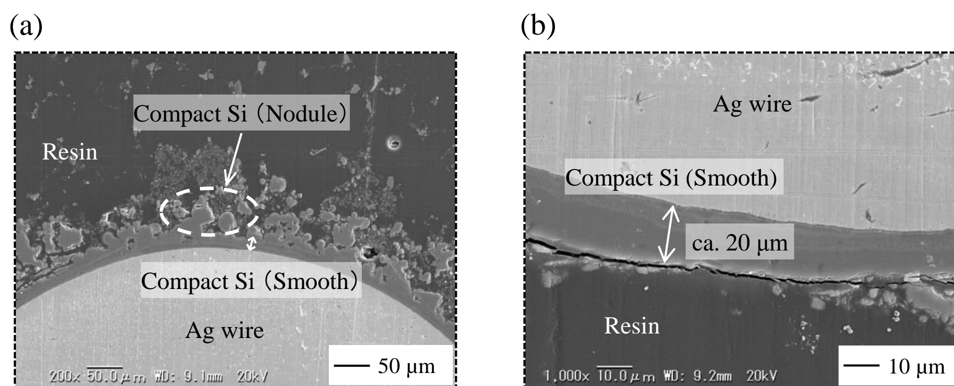

Figure 4 Cross-sectional SEM images of the sample obtained by the galvanostatic electrolysis of a Ag wire electrode at −155 mA cm^{-2} for 20 min in molten KF–KCl at 923 K after the introduction of $SiCl_4$ [8].

and Cl^- ions. The high ratio of Cl^- ions is likely to cause the observed granular morphology. The influence of the anionic fraction on the morphology of Si deposit will be investigated in the future.

Conclusions

We have investigated the electrochemical behavior of Si(IV) ions in molten KF–KCl–K_2SiF_6 at 923 K and 1073 K. Cathodic current for Si electrodeposition from Si(IV) ions are observed at the both temperatures. We have obtained adherent, compact and smooth Si deposits on Ag wire substrates at 923 K and 1023 K. The crystallite size of electrodeposited silicon largely increases by the elevation of electrodeposition temperature from 923 K to 1023 K. A feasibility of using $SiCl_4$ gas as a Si source for Si deposition was experimentally confirmed.

Acknowledgments

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