

Electrodeposition of Silicon with a Liquid Gallium Cathode in Molten Salts

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Further development of solar power depends largely on the availability of inexpensive solar grade silicon. Electrodeposition is a candidate method to produce high purity silicon at a reasonable cost. A new approach using a liquid gallium cathode was used to study deposition of silicon from molten salt electrolytes containing K_2SiF_6 . Electrochemical studies and electrolysis to deposit silicon from molten eutectic KCl–KF with additions of K_2SiF_6 were carried out at 650 °C. Silver wire and glassy carbon rod were used as working electrodes, while glassy carbon rod or silver wire were counter electrodes. A silicon plate reference electrode was used. Liquid gallium in a small alumina tube with tungsten lead was the cathode during electrolysis while glassy carbon or silicon was the anode. Silicon was found to deposit inside a liquid gallium cathode during electrolysis. The current efficiency was found to be quite high, and consistently above 80 %.

Introduction

Silicon is by far the most important active material in photovoltaic cells. A total of 99 GW of grid-connected solar energy was installed in 2017, making the total solar power capacity to be more than 400 GW (1). It is expected that this growth will increase significantly if the cost of solar cells is reduced. Therefore there is substantial research to develop new methods for producing solar grade silicon at a lower cost. Industrial processes based on electrolysis are well established for producing large quantities of metals such as aluminium, copper and nickel. Electrodeposition of silicon has been reported in the literature since the 1970s.

Reported experimental studies of electrodeposition of silicon have been carried out mainly in molten salts but also in ionic liquids. In most of the research the aim has been to develop a new process for producing silicon of solar grade quality. Some review papers have been published (2-4). Most of the research on electrodeposition of Si has been carried out in molten salts at relatively high temperatures. Good quality silicon deposits have been obtained in molten fluoride molten electrolytes such as LiF–KF and LiF–NaF–KF (5,6). However, the low water solubility of fluorides represents a challenge for removing adhered salt. Nohira and coworkers (7,8) have used mixed chloride/fluoride molten salts, and molten eutectic KCl–KF has been studied extensively.

Attempts to deposit silicon from ionic liquids with melting points below room temperature is very challenging because silicon is a semiconductor with low electrical conductivity at low temperatures. This may limit the thickness of the deposit. Some promising results have been reported (9, 10).

Some interesting results have been published by Maldonado and co-workers (11-13). They have focused on depositing semiconductor materials of nano size scale by using a novel approach employing a liquid cathode such as gallium or mercury. Successful deposition of silicon nanowires from propylene carbonate electrolyte with SiCl_4 at temperatures as low as 60 °C by using liquid gallium droplets as cathode was reported (13). In this case silicon precipitates inside the liquid Ga cathode from a supersaturated solution and there is very little alloy formation. The active cathode is liquid Ga, so the poor electric conductivity of Si at low temperature will not cause any limitation of the process.

The current approach using molten salt electrolytes is based on the work by Maldonado and coworkers. Gallium does not form alloys with silicon, so solid silicon may be formed inside the liquid Ga cathode also in molten salts. However, an enhanced purification of deposited silicon may take place by alloy formation of certain impurity elements with liquid Ga.

The most important impurity elements for solar grade silicon are boron and phosphorus. Most of the reported results from electrolysis experiments have not been successful in reducing these elements significantly. However, it seems that the use of a liquid anode of Cu-Si may give enhanced purification in electrorefining experiments (14,15) where the initial silicon source is metallurgical grade Si.

Experimental

The used experimental setup and cell design was described elsewhere (16). The electrochemical experiments were conducted in a dry Ar glove box. Anhydrous salts of KF and KCl of reagent-grade were mixed to the eutectic composition (KF:KCl = 45:55 mol%, melting point = 878 K) and loaded into a graphite crucible. The crucible was placed at the bottom of a stainless-steel vessel in an airtight Kanthal container and dried under vacuum at 673 K for 24 h. Electrochemical studies, mainly cyclic voltammetry were performed by using silver wire, glassy carbon rod and liquid gallium in a small alumina tube as working electrode. A silicon plate placed in the electrolyte was used as reference electrode and a glassy carbon rod or silver wire served as counter electrode. The liquid gallium electrode was placed at the bottom of an open small alumina tube with tungsten wire for electrical contact. Electrolysis experiments were carried out by constant current or constant potential by using liquid gallium in alumina tube as cathode and a glassy carbon rod or dissolving silicon anode. A silicon plate reference electrode was used. The potential of the reference electrode was calibrated with reference to the dynamic K^+/K potential. Deposited silicon in the form of powder was found inside or on top of the liquid gallium pool. The sample was exposed to hot water to remove adhering salt and dried under vacuum for 12 h. Si was separated physically from the main part of gallium. The remaining parts of Ga were dissolved in 30 % HNO_3 for several hours. Then the sample was dipped into 10 % HF (aq) for 1 h to remove oxide. SEM with EDS was used to characterise the morphology of deposited Si particles and to detect qualitatively the presence of major impurity elements. The samples were analyzed using scanning electron microscopy (SEM, Keyence Corp., VE-8800) and X-ray diffraction (XRD; Rigaku Corp., Ultima IV, Cu-K α line). Dissolution of Si particles took place in HNO_3 (aq) - HF (aq) mixture, and the solution was analyzed for minority elements by ICP-AES.

The main electrolyte was eutectic KCl–KF at 650 °C with additions of 0.5 and 2 mol% K_2SiF_6 . Also electrolytes of NaCl–NaF and LiCl–LiF were tried. In the sodium

system evaporation of silicon compound was found to cause difficulties. In the lithium system significant alloy formation between Li and Ga was impossible to avoid.

Results and discussion

Figure 1 shows cyclic voltammograms in the pure KCl–KF melt obtained on electrodes of silver and liquid gallium. The cathodic current observed on Ga is due to alloy formation with potassium. The small cathodic current on Ag is likely to be due to formation of dissolved potassium in the electrolyte. Figure 2 shows corresponding voltammograms after addition of 0.5 mol% K_2SiF_6 . The cathodic current on Ga prior to the deposition of pure Si may be due to alloy formation with Si. Again the small cathodic background current on Ag prior to the deposition of pure Si may be due to formation of dissolved K. Figure 3 shows cyclic voltammograms obtained on liquid Ga after addition of 2.0 mol% K_2SiF_6 . The results suggest that pure Si was deposited in the potential range from $\sim 0.78 - 0.93$ V vs K^+/K .

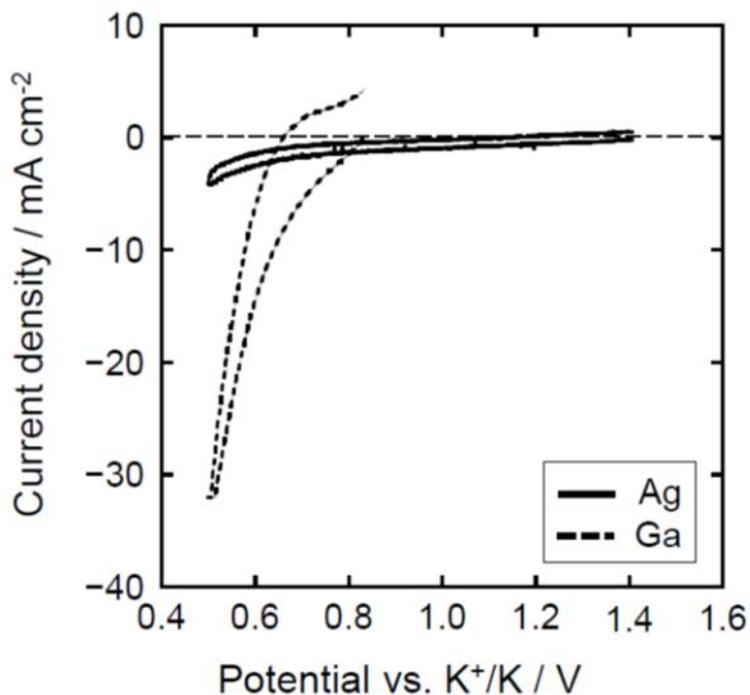


Figure 1. Cyclic voltammetry in molten KCl–KF at 650 °C on Ag and liquid Ga electrodes at 100 mV s⁻¹.

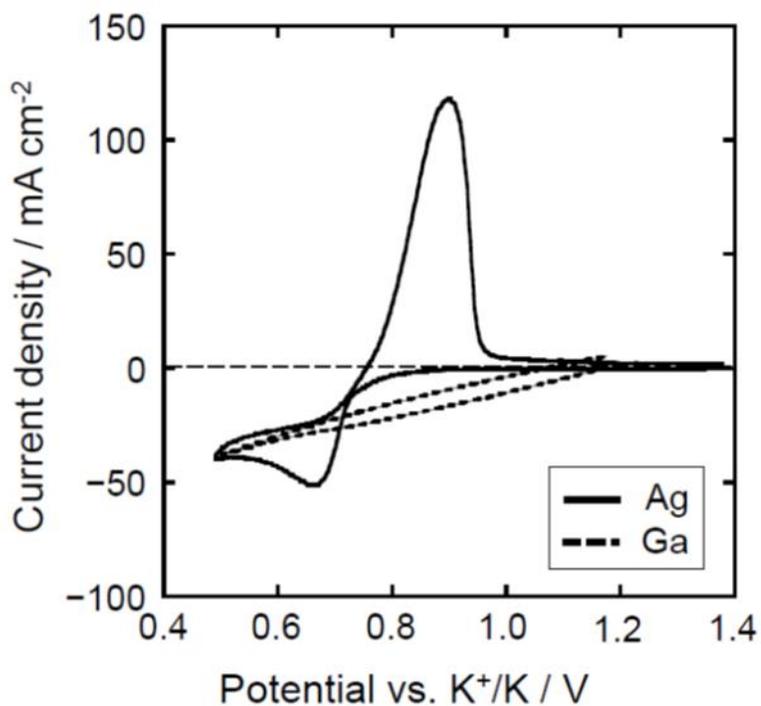


Figure 2. Cyclic voltammetry in molten KCl–KF with 0.5 mol% K₂SiF₆ at 650 °C on Ag and liquid Ga electrodes at 100 mV s⁻¹.

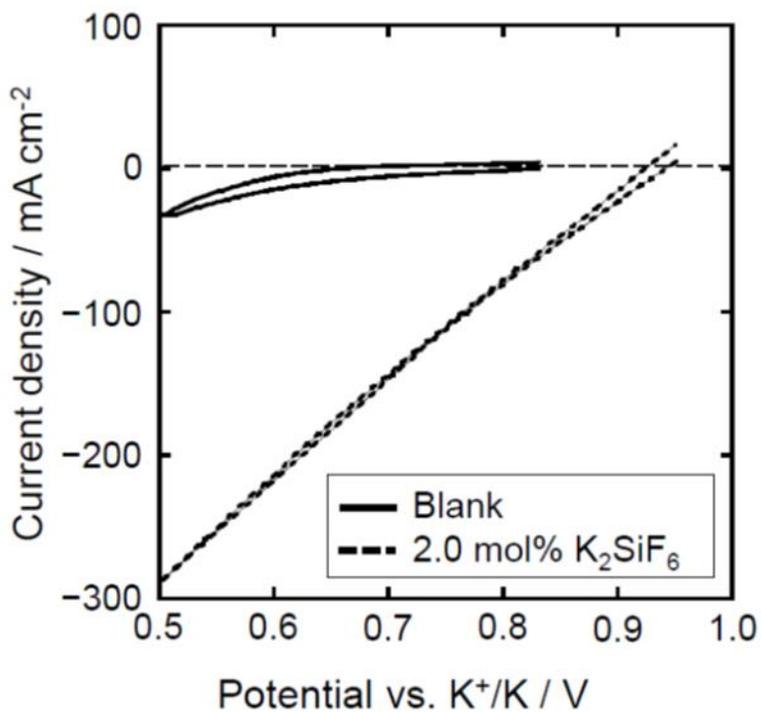


Figure 3. Cyclic voltammetry in molten KCl–KF with 0.5 mol% K₂SiF₆ at 650 °C on liquid Ga electrode at 100 mV s⁻¹.

The results confirmed that deposition of Si on silver and glassy carbon electrodes was diffusion controlled. Deposition of Si on liquid Ga seemed to be charge transfer controlled. The reversible potential for deposition of potassium was estimated by linear sweep voltammetry at low scan rate using a silver electrode. The diffusion coefficient of dissolved Si (IV) complexes was determined to be $5.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in molten KCl–KF at 650 °C with 0.1 mol% K_2SiF_6 , obtained in a previous study by chronoamperometry using a silver cathode (8).

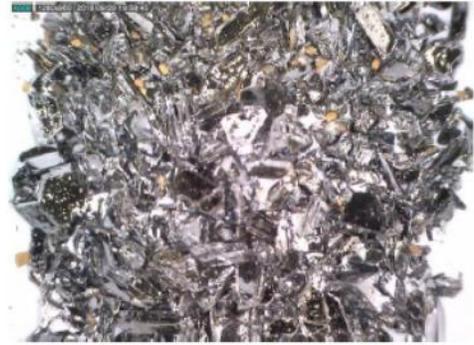
Silicon was found to deposit using a liquid gallium cathode, both during galvanostatic and potentiostatic electrolysis. Some silicon particles were found on top of gallium after cooling down. Preliminary electrolysis experiments to deposit Si showed that applying constant current gave rise to occasional unstable potentials between gallium and reference electrodes during electrolysis, which could be due to co-deposition of potassium followed by oxidation of produced potassium. Controlling the potential was found to improve the conditions for depositing silicon. After cooling down the deposited silicon was collected from inside and top of the liquid gallium pool. In more recent experiments the alumina container was made a little larger and the amount of gallium was significantly increased. This helped in establishing more stable conditions, and constant current electrolysis experiments was run successfully. The current efficiency for silicon deposition using liquid gallium cathode was found to be quite high, and consistently above 80 %.

Some of the Si particles found on top of liquid Ga were of brown colour while particles found inside Ga were larger and crystalline. Figure 4 shows photos of obtained Si particles after washing. It can be suggested that the smaller brown particles were covered by SiO_2 possibly formed during water washing. Before element analysis the brown particles were separated by sieving to remove particles smaller than 216 μm . Results from analysis of deposited Si by ICP-AES are shown in Table 1. The content of boron is quite low, but the content of phosphorus is surprisingly high. It was expected that phosphorus could form gallium phosphide and lead to an extra refining. A modified experimental design and further treatment of the deposit may be beneficial in removing phosphorus.

The approach to use an inert liquid cathode to deposit metals in molten salts may be extended to deposition of other metals or alloys. Gallium has several advantages as a cathode but it forms alloys with many elements.



— 10 mm



— 1 mm

Figure 4. Photos of obtained Si produced by electrolysis.

TABLE I. Element analysis (ICP-AES) of deposited Si.

Impurity element	ppmw
B	7.98
P	41.55
Al	5.19
Cr	0.16
Fe	3.63
Mn	0.83
Ni	5.50
Mo	9.75
Mg	0.87
Zn	46.76
Cd	1.35
Co	1.16
K	0.74
Na	0.50
Sb	8.64

Conclusions

Silicon was found to deposit inside a liquid gallium cathode during electrolysis in molten KCl–KF at 650 °C. Large crystalline particles of relatively high purity were obtained. The current efficiency for Si deposition was found to be more than 90 % in successful experiments. The contents of boron and especially phosphorus must be reduced significantly for solar cell applications. The use of a liquid gallium cathode is promising for the prospect of developing a new process for producing high purity silicon by electrolysis in molten salts.

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