EFFECT OF OXYGEN ON THE STRUCTURE OF SILICON ELECTRODEPOSITED FROM HALIDE MELTS

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ABSTRACT

Silicon electrodeposition from the KF-KCl-K$_2$SiF$_6$ and KF-KCl-K$_2$SiF$_6$-SiO$_2$ melts on the graphite substrate was studied. The composition and structure of the deposits obtained were examined using scanning electron microscopy (SEM), X-ray spectrum analysis, X-ray diffraction analysis. Silicon coatings and nanofibers were produced by halide and oxide-halide melts electrolysis. The analysis of the electron microscopy and X-ray phase analysis data allowed determining the oxygen effect on the cathode silicon structure.

1. INTRODUCTION

Silicon is a primary material for photovoltaic cell production. It is widely used in electron and metallurgical industries. Silicon nanomaterials provide a significant efficiency upgrading of lithium-ionic chemical current sources (1) and photoelectric elements (2). As silicon is used in modern devices, the purity requirements became more stringent. The main technique of high purity silicon and silicon-based nanomaterial production is gas phase deposition method (3). This method has high effective costs and requires complex instrumentation. That is why the development of new silicon production techniques is a topic issue. The electrolysis of molten salts is a perspective method of silicon and silicon-based nanomaterial production (4, 5). This work describes silicon electrodeposition from halide and oxide-halide molten salts and represents the results of the KF-KCl-K$_2$SiF$_6$ and KF-KCl-K$_2$SiF$_6$-SiO$_2$ melts galvanostatic electrolysis.

2. EXPERIMENTAL

Fluoride-chloride electrolytes were prepared from KCl (“chemically pure” grade) and KF-HF (“chemically pure” grade) individual salts and K$_2$SiF$_6$ (“analytically pure” grade). Potassium chloride was supplied by Uralkalii, and KF-HF and K$_2$SiF$_6$ were supplied by Vekton.

Before the experiment, potassium chloride was dried under vacuum at 773 K in a glassy carbon crucible for 4 h to 6 h. Then the salt was melted at 1073 K and kept at this temperature for 1 h, and then cooled. To remove the oxide impurities from K$_2$SiF$_6$, the salt was mixed with 2 wt. % of NH$_4$F and kept in the glassy carbon crucible for 6 h at 673 K. The following reaction takes place:

$$\text{NH}_4\text{F} + \text{SiO}_2 = 4\text{NH}_3\text{F} \uparrow + \text{SiF}_4 \uparrow + 2\text{H}_2\text{O} \uparrow$$  \[1\]

The mixture of KCl and KF-HF was heated in the glassy carbon crucible up to 973 K and dwelled for 5 h. All HF was removed due to the thermal decomposition of KF-HF.
at 512 K. Then the needed amount of K₂SiF₆ was added. The melt was constantly stirred for 30 min and then was emptied into the graphite crucible. The absence of HF was checked by measuring the pH of the water solution of the mixture prepared. The content of admixtures in the salts prepared was analyzed by mass spectroscopy method. The amount of principal component in the melt was more than 99.9 wt. %. The prepared electrolytes were stored in a dry box. Fine powder silica (Russian Magnesium Company) was used to prepare the KF-KCl-K₂SiF₆-SiO₂ electrolytes. It was preliminary dried in the quartz crucible for 3h in air at 773 K. The content was checked by the mass spectroscopy.

2.1. Cell for silicon electrodeposition

Silicon electrodeposition was carried out in the KF-KCl-K₂SiF₆ melt both with the addition of 2 mol % of SiO₂ and without it. Figure 1 demonstrates the scheme of the cell for the KF-KCl-K₂SiF₆ and KF-KCl-K₂SiF₆-SiO₂ melts electrolysis. The electrolysis was carried out in a graphite container (an anode) 2 with the nickel current leads 1, 9. The current lead 9 was protected by the quartz case 10. The upper part of the cell was protected by the quartz barrier ring 6 with the intermediate layer made of the graphite crumb 7. The electrochemical cell was closed by a lid 14 made of dense graphite. The cathode 16 was fixed at the nickel current lead 11. The melt 3 in the graphite container 2 with current leads 1, 9 were placed into a resistance furnace and heated up to the required temperature and dwelled in the molten mixture. The purification electrolysis with the additional electrode, which was then changed on the working electrode, was carried out in the molten mixture. Before the electrolysis started the cathode 16 at the nickel current lead 11, protected by the quartz case 13, was immersed into the melt. The working area was then closed by the lid 14, in which a quartz stopper 12 and a thermocouple case 11 were mounted, and then the electrolysis was started. Silica or potassium hexafluorosilicate, which were loaded into the graphite container together with the melt as a powder through the quartz feeder 15, were used as a feed addition. The temperature in the cell was controlled using platinum-platinumrhodium thermocouple 5. A quartz case 4 was used in the experiments with the SiO₂ additions. In the experiments with the KF-KCl-K₂SiF₆ melt the thermocouple was immersed directly into the melt on a short period of time to measure the temperature. The furnace temperature was maintained using the VARTA TP703 thermal regulator. The melt composition was controlled by the chemical analysis of probes collected before and after the experiment.
Fig. 1 Scheme of cell for electrolysis: 1 – nickel crucible; 2 – graphite container (anode); 3 – melt; 4 – thermocouple protection case; 5 – thermocouple; 6 – quartz barrier ring; 7 – graphite powder; 8 – quartz tube; 9 – nickel current lead (for anode); 10 – quartz protection case; 11 – cathodic current lead; 12 – quartz stopper; 13 – quartz protection case; 14 – graphite cover; 15 – quartz feeder; 16 – cathode.

2.2. Techniques

As the electrolysis terminated the substrate with silicon deposit was taken out of the furnace. The powder-like cathode deposit was grinded in the agate mortar and washed by the HCl water solution at 353 K. The obtained pulp was poured over into the vessel made of heat-resistant glass and was stirred for 2.5 hours using the magnet agitator at 333 K. Later the pulp was divided in the centrifugal separator and the washing cycle repeated. The deposit was washed to remove the electrolyte completely. The powder-like silicon, deposited in the centrifugal separator was dried in the polyethylene tube in air with the addition of alcohol. Dried powder-like silicon was weighted and analyzed. The electrolyte at the surface of the coatings was removed by the HCl solution and then the deposit was examined.

The admixtures in deposits were determined by the atomic-emission method with inductively bound plasma using the indicator of the iCAP6300 Duo series of the Thermo Scientific Company. The specific silicon powder surface value was determined using the indicator Sorbi № 4.1. The micro X-ray spectral analysis and micro photographing of silicon samples were made using the scanning electron
microscope JMS-5900LV. The X-ray phase analysis of the silicon powders was performed using the Rigaku DMAX-2200/pc.

3. Electrolysis of KF-KCl-K₂SiF₆ and KF-KCl-K₂SiF₆-SiO₂

The electrolysis was performed in the KF(40.5 mol %)-KCl(49.5 mol %)-K₂SiF₆(10 mol %) melt, on the graphite substrate at iₖ = 0.02 A∙cm⁻² and 973 K. Figure 2 represents the data on the X-ray phase analysis of the obtained cathode deposit. Figure 3 shows the results of the electron microscopy of the cross-section of the electrode with the electrolytic deposit. The obtained data demonstrate that silicon deposits on the graphite substrate in the form of coatings under these conditions.

![Figure 2](image1.png)

**Fig. 2** X-Ray analysis data of cathodic deposit produced by electrodeposition from KF-KCl-K₂SiF₆ melt at iₖ = 0.02 A∙cm⁻², T = 973 K

![Figure 3](image2.png)

**Fig. 3** SEM data of silicon electrodeposited from KF-KCl-K₂SiF₆ melt at iₖ = 0.02 A∙cm⁻² and T = 973 K: a – cross-section observation b – surface of deposit;
The surface of the continuous deposit (Figure 3b) is formed in n-side pyramids, which denotes the columnar structure of the deposit. The average size of the continuous silicon coating grains was 100-150 μm.

To estimate the effect of the silica additions on the cathode deposit structure the electrodeposition from the [KF-KCl-K₂SiF₆]+SiO₂ melt on the graphite substrate was performed. The [KF(40.5 mol %)-KCl(49.5 mol %)-K₂SiF₆(10 mol %)] melt was used as the base of the mixture. The silica concentration in the mixture was maintained at 2 mol %. Figures 4 and 5 demonstrate the data of the X-ray phase analysis and electron microscopy of the obtained deposit.

**Fig. 4** X-Ray analysis data of cathode deposit produced by electrodeposition from KF-KCl-K₂SiF₆-SiO₂ melt at $i_k = 0.02 \text{ A} \cdot \text{cm}^{-2}$, $T = 973 \text{ K}$

**Fig. 5** SEM data of silicon electrodeposited from KF-KCl-K₂SiF₆-SiO₂ melt at $i_k = 0.02 \text{ A} \cdot \text{cm}^{-2}$ and $T = 973 \text{ K}$. Zoom: a – x 20000; b – x 2000;
The results of the X-ray phase method and electron microscopy show that the silicon deposits formed in the melt with the addition of 2 mol % of SiO$_2$ were fiber-like. The fiber length can reach several micrometers. The average diameter of the fiber does not exceed 200 nm. The average size of the crystals, determined by the X-ray diffraction analysis data, was 30 nm. The silicon deposit specific surface was 14.19 m$^2$·g$^{-1}$.

Silicon was found to crystallize in the form of silicon nanofibers under these conditions.

Silicon deposit produced by the electrolysis of the KF-KCl-$K_2$SiF$_6$-SiO$_2$ melt has a larger specific surface than that, produced by electrolysis of the KF-KCl-$K_2$SiF$_6$ melt. The average size of the silicon crystal significantly decreases as silica is present in the melt. Oxygen promotes the crystallization of the electrolytic deposit with developed specific surface.

To prove aforesaid assumptions the electrolysis in the KF(40.5 mol %)-KCl (49.5 mol %)-$K_2$SiF$_6$(10 mol %) melt was performed at cathode current density of 0.02 A·cm$^{-2}$ and 973 K. as the continuous layer deposited on the cathode SiO$_2$ was added to the melt and the silicon deposition was continued. The SiO$_2$ concentration in the melt was 2 mol %.

Figure 6 represents a microphotography of the experimentally obtained electrolytic deposit cross-section. The silicon crystallization on the graphite substrate during the KF-KCl-$K_2$SiF$_6$ melt electrolysis without SiO$_2$ addition was in the form of continuous layers, as expected. The SiO$_2$ addition to the KF-KCl-$K_2$SiF$_6$ melt during electrolysis (see Figure 6) resulted in the deposit structure changes. The deposit with developed surface started crystallizing on the silicon continuous layer.

**Fig. 6** Cross section SEM observation of silicon deposit obtained by electrolysis at $i_k = 0.02$ A·cm$^{-2}$, $T = 973$ K

**4. CONCLUSIONS:**

Silicon coatings were successfully electrodeposited from the KF-KCl-$K_2$SiF$_6$ melt onto the graphite substrate. Crystalline silicon nanofibers were produced by electrolysis of KF-KCl-$K_2$SiF$_6$-SiO$_2$ melt. It was determined that the addition of SiO$_2$ into the melt promotes the crystallization of silicon deposits with large specific surface area. Average size of electrodeposited silicon crystalline is significantly reduced with the appearance of oxygen in the KF-KCl-$K_2$SiF$_6$ melt composition.
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REFERENCES