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# Silicon electrodeposition in molten fluorides

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ABSTRACT

Silicon nucleation process was investigated in molten NaF–KF (40–60 mol%) on silver electrodes in the 820–950 °C temperature range in order to optimize silicon coating operating conditions. Chronoamperometric measurements evidenced that silicon electrodeposition process involved an instantaneous nucleation with diffusion-controlled nuclei growth whatever temperature and Si(IV) ions concentration in the mixture. The overpotential and temperature influence on nucleation sites number was also studied.

Silicon deposits were obtained using the same temperature range as nucleation study, for different current densities on substrates: Ni, Ag, $C_{graphite}$ and $C_{vitreous}$. A sensitive influence of the cathodic substrate on the deposit adherence and roughness was observed and discussed.

## 1. Introduction

Photovoltaic technology is emerging as a major source of electrical energy [1], and the most common base material for photovoltaic cell is solar grade silicon (SoG-Si). Due to a constantly growing demand for SoG-Si, the development of new processes allowing the production of cheap SoG-Si is a main issue for the solar energy industry.

In the 1980s, silicon electrodeposition in molten salts has been considered as an attractive option for SoG-Si production [2]. Indeed, silicon metal is more reductive than hydrogen meaning that silicon electrodeposition has to be carried out in non-aqueous electrolytes such as alkali metal halides. However, no electrolytic Si production process has found commercial application up to now. Considering more recent concerns about carbon-free energy production and growing needs for SoG-Si, such kind of process is nevertheless being reassessed, and, for that purpose, basic investigations on the salts properties, Si(IV) reduction mechanism and silicon deposition strategies are needed.

In the frame of a production route based on electrorefining (either from MG–Si or from Si cutting remains [3]), it was decided to focus on the electrodeposition process of dissolved Si(IV) in molten fluoride. The main objective was to evaluate the feasibility of such reaction and to provide an academic study of the Si(IV) reduction reaction, thanks to specific electrochemical techniques [4,5]. At this point of the study, the purity of the obtained deposits was not considered as an issue.

It was shown, in a previous work [6], that the volatility of Si(IV) compounds greatly depends on the nature of the fluoride mixture. The NaF–KF eutectic mixture, which highly stabilizes Si(IV) compounds, was thus selected as the electrolyte for the present study.

The article describes a next stage in the preparation of silicon layers for solar energy which is the demonstration of the electrolysis technique validity in molten salts technique to recover pure silicon on a cathode.

For this purpose, the nucleation process and the silicon nuclei growth on silver are investigated using cyclic voltammetry and chronoamperometry and these results are compared with suitable models [4,7] in order to state whether the nucleation is instantaneous or progressive. Meanwhile, the overvoltage and temperature influence on the nucleation mode and nucleation sites number were examined. Then, silicon deposition runs were carried with various electrode substrates (Ni, Ag, $C_{graphite}$ and $C_{vitreous}$), current densities ($-20$ to $-200\,\mathrm{mA\,cm^{-2}}$ range) and temperatures (820–900 °C range). The influence of each parameter on the coating adherence and roughness was observed by scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Cell

The cell was a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled by circulating water. The description of this cell has been

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detailed in previous work [8]. The experiments were performed under an inert argon atmosphere (Linde). The cell was heated using a programmable furnace and the temperature was measured using a chromel–alumel thermocouple.

The electrolytic bath consisted of the NaF–KF (40–60 mol%) eutectic mixture (Carlo Erba 99.995%). As mentioned earlier, the choice of this specific solvent was based on its stabilizing properties regarding to the volatility of Si(IV) compounds [6]. The mixture was initially dehydrated by heating under vacuum ($7 \times 10^{-2}$ mbar) from ambient temperature up to its melting point during one week. Silicon ions were introduced into the bath in the form of sodium hexafluorosilicate $Na_2SiF_6$ (Alfa Aesar 99.99%) powder.

### 2.2. Electrodes

Silver wires (1 mm diameter), vitreous and graphite carbon rods (3 mm diameter–Mersen spectroscopic quality) and nickel plates (50 mm × 10 mm × 1 mm) were used as working electrode. The surface area of the working electrode was determined after each experiment by measuring the immersion depth in the bath. The auxiliary electrode was a silicon thick plate (4 mm × 8 mm × 11 mm) with a large surface area ($3\,cm^2$). The potentials were measured with reference to a silicon plate immersed in the molten electrolyte.

### 2.3. Techniques

The electrochemical techniques used for the silicon nucleation and deposition investigation were cyclic voltammetry and chronoamperometry. All the electrochemical measurements were performed with an AutolabPGStat 30 potentiostat/galvanostat controlled by a computer using the research software GPES.

The silicon deposits were observed by SEM coupled with EDX probe, after cleaning in a $HCl–AlCl_3–H_2O$ mixture at 50 °C with ultrasonic waves.

## 3. Results and discussion

### 3.1. Si(IV) ions reduction mechanism

The silicon ions reduction in fluorides media was found to be a single step process exchanging 4 electrons (as already presented in Ref. [6]):

$$\mathrm{Si(IV)} + 4e^- = \mathrm{Si} \tag{1}$$

Cyclic voltammetry was carried out on a silver electrode in $NaF–KF–Na_2SiF_6$ system in the 820–950 °C temperature range. Fig. 1 presents a typical cyclic voltammogram of the $NaF–KF–Na_2SiF_6$ ($0.24\,mol\,kg^{-1}$) system at 850 °C on silicon electrode. This cyclic voltammogram exhibits only one reduction peak at −0.15 V vs Si and its associated reoxidation peak at 0.15 V vs Si. The linear relationship between Si(IV) reduction peak intensity and the square root of the scan rate has been verified (see the inset of Fig. 1), proving that the electrochemical reduction process is controlled by the Si(IV) ions diffusion in the bath (Berzins–Delahay [9] valid for a reversible soluble/insoluble system):

$$I_p = -0.61 nFSc^0 \left(\frac{nFD}{RT}\right)^{1/2} v^{1/2} \tag{2}$$

where $n$ is the number of exchanged electrons, $F$ is the Faraday's constant ($C\,mol^{-1}$), $S$ is the electrode surface area ($m^2$), $c^0$ is the solute concentration ($mol\,m^{-3}$), $D$ is the diffusion coefficient ($m^2\,s^{-1}$), $T$ is the temperature ($K$) and $v$ is the potential scan rate ($V\,s^{-1}$).

Furthermore, the diffusion coefficient $D$ can be calculated using Eq. (2) and the results obtained from the inset of Fig. 1. At the temperature of 850 °C, its value is $2.9 \times 10^{-9}\,m^2\,s^{-1}$. The temperature dependence of the diffusion coefficient, in the 820–950 °C temperature range, is given in Eq. (3):

$$D = 1.13 \times 10^{-5} \exp\left(-\frac{77.2 \times 10^3}{RT}\right) \tag{3}$$

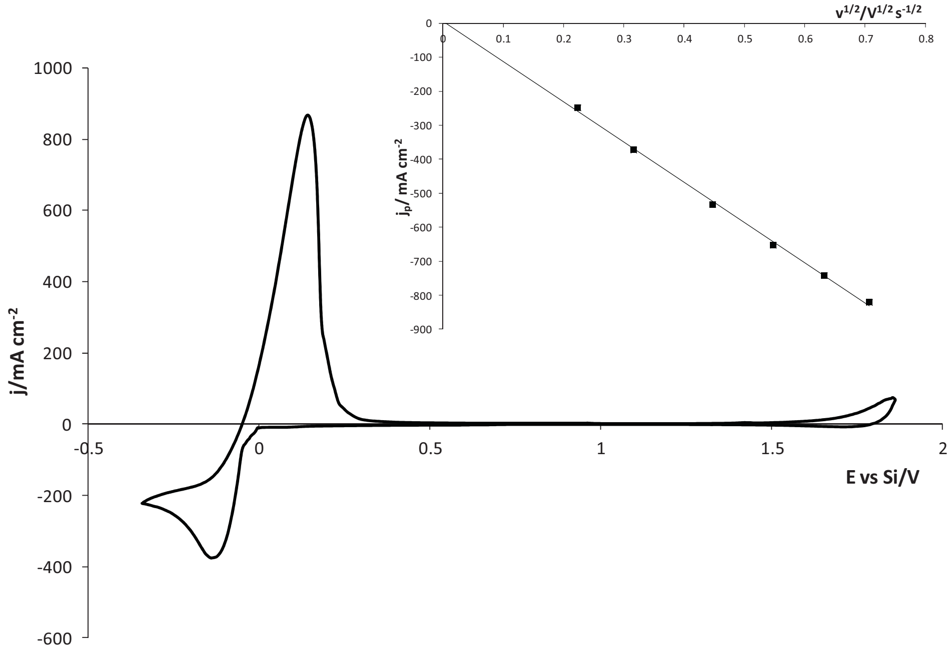

**Fig. 1.** Cyclic voltammogram of $NaF–KF–Na_2SiF_6$ ($c_0 = 0.24\,mol\,kg^{-1}$) at 850 °C; working electrode: Ag; auxiliary electrode: Si; reference electrode: Si; Scan rate = $100\,mV\,s^{-1}$/Inset: Linear relationship of Si(IV) reduction peak current density versus the square root of the scanning potential rate.