

Electrodeposition of Silicon in Fluoride Melts Production of Silicon Films

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IN

ELECTROLYSIS AND MATERIAL SCIENCE

Electrodeposition of Silicon in Fluoride Melts

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DECLARATION

I hereby declare that this thesis is my own effort and guidance from my supervisors. The ideas, concepts and theories of other authors have been appropriately recognized with references. This thesis has not been submitted for any degree or examination in any other university, learning institute or industrial organization. The thesis was carried out in accordance with the rules and regulations for the Master of Science program at Norwegian University of Science and Technology.

Trondheim, 15th July 2011

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DEDICATION

This work is dedicated to my beloved wife Rebecca Nemi, and son Magnus Ndede Amihere. May the almighty God richly blesses both of you and grant your heart desire.

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ABSTRACT

There has been considerable interest in electrodeposition of silicon from fluoride melts on a suitable substrate for its application in thin film solar cells. The goal of this work is to produce a high purity silicon films from LiF-KF-K₂SiF₆ (mol %) that could be suitable for solar grade applications, and to study electrodeposition of silicon in the same melt by performing electrochemical measurements.

Cyclic voltammetry was carried out both in pure melt LiF-KF and LiF-KF-K₂SiF₆ (0.13mol/kg) at 750°C on Ag electrode to study the reduction mechanism of fluorosilicate. The reduction mechanism was found to be mass transport diffusion controlled. The diffusion coefficient was estimated to be 1.1×10^{-5} cm²/s from Randles-Sevcik equation.

Chronoamperometry was also carried out in LiF-KF-K₂SiF₆ (0.13mol/kg) at 750°C on Ag electrode at different cathodic potentials and the current-time response, reduction mechanism of silicate ion was studied. It was also found again that the reduction mechanism of fluorosilicate is diffusion controlled. The diffusion coefficient was calculated to be 4.6×10^{-4} cm²/s using the Cottrell equation.

The influence of electrolytic parameters such as temperature, concentration of the electroactive species K₂SiF₆, and current density on the morphology and purity of the deposits and the current efficiency of the electrolytic process was studied. Effect of temperature and concentration was studied on Ag substrate and current density on both Ag and Si substrate. The influence of the substrate (silver and silicon) was also studied. Before the start of each electrodeposition experiment pre-electrolysis was carried out to remove moisture and reduce impurities concentration to ppm level. The deposits obtained were cleaned in ultrasonic bath to get rid of salt inclusions. It was observed that not all the salt inclusions were completely removed and therefore the current efficiency calculated was described to be apparent (not accurate). A few selected deposits were characterized using scanning electron microscope and energy dispersive spectroscopy, the results are shown below. It was observed that at a temperature of 800°C the deposit was dense, coherent, good adhesion to the silver substrate and with less impurities and salt inclusions but at 550°C the deposit was powdered or dendritic with high content of impurities and salt inclusions. At 5mol% of K₂SiF₆ the deposit consists of homogeneous structure with less impurities and salt but at 20mol% on the microstructure seems to be elongated and contain high content of impurities and salts. On silicon substrate, at current density 101.5mAcm⁻² the deposit was dendritic with no grains,

weakly adhered to the silicon substrate and also contains more impurities and salts but at 35.5mAcm⁻² the deposit contains large grains with columnar microstructure and less impurities and salts. On silver substrate, at 83.8mAcm⁻² the deposit consists of fine microstructure with high content of impurities and salts but at 42.9mAcm⁻² the deposit consists of bigger and elongated with high porosity and small content of impurities and salts. For the influence of the substrate, it was observed that on sliver the deposit was insoluble with fine microstructure but on silicon it was soluble and weakly adhered with non uniform microstructure which is powdered and dendritic. The deposit obtained on both silver and silicon contains high content of impurities and salts because of the high current density applied (83.8mAcm⁻² on Ag and 80.5mAcm⁻² on Si).

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LIST OF SYMBOLS

The meaning of important symbols used in the text is shown below. Symbols omitted from the list are explained in the text.

SYMBOL	MEANING/UNIT
\mathbf{C}^{∞}	concentration in the bulk solution [molcm ⁻³]
Co	surface concentration [molcm ⁻³]
D	diffusion coefficient [cm ² s ⁻¹]
E	(1) potential [V]
	(2) chemical equivalence [g]
E _{pc}	cathodic peak potential [V]
E _{pa}	anodic peak potential [V]
F	Faraday constant (96485) [Cmol ⁻¹]
$\Delta \mathrm{G}^{*}$	free energy "cost" or activation energy [J]
ΔG	free energy change of the nuclei [J]
η	overpotential [V]
i _p	peak current density [Acm ⁻²]
i _{pc}	cathodic peak current density [Acm ⁻²]
i _{pa}	anodic peak current density [Acm ⁻²]
Ι	current [A]
m _{act}	actual mass of the material deposited [g]
m _{theo}	theoretical mass from Faraday's laws [g]
Μ	molecular weight [gmol ⁻¹]
n	(1) number of electrons [-]
	(2) amount of substance [mol]
Po	theoretical production rate [gs ⁻¹]
р	measured production rate [gs ⁻¹]
q	quantity of electricity/charge [C]
r	radius [cm]
r*	critical radius [cm]

R	molar gas constant (8.314) [JK ⁻¹ mol ⁻¹]
t	time [s]
Т	temperature [K]
v	potential sweep rate [Vs ⁻¹]
Z	electrochemical equivalence [-]

ABBREVIATIONS

Abbreviations used in this report are explained below. Few of them are already explain in the text.

BSE	Backscattered electrons
CZ	Czochralski
CL	Cathodoluminescence
CV	Cyclic voltammetry
CTE	Counter electrode
CE	Current efficiency
EDS	Energy-dispersive spectroscopy
EBSD	Diffracted backscattered electrons
EPMA	Electron probe micro-analyzer
GC	Glassy carbon
NTNU	Norwegian University of Science and Technology
PV	Photovoltaics
SE	Secondary electrons
SCM	Simple classical model
SEM	Scanning electron microscopy
WDS	Wavelength dispersive spectroscopy

CHAPTER 1

1.0 INTRODUCTION

1.1 Solar energy in the future

Development of clean energy sources as an alternative to fossil fuels has become a major concern in the world today. Fossil fuel remains a major source of electricity production, providing reliable source of power at a cost effective price. The major drawbacks to burning fossil fuel are the emission of carbon dioxide (CO_2) and other green house gases into the atmosphere leading to global warming, and also there is the possibility of fossil fuel depleting with time. It is predicted that fossil fuel for electricity generation will be extremely scarce and expensive over the coming years as it becomes depleted. Taking all these drawbacks into consideration the question where energy for electricity production will be sourced in future is under serious investigation. Renewable energy has the advantage of being constantly replenished and therefore provides a sustainable energy supply without or with less CO₂ emission. Solar power is an ideal energy solution, which theoretically has the capacity to meet the world's energy demand. Energy from the sun can be converted into usable energy or electricity by the use of solar cells or modules. The major drawback with use of solar energy is the high price of solar-cell modules in the world today. Even though prices of solar-cell modules keep on decreasing, it is still not cheaper in comparison to conventional ways of generating electricity, e.g. Fossil fuel. A remarkable reduction of solar-cell modules prices from \$4.66 to \$2.01 per Wp has been recorded between 2004 and 2010 [1]. This reduction in prices may be due to several reasons such as an increase in efficiency of solar-cell modules (from 10% in 1956 to 19.5% in 2010 with a target of 23% in 2020), the use of thin film wafers (180-200µm today with a target of less than 100µm in 2020) and the use of environmentally friendly materials to replace scarce resources such as silver, indium tellurium, lead and cadmium [2]. The high prices of solar-cell modules is due to the high cost contribution from the production of polysilicon (99.9999% pure) feedstock from metallurgical grade silicon (98.5 to 99% pure) by Siemens process and significant wastage of about 50% (contributing 40% of the cost of the module) during ingot slicing using wire saw. Monocrystalline and multicrystalline ingots are predominantly grown by Czochralski (CZ) and directional solidification respectively. In order to make solar cells and modules more accessible and affordable it is important that production costs are reduced and efficiency improved significantly. Ways to reduce production cost is to use a cheaper growth technique and raw material as the feedstock. A growth technique that can be applied to deposit a pure thin film of the solar material will contribute significantly to the reduction of the production cost. Several growth techniques exist but electrodeposition appears to be cost saving technique since solidification and sawing steps which contribute significantly to the overall cost of solar cells will be bypassed. A thin film of the solar cell material (e.g. Si, CdTe, etc.) can be deposited on a substrate by electrodeposition for it to be used directly as wafers in solar cells. Electrodeposition also has the benefit of being scalable enabling various substrate shapes and sizes to be deposited. Again if polysilicon could be produced by electrorefining, energy and cost will be saved by side stepping energy consuming Siemens process.

PV technology in the market today is dominated by 80% of crystalline silicon. Even with greatly increase in production volume and significant reduction of cost it is doubtful that crystalline silicon will ever meet the long-term cost goal for utility scale power generation. If one accept this is rationale, it will be useful to see whether thin-film technologies can realistically meet this goal. There is reason to be very optimistic particularly in view of remarkable progress that has been made in the recent years in terms of high energy conversion efficiency, long-term stability, and demonstrated large scale manufacturing capacities in several thin-film technologies. Thin-film technologies have a significant cost advantage in comparison to traditional wafer-based crystalline silicon due to a number of factors such as: (i) fewer processing steps, (ii) low material use, (iii) simpler device processing and manufacturing technology for large area modules and arrays [3]. Most of the thin-film technologies have similar manufacturing cost because of their nature of design and construction. The choice of a suitable technology is basically dependent on several factors which include reliability of the material, highest achievable efficiency and ease of manufacturing and environmental sensitivity.

1.2 Objective(s) of the research

1. To deposit silicon films from LiF-KF-K₂SiF₆ melts on silver and silicon substrate.

2. To study the behaviour of silicon in LiF-KF- K_2SiF_6 melts by applying electrochemical techniques such as cyclic voltammetry and chronoamperometry.

3. To characterize the silicon deposits by scanning electron microscope and energy-dispersive spectroscopy.

4. To determine current efficiency for electrodeposition of silicon on silver and silicon substrates at different electrolytic parameters such as current density, temperature, concentration of K_2SiF_6 .

CHAPTER 2

2.0 BACKGROUND OF THE RESEARCH

2.1 Silicon production

2.1.1 Quartz to Metallurgical grade silicon

Silicon is produced industrially by carbothermal reduction of silicon dioxide (SiO₂) in submerged electric-arc furnaces. The feed materials include quartz, reluctant blending materials such as coke, coal, charcoal and wood chips. Purity of these raw materials is important for the purity of the silicon produced. Three pre-baked carbon electrodes, submerged into the charge materials, supply a three-phase current that heats the charge material to approximately 2000°C. At this temperature the silicon dioxide is reduced to molten silicon according to the reaction: $SiO_2(s) + 2C(s) = Si(s) + 2CO$ (g). The amount of CO_2 emitted depends on the source of electricity used. The furnace is operated such that there is a layer of solid material on top of the molten bath to maximize the silicon yield. The silicon is tapped from the furnace through a tap-hole at the bottom. Impurities commonly present in metallurgical-grade silicon include carbon, alkali earth-metals and transition metals, as well as boron and phosphorus [4]. A typical electric arc furnace for industrial production of metallurgical-grade silicon is shown in Figure 1 below.



Figure 1: Typical plant lay out for industrial production of MG-Si [5].

The electrical energy consumption for the production of metallurgical-grade silicon is 11-13MWh/ton of silicon metal. The energy consumption per ton of alloy is reduced significantly with increasing iron content in the silicon alloy product. The off-gas from the silicon furnace has an energy content of the same order of magnitude as the electrical energy input of the furnace. The off-gas may be directed into an energy recovery system, and can be used to produce hot water or saturated steam for heating, or superheated steam for electricity generation. Demand for metallurgical-grade silicon is primarily from aluminium and chemical industries, and a small fraction is refined into polysilicon.

2.1.2 Metallurgical grade silicon to polysilicon

Polysilicon is produced either by Siemens process, chemical deposition or fluid bed reactor technology (FRB). Polysilicon is produced predominantly by Siemens process. Around 80% of the world polysilicon is produced by the Siemens process that utilizes trichlorosilane [5]. Trichlorosilane has many advantages which include high deposition rate and volatility which makes it easier to remove boron and phosphorous. One disadvantage of using SiHCl₃ is the high electricity requirement to maintain process temperatures. A brief outline of the Siemens process is shown below:

The first step is to react HCl with MG-Si to form liquid SiHCl₃ according to the reaction: Si(s) + 3HCl (g) \rightarrow SiHCl₃ (g) + H₂ (g).

Liquid SiHCl₃ is purified by distillation process until the resulting impurity levels are at few ppb. The impurities which remain in the purified SiHCl₃ include SiH₂Cl₂, Fe, Ca, Al, C, and SiCl₄.

Polysilicon is deposited onto a thin monosilicon seed from purified SiHCl₃. The reaction for production of polysilicon can be represented as: SiHCl₃ (g) + H₂ (g) \rightarrow Si(s) + 3HCl (g).

The energy requirement for production of polysilicon via the Siemens process is about 145KWh/KgSi [6].

The flow sheet shown in Figure 2 outline in details the steps involve in the production of polysilicon by the Siemens process.



Figure 2: Flow sheet for industrial production of polysilicon via Siemens process [7].

2.2 Thin film growth techniques

There are several thin film growth techniques namely sputtering, chemical bath deposition, electrodeposition, physical vapour deposition (PVD), liquid phase epitaxy, plasma spray. Some of these techniques rely on high vacuum (HV) or ultra high vacuum (UHV) systems at high temperature. Such conditions yield superior quality material or deposit despite the high production cost arising from the initial cost of the equipment and power required for vacuum production and growth [8].

2.2.1 Electrodeposition

Electrodeposition is the process of coating a thin layer of a material (e.g. metal, metalloid) on top of another material or substrate to modify it surface properties. It is normally done to achieved electrical and corrosion resistance, reduce wear and friction, improve heat tolerance, for decoration and for depositing semiconductor material to be used in the area of photovoltaics. The morphology and composition of the coating material vary significantly, and depends on the current density, operating temperature, concentration of the solution, bath composition, presence of impurities, physical and chemical nature and geometry of the substrate. The quantity of the material deposited on the substrate also depends on the total charge passing through the electrolyte. During electrodeposition electric current is applied between electrodes immersed in the melt. For example when current is applied using a dissolving silicon anode and a cathode such as silver, graphite or silicon plate and a reference electrode such as coiled platinum wire immersed in LiF-KF-K₂SiF₆ silicon is electrodeposited at the cathode. For this work silicon is electrolyte and potassium fluorosilicate (K₂SiF₆) as the source of the electroactive silicon. LiF-KF was selected as the electrolyte because of their unique properties such as low viscosity, high ionic conductivity, low melting point eutectics, large decomposition potential range, low vapour pressure and high stability of the fluoride ion complexes which help to decrease diffusion controlled effect which is responsible for porous, dendritic or powdery growth. Potassium fluorosilicate seems to be the best electroactive source of silicon because of its low cost and availability, and low volatility [9].

Electrodeposition of semiconductors (e.g. Si) has relatively recent history dating back only to the 1970s [8]. This method is attractive from both fundamental and practical perspectives in terms of applicability to large and irregular device areas and ability to prepare composite (e.g. metals/semiconductors) structures and unique semiconductor morphologies (e.g. Nanotubes, nanodots). The application of electrodeposition in the preparation and purification of semiconductors for PV industry has become very necessary because of the need to develop a technique which is economical in solar cell fabrication. Electrodeposition offers the hope of a means of conveniently producing large area samples at low cost by making use of a technique which is readily adapted to industrial production. Again electrodeposition has been found to be an alternative technique for preparation of semiconductors for certain electronic devices, particularly thin film transistors for flat panel displays [10]. Electrodeposition has the advantage of being a non-vacuum technique and can be used to electrorefined silicon enabling the removal of impurities from the solution before growth of the layer begins. From electrorefining viewpoint impurities more than silicon will remain at the anode or will not dissolve anodically whiles impurities less noble than silicon (e.g. B, P, and Ca) remain in the electrolyte or will not deposit at the cathode [6]. The principle of electrorefining of the silicon can be understood from Figure 3 below.



Figure 3: Electrorefining of silicon

2.2.1.1 History and earlier work on electrodeposition of silicon from fluoride melts

The successful attempts to deposit silicon electrochemically were performed in the 1865 by Ullik [11] using K_2SiF_6 dissolved in molten KF at temperatures in excess of 1000°C, but a detailed study of silicon electrodeposition was performed in 1930s.

Cohen and Huggins were the first to prepare both mono and polycrystalline silicon deposits by electrolysis of 5mol% K₂SiF₆ in LiF-KF eutectic at 750°C [12, 13]. Epitaxial layers of silicon were obtained on a single crystal silicon substrate. An anodic pulse of 50mAcm⁻² was applied to the substrate for 1 second to etch the surface of the substrate prior to deposition. The cathodic current density required for epitaxial deposition was in the range 1-10mAcm⁻². Low current densities in this range give rise to isolated hillocks, the optimum value for uniform layers being around 4-6mAcm⁻². Above 10mAcm⁻² a polycrystalline layer was deposited on epitaxial layer of about 10µm in thickness. The layers had a resistivity of 0.05– 0.10Ω cm, corresponding roughly to 10^{18} carriers/cm³. The cathodes used for the study include tungsten, niobium, and silicon and anode is dissolving silicon.

Rao et al² reported on electrodeposition of silicon from a solution of potassium of fluorosilicate in a fluoride melts at 750°C on silver and graphite substrate[14]. A constant potential of (-0.73 \pm 0.03) V on silver and (-0.75 \pm 0.05) V on graphite was applied during deposition for two to four days. The observed current densities were 10 to 100mAcm⁻²

depending on the solute concentration. The cathodic current efficiencies were up to 70 and 80% for electrodeposition of silicon and graphite respectively. Shiny, dense, coherent and well-adherent silicon layers up to 4mm thick on silver and about 2mm thick on graphite. The films have columnar structure with grain size up to 100 μ m for electrodeposits on silver and up to 250 μ m for silicon on graphite. The surfaces are not microscopically smooth, but an irregular surface would have a beneficial effect in solar cells because of an increased surface area of sunlight absorption [14]. Elwell also reported the possibility of electrodepositing Si layer from molten salts using SiO₂ as the precursor. As electrolyte, the use of LiF was avoided due to its low solubility in water and acids, which makes it difficult to eliminate the excess of salt adhered to the electrodeposited silicon. The eutectics between NaF or KF and CaF₂, BaF₂ and MgF₂ were used. Elwell focused his work on the use of Ag substrates [15].

Moore et al. reported the production of crystalline silicon layers 5-50 μ m thick onto silicon substrate at growth rates of 60 μ m/hour by electrodeposition from fused salt [15]. The electrolyte was equimolar LiF-KF mixtures containing 10wt% K₂SiF₆ and the working temperature ranged from 750-800°C. Heavy doped p-type (111) Czochralski silicon and polished silver were used as the substrate.

Boen and Bouteillon in 1982 prepared electroactive silicon from LiF-KF-K₂SiF₆ on silver, silicon, platinum and graphite cathode [13]. The melt was purified by pre-electrolysis and treatment with HF. It was observed that the product formed on silver and graphite cathode was insoluble in the substrate. This indicates that both silver and graphite could be used for electrolytic deposit of silicon. The main focus of their work is to prepare thin layers of silicon by electrolytic means. The mechanism of reduction of silicon and the influence of electrolytic parameters such as current density was studied. Lepinay and Bouteillon proposed that the reduction of silicon occurs in two steps and coupled by con-proportionation chemical reaction shown in equation (1) and (2) respectively.

$$Si (IV) \rightarrow Si (II) + 2e \rightarrow Si$$
(1)

$$Si (IV) + Si \leftrightarrow Si (II).$$
 (2)

Boen and Bouteillon found out that it was impossible to obtain electrolytic silicon on graphite or silver electrodes using a non purified solvent. X-ray analysis indicates that the parts of the electrode surface were covered by an iron deposit. The presence of iron seems to inhibit to inhibit silicon nucleation. Boen and Bouteillon later showed that improvements in deposit morphology and the purity of silicon could be achieved by pulsed electrolysis [13].

In 1984 Stern and McCollum electrodeposited silicon coatings at 750°C from ternary eutectic LiF-KF-K₂SiF₆ (FLINAK). The main focus of their work is to prepare high purity crystals for photovoltaic applications and also deposit refractory material SiC and silicide wear coatings onto structural metals. The cathode used is inconel (76wt% Ni, 16wt% Cr, 8wt%Fe); anode is silicon or SiC rod and coiled platinum wire as the reference. It was observed by Stern and McCollum that the morphology of the deposits depends on the applied voltage. At lowest voltage the coatings consist of densely packed small crystals (less than 1 μ m) but at high voltage the coating structure consist of densely packed network of lacy rounded crystals [12].

In 1985 Shama and Mukherjee studied electrorefining of metallurgical-grade silicon in a semicontinuously electrolytic cell which consisted of a lower electrolytic chamber and upper receiver chamber with a slide valve paced in between for the purpose of isolation of the two chambers. Freshly crushed metallurgical grade silicon was charged as the anode feed at the bottom of vitreous carbon crucible of 65mm internal diameter, 70mm outer diameter and height 10mm which contain the electrolyte. The cathode used was graphite strips of dimension 125mm long x 25mm wide x 6mm thick. The salt that forms the electrolyte was chemically pure and vacuum dried at 350°C for 48 hours. The electrolyte used is a mixture of LiF, KF, and K₂SiF₆ which was melted at 750°C under flowing argon atmosphere to form the electrolyte and pre-electrolyzed at cell potential of 1.9 to 2V for about 8 hours to reduce the background current density to a quite low value. Electrolytic deposition of silicon was initiated by adding the anode feed and passing current corresponding to the desired current density. After each silicon electrodeposition the current efficiency was estimated. Effect of current density (7.75 to $23.25 \times 10^2 \text{A/m}^2$) on current efficiency for electrodeposition of silicon on graphite electrode was studied in 42.5 mol% of LiF, 42.5mol% of KF and 15mol% of K₂SiF₆ at constant temperature 750°C. Current efficiency of about 98% was recorded at current density $13.5 \times 10^2 \text{A/m}^2$. Current density greater than $13.5 \times 10^2 \text{A/m}^2$ leads to a decrease in the current efficiency. Again effect of temperature (650 to 800°C) was studied in the same melt and electrode mentioned above at constant current density $13.5 \times 10^2 \text{A/m}^2$. The highest current efficiency of about 96% was obtained. The influence of current efficiency by K₂SiF₆ concentration in the electrolyte (6 to 18mol %) was studied in equimolar LiF-KF electrolyte at constant temperature and current density 750°C and 13.5x10²A/cm² respectively. The highest current efficiency of about 95% was obtained at 15 mol% K₂SiF₆, but beyond this concentration the current efficiency decreases [17].

NTNU in collaboration with SINTEF has performed experiments on electrodeposition of silicon in molten LiF-KF-K₂SiF₆ (5mol %) on Ag and Si substrates at 550°C and 800°C. On silver dense coherent films with good adhesion and no inclusion of salts were obtained at 800°C at growth rate of 52μ m/hour. On silicon small "randomly" oriented silicon layers were observed. At 550°C powderish deposits on both Ag and Si were observed [18].

CHAPTER 3

3.0 THEORY

3.1 Electrochemical methods

3.1.1 Cyclic Voltammetry

In 1938 studies on cyclic voltammetry (CV) was first reported and described theoretically by Randles [19]. Cyclic voltammetry is a common electrochemical method that is employed to give qualitative information about electrochemical reactions. It is an important tool for the study of the nature and mechanisms of electrode reactions. In cyclic voltammetry, the cathode potential ramps linearly with time as shown in Figure 4. Cyclic voltammetry is especially useful for studying diffusion controlled electrode reactions



Figure 4: Cyclic voltammetry waveform: Variation of cathode potential with time

The ramping is known as the experiment scan rate (v). The potential is applied between the reference electrode (RE) and the working electrode (WE) by a potentiostat and the corresponding current is measured between the working electrode and the counter electrode (CTE). The current measured is often normalized to the electrode surface area and referred to as current density. The forward scan produces a current peak for any analyte that can be

reduced or oxidized (depending on the initial scan direction) through the range of the scanned potential. The current increases as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. If the redox couple is reversible then the applied potential is reversed, it will reach the potential that will reoxidized the product formed in the first reduction reaction, and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. Information about the redox potential and the electrochemical reaction rates of the compounds are obtained. A peak in the measured current is seen at a potential that is a characteristics of any electrode reaction taking place. From the scan rate dependence of the peak amplitudes, widths, peak currents or the potential of the peaks observed makes it possible to investigate the role of adsorption, diffusion, and coupled homogeneous chemical reaction mechanisms. For instance if the electronic transfer at the surface is fast and the current is limited by diffusion of the species to the electrode surface, then the cathodic peak current density will be proportional to the square root of the scan rate $(v^{1/2})$.

Consider a solid deposition or simple electrode reaction:

$$X^{n+} + ne^- \to X \tag{3}$$

It is appropriate to assume that X is deposited with a constant unit activity which corresponds to the assumption that the electrode surface is immediately covered by at least one monolayer of X once the reversible potential is reached. The problem was first treated by Berzins and Delahay [20]. The current density is given by

$$i = -2nF(D\sigma/\pi)^{1/2}C^{\infty}\Phi[(\sigma t)^{1/2}]$$
(4)

Where

$$\Phi(X) = e^{-X^2} \int_0^X e^{t^2} dt$$
(5)

 $\Phi(x)$ known as Dawson's integral, and has a maximum value of 0.5410 for x=0.9241. Solving equation (3) and substituting into equation (2) gives

$$i_{Pc} = -\frac{0.6105 \cdot (nF)^{\frac{3}{2}} \cdot c^{\infty} \cdot D^{\frac{1}{2}} \cdot v^{\frac{1}{2}}}{(RT)^{\frac{1}{2}}}$$
(6)

Equation (6) is Randles-Sevcik equation for deposition of a solid [19].

A plot of the cathodic peak current density (i_{pc}) vs. the square root of the scan or sweep rate gives a straight line passing through the origin. This is an indication that the reduction is controlled by diffusion. The diffusion coefficient can then be estimated knowing the slope. A plot of the current density (i) or current (I) vs. potential (E) gives a voltammogram as shown in Figure 5. The voltammogram helps to determines the potentials at which electrochemical processes occurs.



Figure 5: The expected response of a reversible redox couple during a single potential cycle

3.1.2 Chronoamperometry

Chronoamperometry was reported in 1954 by Gerischer and Vielstich for determination of kinetic parameters of simple electrode reactions from the plot of current density (i) vs. the square root of the time $(t^{1/2})$ [21]. Chronoamperometry is a potential step technique in which the working electrode (cathodic) potential is changed instantaneously from an initial cathodic potential (E₁) to a final cathodic potential (E₂) and corresponding current - time response is noted. This is illustrated in figure 3 and 4 below.


Figure 6: Potential – time profile for cathodic step chronoamperometric experiment



Figure 7: Current - time response for diffusion controlled cathodic step experiment

The initial potential is chosen at a region where there is no current flowing (non Faradaic reaction occurs) to a potential region where current flows (reaction occur). This current is larger at first, but it rapidly decays as the analyte near the electrode surface is consumed, and a transient signal is observed. This technique is by far the most useful for quantitative study of nucleation processes. Imposing a sudden potential change allows for the investigation of the process, qualitatively by studying concentration profiles and quantitatively by solving differential equation that describe mass transport or possible homogeneous reactions on the

electrode surface. These differential equations are solved before and current response for absolute mass transport controlled reaction could be obtained. Solving Fick's second law with appropriate boundary conditions gives Cottrell equation which shows how current density (i) varies with time (t).

Fick's second law:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \tag{7}$$

Boundary conditions

1.
$$t = 0, x \ge 0$$
 $C_0 = C_0^{\infty}$ (8)

2.
$$t \ge 0, x \to \infty$$
 $C_0 = C_0^{\infty}$ (9)

3.
$$t > 0, x = 0$$
 $C_0 = 0$ (10)

Laplace transformation makes it easy in solving the boundary value problems.

Cottrell equation [20] given as:

$$i = \frac{nFD^{\frac{1}{2}}C^{\infty}}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}}$$

(11)

A plot of the limiting current density (i) against inverse of the square root of time $(t^{-1/2})$ gives a straight line passing through the origin indicating the reaction is diffusion controlled. The diffusion coefficient (typically 10^{-5} cm²/s) is determined from the slope of the line.

3.2 Phase formation

In electrode reactions such as electrodeposition of metals in plating, electrorefining and electrowinning, bubble formations when the product is gas or transformation of one solid to another there is formation of a new phase. The formation of a new phase first begins with nucleation followed by subsequent growth. Furthermore electrodeposition of metal on a suitable substrate involves both diffusion of the metal across the surface and incorporation of the ad-atom into an appropriate site in the lattice. For electrode reactions which involve transfer of many electrons there is the possibility of adsorption, coupled chemical reaction and phase transformation to occur sandwiched between followed by electron transfer.

3.2.1 Electrochemical phase formation

The electrode reaction shown in equation (3) is heterogeneous reaction since the reactant and the product are at different phases. The formation of the deposit (X) involves a number of steps. If the material is deposited on a foreign substrate then the following processes are likely to occur [20].

- 1. Bulk diffusion of X^{n+} ions on the electrode surface
- 2. Electron transfer
- 3. Adsorption of the material, X_{ads}
- 4. Surface diffusion of the adsorbed material
- 5. Clustering of the adsorbed material leading to the formation of nuclei of critical size
- 6. Development of macroscopic deposit with incorporation of adsorbed material at the lattice site.

Any of the above mention steps is likely to be rate determining. In electron or charge transfer reactions in molten salts such as alkali halides, the process is extremely fast and therefore step 2 and 3 mention above are not likely to occur. Step 4 is the rate determining step during electrocrystallization of a material on a substrate of its kind for example Si deposited on Si substrate. On the other hand if the electrocrystallization occurs on a foreign substrate for example Si deposited on Ag substrate then rate is likely to be limited by the number of nuclei present and the rate at which new ones appears.

3.2.2 Nucleation and growth

Nucleation with the exemption of electrochemical nucleation is a physical reaction which occurs when components in a solution start to precipitate out, forming nuclei which attract more precipitate (i.e. growth). Nucleation frequently occurs at the nucleation sites (e.g. phase boundaries) on surfaces contacting the liquid or vapour and this is called heterogeneous nucleation. Nucleation can also occur less frequently without preferential nucleation sites and this is referring to us homogeneous nucleation. Nucleation of crystalline, amorphous and even vacancy clusters in solid is crucial to semiconductor industry. Electrochemical nucleation of a new phase, in which the nuclei grow due to mass transport mechanism, is very essential in many areas such as electrowinning, hydrometallurgy, and formation of anodic films, electrodes and high-density batteries, deposition of organic layers and anodic plating and stripping voltammetry [22]. Electrochemical nucleation takes place predominantly at the edges of an electronic conducting material and the solution of the electrolyte; where interfacial charge transfer occur as single ions are reduced to metal atoms which adsorb on the cathode substrate and form a cluster.

An electrochemical nucleation process can either be instantaneous or progressive. The grain size of the deposited material is best optimized by the time dependence of the nucleation. For progressive nucleation the nuclei form continuously and grow making it difficult for the grain size to be controlled. On the other hand, if the nucleation process is instantaneous then the nuclei form at the same time making it easy for the grain size to be optimized. The number of nuclei formed depends on the applied potential and the constant current growth conditions. During instantaneous nucleation, the initial current density helps in the determination of the average density of the nuclei since there is no nucleus formed after the initial nucleation process. The density of the nuclei gives a clue about the time the nuclei will coalesce thereby knowing the ultimate grain size. It has been found that both time dependence of nucleation process and mode of growth of the nuclei can be evaluated by taking into consideration the initial shape and size of the heterogeneous deposits. The size of the nucleus varies linearly with the time it takes for it to be formed. This indicates that the nucleation process is progressive if the size of the nuclei differs but if the size is similar then the process will be described to be instantaneous. Again it is possible to determine the time dependence of the nucleation process by comparing theoretical models to chronoamperometric experiment results.

A simple classical model (SCM) was developed by Volmer and Weber and later Becker and Döring [23] for the study of the kinetics of the nucleation processes by assuming that the new phase contains the same composition, structure and thermodynamic properties as the bulk material. This model work well for clusters in the other of 100 atoms or more but experimental results show that most often the critical nuclei contain less than 10 atoms [20]. This contradiction was solved by the model proposed by Walton which is based on statistical mechanics that contains no macroscopic physical quantities. The model characterized the size of clusters by the number of atoms it contains instead of its radius.

Consider a simple electrode reaction in equation (1) shown above. The reaction is dominated by heterogeneous nucleation and therefore it will be appropriate to take into account the interactions between the substrate and the growing phase. These interactions may be ignored when the growth centres are spherical small droplet with small vanishingly contact area with the substrate. This phenomenon is similar to homogeneous phase formation from vapour phase in which a solid or liquid is normally in contact with its vapour, this can be represented as: $X_{(g)} \leftrightarrow X_{(s)}$

It has been mentioned earlier that the formation of a nuclei is due to clustering of ad-atoms. Ions in the solution, X^{n+} and ad-atoms, X_{ads} create an equilibrium condition at the electrode surface due to effect of charge transfer reactions.

The overall free energy change of the nuclei is a function of the radius of the nuclei, free energy per unit volume and surface tension that results in energy losses. The variation of the free energy change of the nuclei with its radius according to simple classical theory is shown in figure 8 below. Maximum or free energy "cost" is obtained at the critical radius. This free energy of critical nucleus can also be called activation energy which needs to be overcome by the nuclei for growth to occur.





Addition of new molecules to clusters with radius larger than the critical radius (r^*) cause a decline in the total free energy. At that point growth of the crystals occur spontaneously and is no longer limited by nucleation, but perhaps by diffusion or by kinetics of the reaction.

3.3 Faraday's laws of electrolysis

Faraday's laws of electrolysis were published in 1834 by Michael Faraday based on his findings on electrochemical deposition of a substance on an electrode during electrolysis [24].

The laws are as stated below:

First law:

The amount of a substance (n_s) deposited at the electrode during electrolysis is directly proportional to the quantity of electricity or charge (q) passed through the electrolyte.

Mathematically:

$n \propto q \text{ Or } n = zq$	(12)

$$q = It$$

$$n = zIt$$

Second law:

When the same quantity of electricity or charge is made to pass through different electrolytes, the masses of the substance liberated or deposited at the electrodes are proportional to their chemical equivalence.

It can also be stated as electrochemical equivalent (z) of a substance is proportional to its chemical equivalent (E)

Faraday's constant can be calculated from the second law as shown below.

$$z \propto E \text{ Or } z = FE \tag{15}$$

$$F = \frac{z}{E} = 96500 \text{ coulomb/equivalent}$$

In electrolytic production, the laws of Faraday can be combined into one equation:

The amount of material produced at the electrode (P) is as shown below:

$$P = \frac{M}{ZF} It$$
(16)

The theoretical production rate (P_o) is as shown:

$$p_o = \frac{P}{t} = \frac{MI}{ZF}$$
(17)

3.4 Current efficiency

In many industrial processes, the process of electrolysis is less efficient than expected from Faraday's laws of electrolysis. This may be due to several reasons such as loss of energy during its flow through the system, side or back reactions, short-circuiting, leakage currents, electronic conduction, and co-deposition of more noble impurities from raw materials etc.

(14)

The efficiency of an electrochemical process is described in terms of its current efficiency, which is defined as:

$$CE = \frac{Actual\ mass\ of\ the\ material\ liberated\ during\ electrolysis}{Theoretical\ mass\ of\ the\ material\ from\ Faraday\ laws} x100\%$$
(18)

$$CE = \frac{m_{act}}{m_{theo}} x 100\% \tag{19}$$

$$m_{theo} = \frac{It}{ZF} xM \tag{20}$$

Current efficiency can also be defined as the ratio of measured production rate to theoretical production rate [25].

$$CE = \frac{measured \ production \ rate}{Theoretical \ production \ rate} x100\%$$
(21)

$$CE = \frac{p}{p_0} x 100\% \tag{22}$$

Current efficiency can also be defined as the ratio of theoretical amount of electric charges (Q_M) for the formation of the amount of the deposit to the total amount of charges (Q_T) in the cell [26].

$$CE = \frac{Q_M}{Q_T} \tag{23}$$

3.4.1. Measurement of current efficiency

There are several methods that can be used to measure current efficiency which include potential coulometry, the use of metallic tracers, the total oxygen balance, and determination of the weight of the material deposited [26]. The method used for this work is discussed briefly below. All the other methods which are not used are not discussed here.

3.4.1.1 Measurement of current efficiency from the weight of silicon deposited

In principle, current efficiency can be determined from the weight of the material deposited on an electrode during electrolysis by taking into consideration the amount of electricity used in a given period of time. Firstly, the weight of the substrate (m_s) must be noted before the start of the electrolysis. After the electrolysis or electrodeposition the deposits must be cleaned in using ultrasonic bath to remove salt inclusions. The weight of the deposit together with the substrate is noted (m_d). The actual mass of the deposit (m_{act}) can then be determined by the difference of the mass of the substrate and the mass of the deposit together with the substrate (i.e. $m_{act} = m_d - m_s$). Knowing the theoretical mass (m_{theo}) of the material deposited from Faraday's laws of electrolysis shown in equation (20), current efficiency of the electrolytic process can then be calculated using equation (19).

3.5 Characterization techniques

There are many characterization techniques but only the techniques used for this work will be described.

3.5.1 Scanning electron microscopy (SEM)

3.5.1.1 Description of scanning electron microscopy

All SEMs contains the following components: Electron source or gun, Electromagnetic lenses, Sample stage, detectors for the all signals of interest, data output devices and infrastructure requirements (power supply, vacuum system, cooling system etc). Photographs of a few of the above components are shown in Figure 9 below.

SEM is used to generate high resolution images of shapes of objects and to exhibit spatial variations in chemical compositions. It is used for discrimination of phases based on atomic

number of the constituent elements in the sample using BSE detector. It is also used for acquiring elemental maps or spot chemical analysis with the help of energy dispersive spectroscopy (EDS) detector and for compositional mapping based on differences in trace elements specifically transition metals using CL detector [27]. It is used widely to identify phases based on qualitative chemical analysis and crystal structure.

Sample preparation in SEM is very simple and also result is obtained in some few minutes.

For most SEMs the sample must be stable in vacuum on the order of 10^{-5} to 10^{-6} torr. Samples that produces gas at low pressures are not good to be characterized with conventional SEMs and therefore low vacuum or environmental SEMs need to be used. Light elements such as H, He and Li are difficult to be detected.



Figure 9: Some components of SEM: (A) detectors, (B) sample stage, (C) objective lens

3.5.1.2 Sample preparation

Sample preparation is very important because it may have a significant influence on the results. Since SEM operates under vacuum and uses electrons to eject electrons and X-rays from the sample special preparations will be very necessary. It is essential that any amount of water present in the sample must be removed because water would vaporize in vacuum and interfere with the movement of the electrons emitted from the electron gun. All metallic samples are conductive and therefore need no special preparation.

CHAPTER 4

4.0 EXPERIMENTAL

4.1 Furnace and experimental cell set up

The furnace for the electrodeposition, cyclic voltammetry and chronoamperometry experiment composed of an outer casing or the body which contain the glassy carbon crucible containing the alkali metal fluorides (LiF, KF) and the source of electroactive silicon (K_2SiF_6). The body is made of steel which is protected from corrosive atmosphere by painting. There is a ceramic refractory material which is made of a mixture of Al_2O_3 and CaO lining inside of the furnace. To ensure uniform temperature distribution around the glassy carbon crucible containing the melt, the temperature gradient across the furnace length was measured. The head of the furnace contain seven holders that accommodate the anode (MG-Si), cathode (Si or Ag), quasi-reference (Pt), thermocouple which is made by joining pure Pt and Pt with 10% Rh, alumina tube for salt addition and two metals to support the radiation shields. The head also contain a pipe that is normally connected to a rubber tube during experiment to allow the flow of argon in and out of the furnace during experiment. The body of the furnace, the head and the device for controlling the power and temperature of the furnace are shown in Figure 10 below.



a. b. c.

Figure 10: Furnace for electrodeposition, cyclic voltammetry and chronoamperometry experiment: (a) body, (b) the head and (c) Furnace power and temperature controlling device

4.2 Chemicals

The individual alkali metal fluorides LiF, KF and the source of electroactive silicon K_2SiF_6 are normally heated to dry and stored at 200°C in an oven to get rid of moisture and other volatile impurities before used for the experiment. Usually the chemicals are grounded into fine powder so that they can be well mixed together. When KF is dried at 200°C the individual particles coagulates making grounding very difficult. LiF and K_2SiF_6 particles remain separated after drying at 200°C.

Photographs of the oven for heating and storing the chemicals at 200°C and the melt after electrodeposition experiment is shown below.



Figure 11: (a) Oven for heating and drying the chemicals at 200° C, (b) LiF-KF-K₂SiF₆ melt after the electrodeposition experiment.

Photograph of individual alkali metal fluorides LiF, KF and the source of electroactive silicon K_2SiF_6 after heating and drying at 200°C are shown below.



Figure 12: Alkali fluorides and the source of electrolytic silicon: (a) LiF, (b) KF, (c) K₂SiF₆

4.3 Electrodes

The electrodes used in the electrodeposition experiment are dissolving silicon anode (A) which is 5cm long and 1x1cm cross section, cathode or substrate which is either 2mm thick Metallurgical Grade (MG) silicon plate (B) or 1mm thick silver (C) which is 99.9% pure and a reference electrode (D) which is about 0.5mm (diameter) coiled platinum wire. Photograph of the above mention electrodes is shown in Figure 13 below.



Figure 13: Electrodes for electrodeposition: (A) dissolving silicon anode; (B) Metallurgical Grade (MG) silicon substrate; (C) Ag substrate and (D) Pt reference electrode.

The electrodes used for the cyclic voltammetry and chronoamperometry experiment are 1mm (diameter) Ag wire which is the working electrode (WE), 3mm (diameter) glassy carbon rod which is the counter electrode (CTE) and 0.5mm (diameter) coiled platinum wire that is the reference electrode (RE). The reference electrode is the same shown in Figure 13.

A Photograph of the glassy carbon rod and Ag wire rod for electrochemical measurement is shown below.



Figure 14: Electrodes for electrochemical studies: (A) glassy carbon rod (B) Ag wire

4.4 Experimental procedure

Normally the anode, cathode, reference electrode, thermocouple, glassy carbon rod, silver wire and the alumina tube for salt additions are cleaned, rinsed with ethanol and allowed to dry before mounted on the head of the furnace as shown in Figure 15. Usually the alumina tubes after the cleaning and rinsing with ethanol they are further heated at a temperature of 1200°C to remove any salt remains before used for another experiment to avoid contamination of the melt. When the furnace is ready to be used the water inlet and outlet are open to allow flow of water through the furnace to cool it since it operates at a high temperature.

Cyclic voltammetry and chronoamperometry was first carried out before the electrodeposition experiment. Cyclic voltammetry was first performed in the pure melt LiF-KF eutectic mixture and LiF-KF-K₂SiF₆ (0.13mol/kg) at different scan rates. To be certain that silicon was reduced the concentration of K_2SiF_6 was increased to 0.26mol/kg and cyclic voltammetry

experiment was performed. Chronoamperometry was also performed in LiF-KF-K₂SiF₆ (0.13mol/kg) at different potential steps. Electrodeposition experiment was performed at different parameters such as current density (11.1 to 122.7mAcm⁻²) and temperature (550 to 800°C) in the melt LiF-KF-K₂SiF₆ (5mol %) at constant temperature of 795°C and average current density 42.4mAcm⁻² respectively. Electrodeposition experiment was again carried out in 41.37g LiF, 92.90g KF, and 5 to 20mol% of K₂SiF₆ at constant temperature of 750°C and average current density of 42.1mAcm⁻². At the start of each electrodeposition experiment LiF-KF eut mixture is heated to a temperature of 200°C by the furnace power and temperature controlling device and allowed staying overnight and further heated to approximately 650°C for about 2 hours to ensure that the salt is molten. This temperature 650°C is not the true temperature of the melt, it is the temperature shown on the furnace power and temperature controlling device. The temperature of the melt is recorded by the thermocouple. The operating temperature is noted before the addition of the source of electroactive silicon K₂SiF₆ and allowed about 1 hour for dissolution. Pre-electrolysis using silicon cathode (1cm into the melt) followed immediately to ensure that moisture, oxygen and other impurities were kept in part per million levels. In each electrodeposition experiment pre-electrolysis was first allowed to take place for about 5 hours. Electrodeposition was performed galvanostatically on silicon and silver substrates in LiF-KF-K₂SiF₆. The same melt was used for several depositions. Immediately after the electrolysis is terminated, the substrates are normally raised above the electrolyte to minimize pitting of the obtained deposit from conproportionation between Si (IV) and Si. After plating the cathode were cleaned in hot ultrasonic bath and further washed with ethanol. The current efficiencies for the electrodeposition experiment were calculated (details shown in appendix C) .All the electrodeposition experiments were carried out under argon atmosphere. The current efficiency for each electrolytic process was calculated. The deposits were characterized by techniques such as scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The photographs of scanning electron microscope with EDS detector in-built in the SEM and sample holder used at the material science building of NTNU are as shown in appendix A. A schematic drawing of the set up for electrodeposition experiment is shown in appendix B



Figure 15: Set up ready to be used for electrodeposition experiment

4.5 Instrumentation

4.5.1 Electrochemical studies and electrodeposition

The electrodeposition experiments and electrochemical measurement were carried out by using a computer controlled potentiostat, Autolab "PGSTAT 20" connected to a 10A current booster. A picture of the potentiostat is shown in Figure 16.



Figure 16: Potentiostat Autolab "PGSTAT 20"

CHAPTER 5

5.0 RESULTS

5.1 Temperature gradient

To ensure uniform temperature distribution along the glassy carbon crucible containing the melt temperature gradient experiment was carried out. This experiment helped to know the exact height to which the crucible must be placed. The result of the experiment is plotted below.



Figure 17: Vertical temperature gradient of the furnace

The plot above shows how temperature (T) around the glassy carbon crucible changes with the height or the position (D) of the crucible from the top of the furnace. From Figure 17, it can be seen that as the glassy carbon crucible is lowered down the furnace its surrounding temperature increases but with time it becomes constant and then finally reduces. The position at which the temperature becomes constant is where the crucible must be placed. The temperature should be as constant as possible along the height of the salt (~3cm). From the plot the temperature is constant between 18 and 21 cm.

5.2 Electrochemical studies

The behaviour of Si in the melt LiF-KF-K₂SiF₆ (0.13mol/kg) was studied by employing electrochemical techniques such as cyclic voltammetry and chronoamperometry. Cyclic voltammetry was also carried out in the pure melt LiF-KF. This electrochemical study was also done in autumn 2010 academic year during the specialization project [28]. The results obtained during the period of this master thesis are consistent with that obtained during the specialization project. The results of cyclic voltammetry and chronoamperometry experiments are shown below.

5.2.1 Cyclic Voltammetry



Figure 18: Cyclic voltammogram on Ag electrode at 750°C, scan rate 200mV/s in: (A) LiF-KF eutectic melt, (B) LiF-KF-K₂SiF₆ (0.13mol/kg)

The voltammograms shown in Figure 18 are the recorded current (I) vs. the potential (E) obtained in pure LiF-KF and LiF-KF-K₂SiF₆ (0.13mol/kg) melt at 750°C and sweep rate 200mV/s on Ag electrode which are represented as A and B respectively. As can be seen from Figure 18, the cathodic limit on Ag in LiF-KF is around -1.7V versus the Pt reference. According to Bouteillon et al [13], the cathodic limit is mainly due to the reduction of the

potassium ion and may be written as: $K^+ +e^- \rightarrow K$. The anodic limit of the electrolyte is also due to oxidation of the fluoride ions (F⁻). However, this would have to be studied on carbon electrode and is not so relevant for this report. The voltammogram (B) shows how fluorosilicate in LiF-KF-K₂SiF₆ (0.13mol/kg) melt are reduced at around -1V versus the Pt electrode. The anodic stripping peak that follows on the return scan is due to the oxidation of silicon. Consistent with the thermodynamic data, the reduction of fluorosilicate takes place at less cathodic potential than those of alkali metal fluorides [13]. To be sure that fluorosilicate is reduced, the concentration of K₂SiF₆ was increased and cyclic voltammetry was carried out. The results are plotted in Figure 19 below.



Figure 19: Cyclic voltammograms on Ag electrode at 0.13 and 0.26mol/kg of K_2SiF_6 at 750°C, sweep rate 200mV/s

The cyclic voltammograms above which is a plot of current vs. the potential indicated how concentration of K_2SiF_6 affects the reduction peak current. From Figure 19, it can be seen that as the concentration of K_2SiF_6 increases the reduction peak current increases. This increase in peak current is due to the diffusion controlled reduction of fluorosilicate, which is in accordance with the results reported by Boen and Bouteillon [13]. The reduction may be written as:

$$Si^{4+} + 4e^- \to Si \tag{24}$$

5.2.1.1 Mechanism of reduction of fluorosilicate from cyclic voltammetry

The Figure 20 below shows the cyclic voltammograms obtained on Ag electrode in LiF-KF- K_2SiF_6 (0.13mol/kg) at different sweep rates. It can be seen from Figure 20 that as the sweep rate increases the cathodic peak and anodic peak height increases. The cathodic current peak of each voltammogram is estimated at each sweep rate. Taking into account the area of the working electrode (Ag wire) which is $0.322cm^2$, the current density of each cathodic peak is calculated and the results shown in Table 1. The shape of the cathodic peak and the corresponding sharp anodic peak for the voltammograms shown in Figure 20 are typical features for a reaction with the formation or deposition of insoluble product on a suitable substrate, as was observed by Lepinay and Bouteillon [18].



Figure 20: Cyclic voltammograms on Ag electrode in LiF-KF-K₂SiF₆ (0.13mol/kg) at 750°C and different scan rate.

I _{pc} [A]	i _{pc} [Acm ⁻²]	-i _{pc} [Acm ⁻²]	v[V/s]	$v^{1/2}[(V/s)^{1/2}]$
-0.10	-0.31	0.31	0.02	0.14
-0.13	-0.41	0.41	0.05	0.22
-0.18	-0.56	0.56	0.10	0.32
-0.24	-0.76	0.76	0.20	0.45
-0.34	-1.06	1.06	0.50	0.71
-0.38	-1.18	1.18	0.70	0.84

Table 1: Cyclic voltammogram data for reduction of fluorosilicate in LiF-KF-K₂SiF₆ (0.13mol/kg) on Ag electrode at 750°C obtained from Figure 20.



Figure 21: Plot of cathodic peak current density vs. square root of sweep rate. The slope of the regression line is shown in the figure.

Figure 21 is used to find out if the reduction of fluorosilicate is diffusion controlled or not. A plot of the cathodic peak current density $(-i_{pc})$ vs. the square root of the sweep rate $(v^{1/2})$ gave a straight line almost passing through the origin indicating that reduction of fluorosilicate is purely diffusion controlled. The same result was reported by Osen et al [18].

5.2.1.2 Diffusion coefficient of fluorosilicate from cyclic voltammetry

Knowing the slope (S) of the regression line to be 1.2708 as shown in Figure 21, the diffusion coefficient can be calculated using equation (6) (Randles-Sevcik equation) to be $1.1x10^{-5}cm^2/s$. A detail of this calculation is shown in the appendix (E number 1)

5.2.2 Chronoamperometry



Figure 22: Chronoamperometry studies in LiF-KF-K₂SiF₆ (0.13mol/kg) on Ag electrode at 750° C and different cathodic potential.

Figure 22 shows current-time response at different cathodic potentials. These potentials are selected at the cathodic region of the voltammogram B shown in Figure 18. From Figure 22 it can be seen that at cathodic potential -800mV the current is approximately zero indicating that there is no reaction taking place. At cathodic potential -1100, -1130,-1150, -1180,-1200 and - 1250mV the current is not zero but rather shows several changes within the period of the experiment. The current-time response at these cathodic potentials is explained below. It can be observed form Figure 22 above that during the first few eighty microseconds the current increases cathodically resulting in charging of the double-layer capacitance. During this -

period of this current increase, there is build-up of supersaturation and formation of critical nuclei. The current then begins to decrease leading to the formation of stable nuclei (also known as growth centres). The nuclei are not thermodynamically stable until they exceed a certain critical size, which depends on the supersaturation of ad-atoms (i.e. the overpotential) [19]. During the period of current decrease the growth centres also increases in size as result of incorporating of atoms on them. The current flowing in each growth centre is proportional to its surface area. The current then becomes approximately constant with time. At this period with a constant current the nuclei grow at diffusion controlled rate. The diffusion process becomes essentially linear and the current decays according to the Cottrell equation.

5.2.2.1 Mechanism of reduction of fluorosilicate from chronoamperometry

Figure 23 which is a plot of the limit current density vs. the square root of inverse of time is use to investigate if a given electrochemical reaction is diffusion controlled or not. From the plot the reduction of fluorosilicate in LiF-KF-K₂SiF₆ (0.13mol/kg) is diffusion controlled since a straight line passing through the origin was obtained.



Figure 23: Plot of limit current density vs. square root of inverse of time at cathodic potential -1200mV. The slope of the regression line is shown in the Figure.

5.2.2.2 Diffusion coefficient of fluorosilicate from chronoamperometry

Using the equation (11) (Cottrell equation) diffusion coefficient of fluorosilicate is calculated to be $4.6x10^{-4}cm^2/s$ knowing the slope (S) of the regression line to be -1.1669. A detail of this calculation is shown in the appendices (E number 2).

5.3 Analysis of the deposits

5.3.1 Influence of temperature on silicon electrodeposition

	Т		i	t	Conc. K ₂ SiF ₆	m _{act}	m _{theo}	"CE"
Exp	[°C]	Substrate	[mA/cm ²]	[hrs]	[mol%]	[g]	[g]	[%]
А	800	Si	35.2	5	5	0.092	0.131	70
1	800	Ag	42.5	3	5	0.065	0.079	82
2	750	Ag	43.2	3	5	0.074	0.079	94
В	800	Si	35.8	5	5	0.094	0.131	72
3	550	Ag	42.6	3	5	0.063	0.079	80
4	550	Ag	41.5	3	5	0.059	0.079	75
С	800	Si	37.2	5	5	0.097	0.131	74
5	750	Ag	41.9	3	5	0.070	0.079	89
6	750	Ag	42.7	3	5	0.072	0.079	91

Table 2: Results for electrodeposition of silicon on Ag substrate at different temperatures.

Table 2 shown is the results and the electrolytic parameters that were used for electrodeposition of silicon in LiF-KF-K₂SiF₆ (5mol %) on silver electrode. The temperature for each electrodeposition experiment was different but other parameters such as concentration of K_2SiF_6 , and time was kept constant. The current density applied was almost constant. The slight difference in the current density is due the differences in the electrode area even though the current applied was constant. The actual mass of silicon deposited was obtained from difference in mass of the substrate and the mass of the substrate together with

the deposit and also the theoretical mass of silicon deposited obtained from Faraday's laws as well as the apparent current efficiency for the electrolytic process is shown in the table. The current efficiency obtained is not the true one because salts and other impurities contributed significantly. The salts were not completely removed when the deposits were cleaned in ultrasonic bath. From the table highest apparent current efficiency of 94% was recorded at 750°C (the detail of calculation of current efficiency is shown in the appendix C). The experiments marked A and B and C are the pre-electrolysis that were performed to remove moisture in the electrolyte and also to reduce the concentration of impurities in the melt to ppm level before the main electrodeposition experiments (1 and 2,), (3 and 4) and (5 and 6) respectively. Experiments 1 and 2, 3 and 4, 5 and 6 were carried in the same melt one after the other. Deposits obtained at 550 and 800°C were characterized by SEM and EDS and the results compared as shown below in Figure 24-28. The potential-time response (chronopotentiograms) for silicon electrodeposition at 550 and 800°C are shown in the appendices (G number 1).

All the EDS micrographs and spectrum were taken from the areas selected in the SEM micrographs.

5.3.1.1 SEM and EDS results for electrodeposition of silicon on silver substrates at 800 and 550°C.



Figure 24: Photograph of silicon deposits obtained on silver substrate at: (a) 800°C, (b) 550°C

The photograph 24 (a) and (b) above are silicon deposits obtained in LiF-KF-K₂SiF₆ on silver substrate at different temperatures 800°C and 550°C respectively. To have an idea about the size of the deposits a scale bar has been put in between them. As can be seen from the photograph the deposits look completely different. The morphology as well as the purity and elemental mapping were studied using SEM and EDS respectively. The results for the SEM and EDS analysis for the two deposits is compared as shown below.



Figure 25: SEM Micrographs of silicon deposits obtained on silver substrate at: (a) 800° C, (b) 550° C, time = 3hrs, average current density = 42mAcm⁻²



Figure 26: EDS Micrographs showing the distribution of the various elements: (a) 800° C, (b) 550° C



Figure 27: EDS spectrum of silicon deposit on silver substrate at temperature 800°C



Figure 28: EDS spectrum of silicon deposit on silver substrate at temperature 550°C.

At 800°C a thin blackish silicon deposit with coherent layer and good adhesion to the silver substrate was obtained but at 550°C a yellowish and powderish or dendritic silicon deposit was obtained (this can be seen in Figure 24). From SEM results shown in 25 (a) and (b) it can

be seen that at 800°C the microstructure of the silicon deposit consist of grains of similar sizes but at 550°C a non uniform spongy microstructure with hindered crystal growth was obtained. The low temperature of the substrate combined with the high current densities applied, probably hampered the growth of crystals. The low temperature affects the kinetics in the way that diffusion, charge transfer and especially crystal growth occurs at lower rates. The high current densities causes high rate of incorporation of Si (high mass transfer kinetics), so there is no time for allowing the crystals to grow [18]. From the EDS results shown in Figure 26 (a) and (b), 27 and 28 it can be seen that the deposit obtained at 800°C is pure with only small amount of salts inclusion whiles at 550°C the deposit contains a high content of salt which was difficult to remove when cleaned in ultrasonic bath. Generally the presence of F⁻, K⁺, Na⁺ and Li⁺ ions gives an indication of the salt content. From Figure 28, it is shown that at 550°C, a lot of fluorine is present, but neither K nor Li is detected. Lithium ion is too light to be detected by EDS; the fact that there is no K implies that the salt remains are mainly LiF. This would be consistent with the general idea that lithium salts are less soluble in water than potassium salts, and thus the hardest salt to be wash away. It can be seen in Figure 27 and 28 again that at 800°C more silicon was deposited in comparison to at 550°C. Figure 26 (a) and (b) also shows that at 800° C silicon were deposited homogenously compared to at 550° C.

5.3.1.2 Current efficiency as a function of temperature



Figure 29: Apparent current efficiency vs. temperature in LiF-KF-K₂SiF₆ (5mol %) at average current density: 42.4mAcm⁻² and time: 3 hours.

The Figure 29 above depicts how apparent current efficiency is influenced by temperature. It can be seen from the plot that apparent current efficiency increases as temperature increases but decrease beyond the optimum temperature (750°C). It can be seen from Figure 29 again that at a temperature 750°C the highest apparent current efficiency of 94% was recorded and then decline at temperature 800°C. The current efficiencies recorded are not the true one and therefore refer to it as apparent current efficiency because the deposits were found to contain salt which were difficult to remove completely by cleaning in ultrasonic bath as stated earlier. To be sure if this high value is truly achievable the experiment was repeated two more times and 89 and 91% apparent current efficiencies obtained at 750°C from the mean value (91.3%) is calculated to be $\pm 2.52\%$. This implies that the correct apparent current efficiency lies within the range 91.3 ± 2.52 . The detail of this calculation is shown in appendix (F number 1).

5.3.2 Influence of concentration of K₂SiF₆ on silicon electrodeposition

Table 3: Results for electrodeposition of silicon on Ag substrate at different concentrations of K_2SiF_6

	Т		i	t	Conc. K ₂ SiF ₆	m _{act}	m _{theo}	"CE"
Exp	[°C]	Substrate	[mA/cm ²]	[hrs]	[mol%]	[g]	[g]	[%]
D	750	Si	35.9	5	5	0.093	0.131	71
1	750	Ag	44.7	3	5	0.062	0.077	80
2	750	Ag	43.5	3	10	0.065	0.077	85
E	750	Si	37.3	3	5	0.096	0.131	73
3	750	Ag	40.1	3	15	0.071	0.077	92
4	750	Ag	39.8	3	15	0.069	0.077	89
5	750	Ag	42.4	3	20	0.042	0.077	74

Table 3 shows the results and the electrolytic parameters that were used for electrodeposition of silicon in LiF-KF-K₂SiF₆ on silver substrate. The effect of concentration of potassium fluorosilicate (K_2SiF_6) on silicon electrodeposition was studied. Other parameters such as

temperature and time were kept constant. The applied current density applied was almost the same for all the experiments. For experiments D and E the pre-electrolysis that was carried out for five hours before the main electrodeposition experiments (1, 2) and (3, 4 and 5) respectively. Experiments 1 and 2 were carried out in the same melt whiles 3, 4 and 5 also in the same melt one after the other. The actual and theoretical masses of silicon deposited and their corresponding apparent current efficiency for the electrolytic process are also shown in the table. The highest apparent current efficiencies calculated as apparent is because the salt inclusions contributed to the weight of silicon species deposited. The deposits obtained again contain traces of salts which were difficult to remove completely when cleaned in ultrasonic bath. The deposits were characterized with SEM and EDS. The results are compared as shown in Figure 30 to 34. Potential-time response (chronoamperometry) during electrodeposition at 20 and 5mol% K₂SiF₆ are shown in the appendices (G number 2).

5.3.2.1 SEM and EDS results for electrodeposition of silicon on silver substrates at 20 and 5mol% concentration of K₂SiF₆.



Figure 30: Photograph of silicon deposits obtained on silver substrate at: (c) 20mol%, (d) 5mol%.



Figure 31: SEM Micrographs of silicon deposits obtained on silver substrate at different concentrations of K_2SiF_6 : (c) 20mol%, (d) 5mol%.



Figure 32: EDS Micrographs showing the distribution of the various elements: (c) 20mol%, (d) 5mol%



Figure 33: EDS spectrum of silicon deposit on silver substrate at 20mol%



Figure 34: EDS spectrum of silicon deposit on silver substrate at 5mol%

From Figure 30 (c) and (d) it can be seen that a thick deposit was obtained at both 20 and 5mol% K₂SiF₆. The deposits obtained at these concentrations were weakly adhered to the

silver substrate. From Figure 31 (c) and (d) it can also be seen that at 20mol% of K_2SiF_6 the microstructure of the deposit seems to consist of elongated grains but at 5mol% a homogeneous structure with no grains was formed. Figure 33 shows that at 20mol % concentration of K_2SiF_6 an impure deposit with high content of salt inclusions which was not completely removed when cleaned in ultrasonic bath. From the same Figure it can be seen that the main salts that are likely to be present KF, K_2SiF_6 . LiF is also likely to be present; lithium is too light to be detected by the EDS. Figure 32 (d) shows that at 20mol% the impurities and the silicon deposited were not uniformly distributed in the deposit. Figure 34 indicate that at 5mol% concentration of K_2SiF_6 the deposit contains fewer impurities and salts inclusion; the only salt likely to be present is LiF provided Li is present. Figure 32 (c) and (d) indicates that at 5mol% the impurities, salts and silicon deposited are uniformly distributed in the deposit. Comparing Figure 33 and 34 it can be seen clearly that at 20mol% of K_2SiF_6 less silicon was deposited compared to 5mol% (40 and 60% silicon respectively).

5.3.2.2 Current efficiency as a function of concentration of K₂SiF₆



Figure 35: Apparent current efficiency vs. concentration of K_2SiF_6 at average current density: 42.4mAcm⁻² and time: 3 hours.

Figure 35 shows how the apparent current efficiency changes with the concentration of potassium fluorosilicate. It can be seen that the apparent current efficiency improved progressively as the K₂SiF₆ concentration increases from 5 to 15mol%, but beyond 15mol% the apparent current efficiency was lower. The highest apparent current efficiency of 92% was obtained at 15mol%. Due to limited time electrodeposition at 15mol% was repeated just once and 89% apparent current efficiency was obtained. A standard deviation of $\pm 2.12\%$ has been calculated from the mean apparent current efficiency (90.5) at 15mol%. This implies the true apparent current efficiency lies with the range 90.5 ± 2.12 . The detail of this calculation is also shown in the appendix (F number 2).

5.3.3 Influence of current density on silicon electrodeposition

Table 4: Results for electrodeposition of silicon on Si and Ag substrates at different current densities, constant temperature and concentration of K_2SiF_6

	Т		i	t	Conc. K ₂ SiF6	m _{act}	m _{theo}	"СЕ"
Exp	[°C]	Substrate	[mA/cm ²]	[hrs]	[mol%]	[g]	[g]	[%]
F	795	Si	35.5	5	5	0.096	0.131	73
	795	Si	27.8	9.5	5	0.177	0.249	71
1	795	Ag	42.9	3	5	0.066	0.079	84
	795	Si	35.5	3	5	0.060	0.079	76
G	795	Si	35.5	5	5	0.093	0.131	71
	795	Si	58.6	9.5	5	0.498	0.498	75
2	795	Ag	83.8	3	5	0.144	0.157	92
	795	Si	80.5	3	5	0.124	0.157	79
Н	795	Si	35.5	5	5	0.097	0.131	74
	795	Si	81.4	9.5	5	0.575	0.747	77
3	795	Ag	122.7	3	5	0.200	0.236	85
	795	Si	101.5	3	5	0.172	0.236	73
Ι	795	Si	35.5	5	5	0.093	0.131	71
	795	Si	11.1	9.5	5	0.076	0.124	61
4	795	Ag	17.2	3	5	0.028	0.039	72
	795	Si	14.2	3	5	0.025	0.039	63

Table 4 shows the results obtained for studying the effect of current density on silicon electrodeposition on both silver and silicon substrates. Parameters such as temperature $(795^{\circ}C)$, concentration of K₂SiF₆ (5mol %) and time (3hours) were kept constant. On silicon substrate electrodeposition was carried out at different times as can be seen from the table but due to limited time allocated for this thesis this was not studied in details. This will be considered in my further studies in this area of research. Experiments F, G, H and I are the pre-electrolysis that was performed for five hours before the main electrodeposition experiments in the melt (1, 2, 3 and 4) respectively. As can be seen from the table in each melt three successive electrodeposition experiments were performed one after the other. The deposits were characterized using SEM and EDS. The results for SEM and EDS are compared as shown in Figures 36 to 40. The potential-time response (chronopotentiograms) during the electrodeposition experiments are shown in the appendices (G number 3)

5.3.3.1 SEM and EDS results for electrodeposition silicon on silicon substrate at 101.5 and 35.5mAcm⁻².



Figure 36: Photograph of Si deposits on Si substrate at current densities: (e) 101.5mAcm⁻², (f) 35.5mAcm⁻²

The photograph above is silicon deposits obtained on silicon substrates at different current densities stated bove. The morphology, purity and elemental mapping of the deposits is respectively determined by SEM and EDS. The results are compared as shown below.



Figure 37: SEM micrographs of Si deposits on Si substrate at current densities: (e) 101.5mAcm⁻², (f) 35.5mAcm⁻²



Figure 38: EDS Micrographs showing the distribution of the various elements: (e) 101.5mAcm⁻², (f) 35.5mAcm⁻²


Figure 39: EDS spectrum of silicon deposit on silicon substrate at 101.5mAcm⁻²



Figure 40: EDS spectrum of silicon deposit on silicon substrate at 35.5mAcm⁻².

It can beeb seen from Figure 37 and photograph 36 (e) show that at higher current density 101.5mAcm^{-2} a thick deposit with no grains and dendritic was formed. The deposit was weakly adhere to the silicon substrate .At current density of 35.5mAcm^{-2} it can be seen in Figure 36 (f) that thin blackish deposit was formed. It can also be seen in Figure 37 (f) that at 35.5mAcm^{-2} the deposit contains large grains with a columnar structure (see appendix I). Figure 38 (f) shows that at 35.5mAcm^{-2} the deposit obtained was highly porous (porosity is the dark regions shown in the micrograph). Comparing Figure 39 and 40 it can see that at higher current density 101.5mAcm^{-2} the deposit contains less silicon and more impurities but at 35.5mAcm^{-2} it contains a high content of silicon and less impurities. Figure 39 again shows that at 101.5mAcm^{-2} that the salts likely to be present are KF, K₂SiF₆ and LiF provided Li is present. As mentioned earlier Li is too light to be detected by EDS. Figure 43 also indicate that at 35.5mAcm^{-2} the only salt likely to be present is LiF (if Li is present) since no K was detected. Figure 38 (e) and (f) shows that at 101.5 mAcm^{-2} the impurities and silicon are homogeneously distributed in the deposits.

5.3.3.2 SEM and EDS results for electrodeposition of silicon on silver substrate at 83.8 and 42.9mAcm⁻².



Figure 41: Photograph of Si deposits on silver substrate at current densities: (g) 83.8mAcm⁻², (h) 42.9mAcm⁻²

The deposits above does not differ much in dimension compared to those with scale bar.



Figure 42: SEM micrographs of Si deposits on silver substrate at current densities (g) 83.8mAcm⁻², (h) 42.9mAcm⁻²

The scale for the SEM micrographs 42 (g) and (h) is the same as the ones already explained above or as shown in Figure 47 (i) and (j).



Figure 43: EDS Micrographs showing the distribution of the various elements: (g) 83.8mAcm⁻², (h) 42.9mAcm⁻²



Figure 44: EDS spectrum of silicon deposit on silicon substrate at 83.8mAcm⁻².



Figure 45: EDS spectrum of silicon deposit on silicon substrate at 42.9mAcm⁻²

From Figure 41 (g) and (h) it can be seen that at 83.8mAcm⁻² a thick gray deposit was obtained but at 42.9mAcm⁻² a thin blackish deposit was formed. The deposits obtained at these current densities were strongly adhered to the silver substrate. Figure 42 (g) and (h) show that the deposit obtained at 83.8mAcm⁻² consist of fine microstructure but at 42.9mAcm⁻² it consist of bigger and elongated grains. It can be seen from Figure 44 and 45 also that at current density 83.8mAcm⁻² the deposit contains a high content of impurities and salt inclusions. The salts likely to be present are KF, K₂SiF₆ and LiF (if Li is present) but at current density 42.9mAcm⁻² the deposit contains less impurities and salt inclusions which is likely to be only LiF again if Li found to be present. The deposit obtained at 42.9mAcm⁻² contains higly porosity compared to that obtained at 83.8mAcm⁻² (porosity is the dark regions shown in the micrograph 43(h)).

5.3.3.3 SEM and EDS results for electrodeposition of silicon on both silicon and silver substrate.



Figure 46: Photograph of silicon deposits on different substrates: (i) Si, 80.5mAcm⁻² (j) Ag, 83.8mAcm⁻²

Figure 46 (i) is silicon deposit on silicon substrate at current density 80.5mAcm⁻² and (j) on silver substate at at current density 83.8mAcm⁻². The comparison of these deposits is basically based on the influence of the substrates since all parameters were kept almost constant. SEM and EDS results are compared as shown below.



i. j. Figure 47: SEM micrographs of Si deposits on: (i) Si substrate, (j) Ag substrate



Figure 48: EDS Micrographs of silicon deposits on: (i) Si, 80.5mAcm⁻², (j) Ag, 83.8mAcm⁻²



Figure 49: EDS spectrum of silicon deposit on silicon substrate



Figure 50: EDS spectrum of silicon deposit on silver substrate

As can be seen in Figure 46, the deposit obtained on silver and silicon substrate at 83.8 and 80.5mAcm^{-2} are gray in colour. The deposit on silver substrate was found insoluble and strongly adhered to the silver substrate but that on silicon substrate was soluble and weakly adhered to the silicon substrate which resulted in excessive loss of deposit when cleaned in ultrasonic bath. Again the microstructure of the deposit on silicon substrate is non uniform and dendritic with no grains but on silver substrate it consist of fine grains as shown in Figure 47 (i) and (j) respectively. From Figure 49 and 50 it can be seen that the deposit obtained on both silicon and silver substrate consists of high impurities and salt inclusions which can possibly be KF, K₂SiF₆ and LiF (if Li is present). It can be seen clearly in Figure 49 and 50 that on silicon substrate less silicon was deposited as compared to that on silver substrate (2 and 35% silicon respectively).

5.3.1.1 Current efficiency as a function of current density





Figure 51 above depicts how current density influences current efficiency (apparent) for electrodeposition of silicon on silver substrate. For the first experiment it can be seen that the apparent current efficiency increases as current density increases but begins to decrease beyond the optimum current density (83.8mAcm⁻²). The highest apparent current efficiency obtained at 83.8mAcm⁻² is 92% which decreases to 85% at current density 122.7mAcm⁻². To find out the consistency in these reported apparent current efficiencies the whole experiment was repeated. The trend observed for the second experiment looks quite different than the first experiment. For the second experiment the apparent current efficiency increases as the current density increases and then remains almost constant. Comparing the two sets of experiments it can be seen that the apparent current efficiencies obtained at the same current densities do not differ much implying that the apparent current efficiency reported seems quite reliable.



Figure 52: Plot of current efficiency vs. current density for electrodeposition of Si on Si substrate.

Figure 52 shows how current efficiency (apparent) changes with current density for electrodeposition of silicon on silicon substrate. For the first experiment it can be seen that increasing current density leads to an increase in the apparent current efficiency but decline at the optimum current density (80.5mAcm⁻²). The apparent current efficiency at the optimum current density is 79% which decreases to 73% at current density 101.5mAcm⁻². Electrodeposition at 35.5 and 80.5mAcm⁻² was repeated (referred to as 2nd experiment shown

in Figure 52) and 70 and 75% apparent current efficiencies were recorded respectively but 76 and 79% apparent current efficiencies were recorded at 35.5 and 80.5mAcm⁻² respectively for the first experiment. The difference in the apparent current efficiency for the first and second experiment is quiet significant and therefore this need further investigation.

CHAPTER 6

6.0 DISCUSSIONS

6.1 Temperature gradient

Performing the temperature gradient experiment to detect the exact height to position the glassy carbon crucible was a wise decision because placing the crucible at any height could have created a lot of difficulties or affected the experimental results since the temperature along the height of the salt was likely to have been different. I strongly recommend that temperature gradient experiment need to be considered necessary when carrying out any experiment where the system to be studied need to be placed in a vertical furnace.

6.2 Electrochemical measurements

Even though electrochemical techniques such as cyclic voltammetry and chronoamperometry were not the main objective of this work, it was found very necessary because reduction mechanism, nucleation and growth fluorosilicate in the melt were understood by studying these techniques. Cyclic voltammetry performed in the pure melt (LiF-KF) resulted in cathodic a limit which is around -1.7V (referring to Figure 18 voltammogram A) versus the platinum reference on using silver electrode. The low cathodic limit obtained in comparison to the thermodynamic value for LiF-KF (4.8V) is in accordance with the results reported by Bouteillon, Osen [13, 18]. This can be explained by the depolarization of potassium ion reduction as a result of incorporation or insertion of potassium ion in silver. The low cathodic limit gave an indication that there is the presence of impurities of the base metal ions (Li⁺ and K^+) and oxygenated specie (F) and therefore pre-electrolysis to reduce the concentration of these ions in the melt before the main electrodeposition experiment was very necessary. Cyclic voltammetry in LiF-KF-K₂SiF₆ (0.13mol/kg) on Ag electrode shows fluorosilicate reduction around -1V (see Figure 18 voltammogram B) versus the Pt reference electrode, which is in accordance with the results reported by Osen et al [18]. The question that came to mind is, is fluorosilicate indeed reduced? This was verified by increasing the concentration of the electroactive species K₂SiF₆ from 0.13 to 0.26mol/kg and again performing cyclic voltammetry. The voltammograms (see Figure 19) at these two concentrations indicates that as the concentration of K₂SiF₆ increases the cathodic peak current also increases due to diffusion controlled reduction of fluorosilicate, which is in accordance with the results reported by Boen and Bouteillon [13]. The reduction mechanism of the fluorosilicate was studied in LiF-KF-K₂SiF₆ (0.13mol/kg) on Ag electrode. Cyclic voltammetry was performed at different sweep rates and the plot of the current (I) recorded versus the potential (E) at different sweep rates gave a voltammograms (see Figure 20) in which the cathodic and anodic currents increased as the sweep rate increased. The plot of the cathodic peak current density (i_{pc}) vs. the square root of sweep rate ($v^{1/2}$) gave a straight line that passes almost through the origin (see Figure 21) indicating that the reaction is diffusion controlled. The same result was reported by Osen et al [18]. The diffusion coefficient of fluorosilicate in LiF-KF-K₂SiF₆ (0.13 mol/kg) at 750°C was calculated from the Randles-Sevcik equation to be $1.1 \times 10^{-5} \text{ cm}^2/\text{s}$ which is in excellent agreement with diffusion coefficients for ions (typically 10^{-5} cm²/s) [30]. Chronoamperometry was also performed in LiF-KF-K₂SiF₆ (0.13mol/kg) on Ag electrode at 750°C for different cathodic potentials. The current-time response (see Figure 22) obtained shows that at low the cathodic potentials (-800mV) no reaction occurred but between (-1100 to -1250mV) it seems that nucleation and growth occurred. At the maximum current nucleation is said to have occurred. Growth (silicon electrodeposition) is also described to have occurred when the current became constant within a certain period of time. Chronoamperometry was also employed to study the reduction mechanism of fluorosilicate. The plot of the limiting current density vs. the square root of inverse of time $(t^{-1/2})$ gave a straight line that passes through the origin (see Figure23). This is an indication that the reduction mechanism is diffusion controlled as was found in the case of cyclic voltammetry. From chronoamperometric data, the diffusion coefficient of the fluorosilicate was calculated using the Cottrell equation to be $4.6 \times 10^{-4} \text{ cm}^2/\text{s}$. This order of magnitude for the diffusion coefficient of fluorosilicate in LiF-KF-K₂SiF₆ (0.13mol/kg) at 750°C is much higher (about 46 times) than diffusion coefficient of ions in molten salts (typically10⁻⁵cm²/s) [30]. The diffusion coefficient of fluorosilicate in LiF-KF-K₂SiF₆ (0.13mol/kg) obtained from cyclic voltammetry looks more reliable than that from chronoamperometry when compared diffusion coefficient of ions.

5.3 Electrodeposition

5.3.1 Effect of temperature

The influence of temperature on the morphology and purity of silicon films or deposits as well current efficiency on silicon electrodeposition in LiF-KF-K₂SiF₆ (5mol %) at average current density of 42.4mAcm⁻² for three hours on Ag substrate was studied. It was observed that at higher temperature (800°C) the deposit obtained consist of dense, coherent layer with good adhesion to the silver substrate, and less impurities and salt inclusions (refer to Figure 26 (a) and 27). EDS and SEM results also shows that the microstructure seems to be columnar with homogeneous distribution of silicon (referring again Figure 26 (a)). This is in accordance with the results reported by Boen and Bouteillon, and Osen et al [13, 18]. The high purity, and nodular structure and homogeneous distribution of silicon appear favourable for direct use of the films in solar cells because of the increase area for sunlight absorption and less impurities trapping at impurities at the recombination centres to minimize the reduction of the efficiency of the solar cells. The deposit obtained at 550°C will not be good to be used in solar cell because it was powdered in nature with high content of salt and impurities and non uniform distribution of silicon (refer to Figure 26 (b) and 28) in comparison to that at 800°C. The current efficiency at each temperature was calculated (details of the calculation is shown in appendix C). The current efficiencies obtained at each temperature are described to be apparent because of the salt remains which were difficult to be removed completely in ultrasonic bath. Referring to the definition of current efficiency as shown in equation 17, the mass of the silicon obtained is high because of the contribution of the salt. The high masses of silicon recorded lead to the high current efficiencies recorded. A plot of the apparent current efficiency vs. temperature shows that as temperature increases the apparent current efficiency also increases but falls beyond the optimum temperature (750°C). The same observation was reported by Shama and Mukherjee [17] when studying the influence of temperature on electrodeposition of silicon in LiF-KF-K₂SiF₆ (15mol %) on graphite electrode and recorded a high current efficiency of about 98% at 750°C. It seems that not much work has been done in the determination of the current efficiency dependency on temperature for electrodeposition of silicon in fluoride melts using silver electrode. An apparent current efficiency of about 94% was recorded at the 750°C which declined to74% at 800°C. Due to limited time for this work only the electrodeposition of silicon at 750°C was verified. The electrodeposition of silicon at the optimum temperature was repeated two more times and 91 and 89% apparent current efficiency was recorded. A standard deviation of about $\pm 2.52\%$ (details of the calculation is shown in appendix F number 1) was calculated from the mean apparent current efficiency (91.3%). The apparent current efficiency decrease at 800°C was presumably due to lowering of K₂SiF₆ concentration by volatilization. A large quantity of condensate was observed beneath the radiation shield (see appendix H). Gopalkrishna M. et al. [14] had reported some loss in weight of LiF-KF binary eutectic containing 13.7mol% K₂SiF₆ at working temperature of 1018K and suggested that the weight loss was due to volatilization of K₂SiF₆. Another possibility for the loss in apparent current efficiency at 800°C is due to the potential drop that persisted for about 2000 seconds during the electrodeposition (see appendix G number 1).

5.3.2 Effect of concentration of K₂SiF₆

The concentration of the electroactive species K_2SiF_6 has a significant influence on the morphology and purity of the deposit as well as the current efficiency of silicon electrodeposition in LiF-KF-K₂SiF₆ (5mol %) on Ag substrate at a temperature of 750°C, average current density of about 42.1mAcm⁻². The deposits obtained at 20 and 5 mol% concentration of K_2SiF_6 were compared. The deposit obtained at 20mol% consisted of elongated grains, high content of impurities and salt inclusion (see Figure 31(c) and (33)) and found weakly adhered to the Ag substrate. The silicon deposited was found not to be uniformly distributed (see Figure 32(c)). The deposit at 5mol% was pure with less content of impurities and salts (see Figure 32(d)). The less impurities and salt content and homogenous distribution of silicon makes it more useful in solar cell because of the high possibility for sunlight absorption in comparison to the deposit at 20mol%. The weakly adhered deposit obtained at these concentrations may possibly be due to secondary reactions between the deposited silicon and the melt as proposed by Gopalakrishna M. et al [13], this can be written as:

$$\operatorname{Si} + \operatorname{Si}^{4+} \leftrightarrow \operatorname{Si}^{2+}$$
 (25)

The plot of the apparent current efficiency vs. the concentration of K_2SiF_6 (see Figure 35) indicated that as the concentration increases the apparent current efficiency also increases but decreases at 20mol%. The possible reason for the decline in current efficiency at 20mol% could be due to chemical dissolution of deposited silicon in the electrolyte as was observed by Shama and Mukherjee [17]. The highest apparent current efficiency of 92% was recorded at 15mol% concentration of K_2SiF_6 . To verify that this high apparent efficiency is realistic the electrodeposition at 15mol was repeated and 89% was obtained given a standard deviation of $\pm 2.12\%$ (details of the calculation shown in appendix F number 2). Shama and Mukherjee [17] reported the same trend for current efficiency as a function of concentration of K_2SiF_6 for electrodeposition of silicon in fluoride melts on graphite electrode. The highest current efficiency of about 95% was reported at 15mol% Shama and Mukherjee [17]. Again it looks like there is not much work done on the influence of concentration of K_2SiF_6 on current efficiency for electrodeposition of silicon in LiF-KF-K_2SiF_6 (mol %) on Ag electrode.

5.3.3 Effect of current density

The influence of current density on morphology and purity of the deposit and current efficiency of the electrodeposition of silicon in LiF-KF-K₂SiF₆ (5mol %) at 750°C on silicon and silver substrate was also studied. On silicon substrate it was found that a high current density (101.5mAcm⁻²) the deposit formed was impure with high content of salt inclusions and powder or dendritic in nature with no grains but at low current density (35.5mAcm⁻²) the deposit consists of large grains and high porosity (show as dark regions on the micrograph) (see Figure 38 (f)). The deposit obtained at 35.5mAcm⁻² is likely to be suitable for direct use in solar cell because of its columnar structure (see appendix I) which will enhance sunlight absorption but the drawback is its high porosity which e recombination centres to trap impurities thereby reducing the efficiency of the solar cell. The powder or the dendritic deposit at high current density is possibly due secondary reaction between alkali metal deposited by the primary deposition as observed by Dodero [14]. This can be written as:

$$4\mathbf{K} + \mathbf{S}^{4+} \leftrightarrow \mathbf{S}\mathbf{i} + 4\mathbf{K}^{+} \tag{26}$$

From Figure 52, it can been seen that apparent current efficiency improved progressively as the current density increases from 14.2 to 80.5mAcm⁻² but decreases at 101.5mAcm⁻². The

highest apparent current efficiency of about 79% was calculated. Electrodeposition at 35.5 and 80.5mAcm⁻² was repeated to determine if the apparent current efficiency calculated is reliable or not. From Figure 52, it can seen that the apparent current efficiencies recorded differ much and therefore the values obtained do not seem to be reliable and therefore this will be considered in my further studies in this area of research. The reason for the decrease in apparent current efficiency at 101.5mAcm⁻² is due to loss of parts of the deposits during when cleaned in ultrasonic bath because at 101.5mAcm⁻² the deposit was powdered in nature and weakly adhered to the silicon substrate.

For electrodeposition of silicon in LiF-KF-K₂SiF₆ (5mol %) at 795°C on Ag substrate, the current density applied is within the range from 17.2 to 122.7mAcm⁻². The deposits obtained at 83.8 and 42.9mAcm⁻² were characterized using SEM and EDS. At 83.8mAcm⁻² the deposit consist of fine microstructure, high content of impurities and salts inclusions but at 42.9mAcm⁻² it consisted of bigger and elongated grains with a columnar structure and less content of impurities and salts. The deposit obtained at 42.9mAcm⁻² will be more useful in solar cells because of it high purity and columnar structure which will enhance sunlight absorption. The presence of porosity in the deposits at 42.9mAcm⁻² is likely to reduce the efficiency of the solar cells because it will act as recombination centres to trap impurities. The apparent current efficiency recorded increases with increasing current density and decreases beyond the optimum current density (83.8mAcm⁻²). The highest apparent current efficiency recorded is 92% but decreases to 85% at 122.7mAcm⁻². The decrease in current efficiency at high current density is due to losses of parts of the observed during cleaning of the deposit in ultrasonic bath and electrodeposition experiment. This could be due the fact that the deposit formed was porous, powdered or dendritic and weakly adhered to the silver substrate. The of loss of deposits during the electrodeposition experiment was seen as a decrease in potential (see appendix G number 3). The whole experiment was repeated and it was found that the apparent current efficiencies recorded in both sets of experiment (1st and 2nd) were consistent (see Figure 51)

5.3.4 Effect of substrate

The influence of the substrate was studied making sure all electrolytic parameters such as temperature (795°C), time (3hours), and current density (80.5 and 83.8mAcm⁻² on silicon and silver substrate respectively) are maintained as constant as possible. It was found that on

silver substrate the deposit formed was insoluble, uniform with fine grains and strongly adhered to the silver substrate but on silicon substrate the deposit was not uniform, soluble and weakly adhered to the silicon substrate. Silicon deposit on silver substrate been insoluble was in consistent with the results reported by Bouteillon et al [13]. According to Cohen et al [18] the less uniform deposit on silicon substrate is because the current distribution on silicon will be uniform due to its poor conductivity. It is expected that the electrical conductivity of silicon should be high at these temperatures set for this work. Silver appears to be a better cathode material than silicon, silicon is reactive at 750°C with other metals and reacts even with carbon. Even though silver is expensive, in commercial process the deposit could be stripped off and the silver re-used. Due current density applied (80.5 on Si and 83.8mAcm⁻² on silver substrate) the deposits obtained on both substrates were impure with a high content of salt inclusions. This implies that it is better to compare the two substrates at low current densities.

CHAPTER 7

7.0 CONCLUSIONS

The reduction mechanism, nucleation and growth of silicon species in LiF-KF-K₂SiF₆ (0.13mol/kg) were successfully studied by employing cyclic voltammetry and chronoamperometry. It was found that the reduction of silicon species is diffusion controlled. Silicon was successfully electrodeposited on both silver and silicon substrate in the melt LiF-KF-K₂SiF₆ (mol %) at all the electrolytic parameters range set for this work. It was observed that at high temperatures, low current densities and low concentration (5mol %) of K₂SiF₆ and less time yield a quality deposit with less impurities and salt inclusions, well-adhered to the substrate, columnar microstructures and homogeneous distribution of silicon deposited. Combination of the following electrolytic parameters gave a quality deposit: Temperature (750-800°C), concentration (5mol %), time (3 hours), current density (15-40mAcm⁻²), substrate (Ag). To be sure whether or not the deposit obtained from the above mentioned parameters range can be used directly in solar cells other properties such as resistivity, concentration of the trace elements and grain size need to be checked. Silver was found to be the best substrate in comparison to silicon for silicon electrodeposition since silver yield insoluble deposits. The current efficiency determined in each electrodeposition experiment was consistently high, but the values were a little too high because of the inclusions of salts from the electrolyte. Even though the deposits were cleaned in ultrasonic bath, the salt inclusions were not completely removed.

For this work direct current electrolysis was applied for the electrodeposition of silicon in LiF-KF-K₂SiF₆ (mol %). I recommend that pulse current electrolysis, resistivity, concentration of trace elements and grain size measurements need to be considered for further research. Effect of time on the morphology, purity and current efficiency of the electrolytic process also need to be considered for further studies .Nucleation and growth of the silicon in LiF-KF-K₂SiF₆ (mol%) need to be studied in details. Reduction steps (one or two) of fluorosilicate need to be checked.

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APPENDICES

APPENDIX A



SEM with in-built EDS detector used at material science department of NTNU



Si deposits on Ag substrate mounted on sample holder

APPENDIX B



Schematic drawing of the set up for electrodeposition experiment

APPENDIX C

Calculation of current efficiency

The current efficiency obtained for each electrodeposition is said not to be the true one because of the salt remains which was difficult to remove when cleaned in ultrasonic bath and therefore refer to it as the apparent current efficiency.

The apparent current efficiency can be calculated as follows:

Consider electrodeposition experiment marked 2 in table 1. The theoretical mass can be calculated using equation 20 shown in the theory section.

I = 0.1A, n=4 (Si⁴⁺+4e⁻ \rightarrow Si), F=96485, M_{Si} = 28.09gmol⁻, t = 3hrs

$$m_{theo} = \frac{0.1x3x60x60}{4x96485}x28.09 = 0.079g$$

Knowing the actual mass m_{act} to be 0.074g, the apparent current efficiency can be calculated using equation (19)

$$"_{CE}" = \frac{0.074}{0.079} x100 = 93.7\% \approx 94\%$$

The same procedure was used for the calculation of "CE" in all electrodeposition experiments and pre-electrolysis as well.

APPENDIX D

Calculation of the bulk concentration $\boldsymbol{C}^{\!\!\infty}$

The density of equimolar LiF-KF at different temperatures is as shown below.

Temperature [°C]	Density [g/cm ³].
700	1.885
800	1.832
900	1.778
1000	1.724
1100	1.671
1200	1.617

Table 5: Density of equimolar LiF-KF at different temperatures

A plot of temperature vs. density gives a straight line shown below. The equation of the line is also shown in the plot. At 750°C the density of LiF-KF can be calculated as:

$$d = -0.0005T + 2.2606$$
$$d = 1.8856g/cm^3$$

Knowing the density the bulk concentration can be calculated.

$$C^{\infty} = \frac{(0.13x1.8856)}{1000}$$

$$C^{\infty} = 0.000245 mol/cm^3$$



Plot of density vs. temperature for equimolar LiF-KF

APPENDIX E

Calculation of diffusion coefficient

1. From cyclic voltammetry data

From equation (24) n = 4, the bulk concentration $C^{\infty} = 0.000245 \text{ mol/cm}^3$ as shown above.

$$D^{1/2} = \left(\frac{(RT)^{1/2} \cdot S}{0.6105(nF)^{3/2}C^{\infty}}\right)$$
$$D = \left(\frac{(8.314x1023)^{1/2}x1.2708}{0.6105(4x96485)^{3/2}x0.000245}\right)^2$$
$$D = (3.268x10^{-3})^2$$
$$D = 1.068x10^{-5}cm^2/s$$

Hence the diffusion coefficient of silicate ion in LiF-KF-K₂SiF₆ (0.13mol/kg) at 750°C is $1.068 \times 10^{-5} cm^2/s$

2. From chronoamperometry data

n = 4. The bulk concentration $C^{\infty} = 0.000245 \text{mol/cm}^3$

$$D = \left(\frac{\pi^{1/2} x S}{n F C^{\infty}}\right)^2$$

$$D = \left(\frac{(3.142)^{1/2}x - 1.1669}{4x96485x0.000245}\right)^2$$

$$D = 4.596 x 10^{-4} cm^2/s$$

Hence the diffusion coefficient of silicate ion in LiF-KF-K₂SiF₆ (0.13mol/kg) at 750°C is $4.596 \times 10^{-4} cm^2/s$

APPENDIX F

Error analysis

1. Standard deviation (S) for electrodeposition at 750°C

Temperature has been found to be an influencing parameter for electrodeposition of silicon in fluoride melts (Table1). Temperature 750°C was found to be the optimum since the highest

apparent current efficiency of 94% was obtained and further increase in temperature leads to a decline in the apparent current efficiency. 89 and 91% apparent current efficiencies were obtained when the experiment was repeated two more times. The standard deviation in these apparent efficiencies is calculated as shown below.

Mean apparent current efficiency (\overline{x}) = $\frac{94+91+89}{3} = 91.3\%$

x	$(x-\overline{x})$	$(x-\overline{x})^2$
94	2.7	7.29
91	-2.3	5.29
89	-0.3	0.09
		$\sum (x - \overline{x})^2 = 12.67$

Table 6: Standard deviation from the mean apparent current efficiency at 750°C

Standard deviation can be calculated from the formula [29]: $\sqrt{\frac{\sum (x-\overline{x})^2}{n-1}}$

where \overline{x} , x and n are the mean apparent current efficiency, apparent current efficiencies and the number of experiments respectively.

$$S = \sqrt{\frac{12.67}{(3-1)}} = 2.52$$

Hence the apparent current efficiency at $750^{\circ}C = 91.3 \pm 2.52\%$

2. Standard deviation (S) at 15mol% concentration of K₂SiF₆

Electrodeposition at the optimum concentration of K_2SiF_6 or 15mol% was carried repeated and the possible apparent current efficiency obtained is 92 and 89%. The standard deviation is calculated as follows. Mean apparent current efficiency (\overline{x}) = $\frac{92+89}{2}$ = 90.5%

x	$(x-\overline{x})$	$(x-\overline{x})^2$
92	1.5	2.25
89	-1.5	2.25
		$\sum (x - \overline{x})^2 = 4.5$

Table 7: Standard deviation from the mean apparent current efficiency at 15mol% K₂SiF₆

$$S = \sqrt{\frac{4.5}{(2-1)}} = 2.12$$

Hence the apparent current efficiency at $15 \text{mol}\% = 90.5 \pm 2.12$

APPENDIX G

Potential-time response (chronopotentiograms) during silicon electrodeposition

1. Effect of temperature



Potential – time response for electrodeposition of Si on Ag electrode at 800° C



Potential – time response for electrodeposition of Si on Ag electrode at 550° C

2. Effect of concentration



Potential – time response for electrodeposition of Si on Ag electrode in LiF-KF- K_2SiF_6 (20mol %)



Potential – time response for electrodeposition of Si on Ag electrode in LiF-KF-K₂SiF₆ (5mol %)

3. Effect of current density



Potential – time response for electrodeposition of Si on silicon substrate at 35.5mAcm⁻²



Potential – time response for electrodeposition of Si on silver substrate at 83.8mAcm⁻²



Potential – time response for electrodeposition of Si on silver substrate at 42.9mAcm⁻²



Potential – time response for electrodeposition of Si on silver substrate at 122.7mAcm⁻²

APPENDIX H



Condensates after high temperature (800°C) electrodeposition experiment

APPENDIX I



Columnar structure of deposit obtained on silicon substrate at 35.5mAcm^{-2}