Electrodeposition of Silicon from Fluorosilicic Acid Produced in Iraqi Phosphate Fertilizer Plant

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ABSTRACT :

The availability, low toxicity, and high degree of technological development make silicon the most likely material to be used in solar cells, the cost of solar cells depends entirely on cost of high purity silicon production. The present work was conducted to electrodeposite of silicon from K_2SiF_6 , an inexpensive raw material prepared from fluorosilicic acid (H_2SiF_6) produced in Iraqi Fertilizer plants, and using inexpensive graphite material as cathode electrode. The preparation of potassium fluorosilicate was performed at (60°C) in a three necks flask provided with a stirrer, while the electro deposition was performed at 750°C in a three-electrodes configuration with melt containing in graphite pot. High purity potassium fluorosilicate (99.25%) was obtained at temperature (60°C), molar ratio-KCl/ H_2SiF_6 (1.4) and agitation (600 rpm). Spongy compact deposits were obtained for silicon with purity not less than (99.97%) at cathode potential (-0.8 V vs. Pt), K_2SiF_6 concentration (14% mole percent) with grain size (130 μm) and level of impurities (Cu, Fe and Ni) less than (0.02%).

Keywords : Silicon, Potassium fluorosilicate, Fluorosilicic acid, Electrodeposition, Molten salt

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1. Introduction

Silicon is an important material in modern semiconductor technology and finding increased use in solar cells for photovoltaic generation of electricity. High-efficiency solar energy conversion has long been the subject of intense attention because this process is environmentally friendly and does not disturb the thermal balance of the planet. The cost of raw material-high purity silicon is to about 20% of the cost of silicon solar modules. To make solar cells less expensive, it is necessary to reduce either the cost of the raw material or the silicon consumption in the fabrication of solar cells. In light of this, reducing the cost of silicon for solar cell continued to be a challenge.¹⁾

In recent years there has been considerable interest in the electrodeposition of silicon from molten salts, the major reason is the highly purity of crystals prepared for photovoltaic application.²⁾ Progress in silicon electrodeposition and possible application of the electrolytic silicon has been reviewed by a number of authors.^{3,4,5,6)} The preparation of high purity silicon could be achieved either by Silica-based or fluorosilicate-based electrolytes. The electrodeposition of silicon from silica-based electrolyte has been reviewed by Monnier.⁷⁾ The melt compositions most likely to serve as electrolytic bathes are molten silicates or solutions of SiO_2 in cryolite at temperature (1370-1450°C). In addition to high temperature, the high purity silicon required the use of a two-stage cell. Electrowinning occurred in the first stage, the cathode of which formed the anode of the second stage.

The electro deposition of silicon from solution of K_2SiF_6

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in the binary LiF/KF or the ternary LiF /NaF/KF (Flinak) eutectics is potentially of considerable importance as an inexpensive method for producing elemental silicon. It is very attractive because 99% pure K_2SiF_6 can be produced cheaply from fluorosilicic acid, an inexpensive by-product of phosphate fertilizer production, and it has been demonstrated that inclusion free silicon films of high purity could be deposited from these solutions.⁸⁾ On the other hand, the deposition of silicon layers on electrically conducting low cost substrate would be a very promising approach to reduce the material processing cost of solar cells.

The first successful attempts to deposit silicon electrochemically were performed by Ullik,⁹⁾ using K_2SiF_6 dissolved in molten KF at temperatures in excess of (1000°C), but detailed study of silicon electrodeposition was not performed until 1960 s by Monnier *et al.*,¹⁰⁾ they employed graphite cathode in their studies and yielded up to (99.99%) pure silicon, but the deposits were in general, powdery and incoherent and required a subsequent separation process to remove entrapped solvent. The deposition of silicon films at temperatures lower than 1000°C using K_2SiF_6 began at the Stanford university center for material research in the early seventies by Cohen *et al.*¹¹⁾ They demonstrated epitaxial silicon electrodeposition on crystalline silicon substrates from a molten KF/LiF solution at temperature as low as 750°C. Although they studied several fluoride solvent systems, only LiF/KF and LiF/KF/NaF melts gave acceptable quality deposits. Deposition rates, however, were relatively low at 1 $\mu\text{m/hr}$, so the method could not be considered as available production method for photovoltaic material. Cohen prepared polycrystalline silicon film onto a metal cathode which is essentially non - alloying with silicon (e.g. Silver and niobium) at 750°C and constant cathode current density 2 mA/cm^2 , the silicon deposits were of large grain diameter (20-50 μm) with good uniformity and adherence.¹²⁾ Rao *et al.*¹³⁾ studied the electrowining of silicon from K_2SiF_6 - Molten fluoride systems at 745°C. After they tried graphite, niobium, nickel, and silver as cathode materials, they recommended using silver as cathode material because of its very low reactivity with silicon in comparison with other materials used. Deposits of silicon up to 3 mm thick were obtained at K_2SiF_6 concentration of (4-6 mole%) having a columnar structure with grain size up to 100 μm . (1 mm) thick dense, well-adherent silicon was successfully deposited at $(-0.75 \pm 0.05 \text{ V vs. pt.})$ using an inexpensive graphite from K_2SiF_6 /LiF-KF molten salt system at $(745 \pm 5^\circ\text{C})$,¹⁴⁾ the polycrystalline silicon has a columnar structure with

normal grain size of (250 μm), the impurities detected were Cu, Fe, and Ni of levels less than 0.005%. A parallel study by Olson *et al.* for the electrorefining of silicon using K_2SiF_6 - Molten fluoride systems at (750°C) and metallurgical grades silicon anode was achieved.¹⁵⁾ A polycrystalline silicon deposits were obtained but with purity lower than those prepared by Rao *et al.*¹³⁾ They stated that the use of Silicon: Cu_3Si semi permeable anode as the silicon source enhanced the purification process.

A Comparison between silver and graphite as cathode materials have been done by Rao *et al.*¹⁶⁾ using K_2SiF_6 /LiF-KF molten salt system, they obtained (4 mm) thick deposition on silver and (2 mm) thick on graphite for two and four days respectively at constant potential of $(-1.73 \pm 0.03 \text{ V vs. pt})$ on silver and $(-0.75 \pm 0.05 \text{ V vs. pt})$ on graphite. They stated that electrodeposition appears to be one of the most promising methods for producing silicon of acceptable purity and cost for solar cell Fabrication. Elwell *et al.*⁴⁾ investigated the mechanism of electrodeposition of silicon from K_2SiF_6 -Flinak using cyclic voltammetry data for stationary and rotating electrodes. They concluded that electron transfer is the main rate. controlling mechanism but that solute diffusion cannot be neglected. The interface process is proceeded by a chemical reaction, probably dissociation of poly nuclear $\text{Si}_n\text{F}_{2n+2}^{+2}$ complex.

Boen *et al.*¹⁷⁾ studied the electrodeposition of silicon in Fluoride melts, they got silicon films at higher rate (30 $\mu\text{m/hr}$). Stern *et al.*¹⁸⁾ deposited of silicon onto Inconel (76 wt%Ni-16 wt%Cr-8 wt%Fe) from the ternary eutectic LiF-NaF-KF containing K_2SiF_6 at 750°C, they found that extensive diffusion of the alloy constituents into the silicon takes place. Moore *et al.*¹⁹⁾ used electrodeposition technique in depositing thin films of silicon on several substrates (MA-Si and metal - coated ceramics), films were grown at temperatures ranging from (750-850°C) at current density between 20-150 mA/cm^2 . They deduced that using large area deposition techniques could be made the process a cost-effective for producing crystalline silicon films suitable for solar cells. The aim of the present work is to determine the ability of electrowining high purity silicon on a low cost substrate(graphite) using potassium fluorosilicate prepared from fluorosilicic acid produced in Iraqi phosphate fertilizer plant.

2. Experimental Work

2.1. Preparation of potassium fluorosilicate

fluorosilicic acid solution from Iraqi phosphate fertilizer

plant in "UKASHAT" location was used in this study. The concentration of this solution was (220 g/l), and having a level of impurities as shown in Table 1. This solution was filtered to remove any suspended solid impurities. A solution containing 40 g (0.537 mol) of potassium chloride in 250 ml dionized water was prepared in Pyrex flask and heated to 60°C. The hot solution was added slowly with stirring to 250 ml fluorsilicic acid (220 g/l, 0.382 mol) at 60°C for 1 hr. A precipitate formed. The mixture was allowed to cool and was then vacuum filtered using puchner filter connected with diaphragm pump equipped with two liquid traps. The solids recovered were rinsed with distilled water, dried in a vacuum oven at 150°C to obtain 60.2 g (71% of theory) of potassium fluorosilicate. Samples of prepared material were characterized for their purities and average particle size. The chemical analysis is shown in Table 2 where purity not less than 99.25% was obtained.

2.2. Electrodeposition of silicon

Binary LiF/KF eutectic(m.p. 492°C) was used, this solvent has the advantages of high conductivity, Low viscosity, high decomposition voltage, and high solubility for oxides which tend to form on the electrode surface.¹⁷⁾

Table 1. Impurity analysis of fluorosilicic acid

Element	Concentration. (ppm)
AL	15
As	21
Fe	28
K	25
Cu	180
Na	320
Mg	72
Zn	31
Ni	10
Pb	24

Table 2. Chemical Analysis of the prepared potassium fluorosilicate

Index name	Index	Index name	Index
Potassium fluorosilicate (K_2SiF_6), %	99.25	Mg, %	0.005
Iron (Fe), %	0.02	Cl, %	0.14
Zn, %	0.007	Cu, %	0.016
Pb, %	0.006	Ni, %	0.011
AL, %	0.02	Average Particle size	73 μm

LiF and KF used were 99.5% (anhydrous), mixed and dried first under flowing argon for several hours prior to fusion, the fused solvent were cooled then K_2SiF_6 was added. The resulting solution was purified by pre-electrolysis for 1 hr under high potential. The electrodeposition was performed at (750°C) in a three . electrodes configuration.

The electrolytic cell consisted of two parts: graphite pot with dimensions (diameter "D" = 10 cm, length "L" = 17 cm) and cover made from poly tetrafluoroethylene (PTFE). Graphite rod with dimensions (D = 1 cm, L = 25 cm) was used as cathode. the graphite rod was enclosed by Teflon screwed tube fixed at the center of cell cover. This assembly provides the mean to lowering and rising the cathode inside the melt. The cover provided with inlet and outlet Teflon tubes for charging and discharging of Argon gas. The inlet tube was connected internally with ceramic tube (D = 8 mm, L = 12 cm) for bubbling argon gas. The graphite pot was used as anode and surrounded at the upper part with copper coils for cooling this part of graphite pot and preventing the damage of Teflon cover. An insulation material inserted between the graphite pot and cover. The cover was tighten with graphite pot by Teflon clamps. A platinum reference electrode was used to measure the cathode potential. Fig. 1 shows the electrolytic cell used in the present work. The electrolysis was achieved using linear voltammetry

Fig. 1. Schematic diagram of electrolysis cell.

with Scan rate = 100 mV/sec.

At the end of electrolysis, a compact spongy deposits of silicon covered by a film of eutectic mixture were obtained which removed from cathode surface, the salt adhering to the deposit were removed by digesting in hot distilled water for 10 hr, followed by ultrasonic cleaning in water, then ethanol for 15 min.

The compact deposits of the final run were pulverized and re-digested in hot distilled water for 4 hr. to remove any access entrapped salts ,filtered then dried under vacuum at 80°C .Samples of prepared silicon were taken and analyzed by EDX and Emission spectrographic for determine their purity. The morphology of deposits was investigated by scanning electron microscopy analysis.

3. Results and Discussion

3.1. Polarizations curves

Fig. 2 shows the polarization curves for electrodeposition of silicon from K_2SiF_6 -KF/LiF system at different concentrations of potassium fluorosilicate (mole present). The general form of the current/potential curves (polarization) for the system is represented as a plot of log current against cathode potential versus platinum reference electrode.

It can be seen that the current increases with increasing K_2SiF_6 concentration. The effect is more pronounced for concentrations between (5-10%) but a slightly increasing in current for concentration between (10-14%) has been

Fig. 2. The cathodic portion of polarization curve for silicon electrodeposition Scan rate = 100 mV/sec, temperature (750°C), KF/LiF(58 g/26.5 g).

occurred. Therefore it is not recommended to use concentration of K_2SiF_6 higher than (14%) or lower than (10%).The former gives higher potential of cell (6.5 V) with no significant increasing in current so large of energy will be dissipated. The later gives lower current yield.

3.2. Effect of cathode potential on the purity of silicon

Table 3 illustrates the effect of cathode potential on the purity of silicon prepared for 6 (hr) potentiostatic operations.

It is cleared that higher electrode potential leads to higher impurity in the prepared silicon and non uniformity or dendrite deposits .Reducing the cathode potential to (-0.8 V) was found to give coherent and strongly adherent deposits. Figs. 3 and 4 show the scanning electron micrograph of deposits at (-0.8 V) and (-1.25 V) vs. Pt respectively. Larger grain size up to (70 μ m) was obtained at (-0.8 V) in comparison with (20 μ m) for electrode potential (-1.25 V).The impurities with a high deposition potential than silicon will be co-deposited with silicon at high potential .The increase in impurity concentration in irregular deposits at higher potentials was confirmed by Rao *et al.*¹³⁾

The most common impurities were Cu, Fe, Ni and Li with a total concentration less than 0.06% at electrode potential -0.8 V(vs. Pt) .The source of Li could be from

Table 3. Effect of electrode potential on the purity of silicon electrodeposited

Electrode potential V(vs. Pt)*	-0.5	-0.8	-1.0	-1.25
Purity (%)	99.98	99.94	99.87	99.7

*Temperature (750°C), KF/Li F(58 g/26 g), K_2SiF_6 conc.(14%)

Fig. 3. The scanning electron micrograph of silicon deposited at -0.8 V (vs. Pt) K_2SiF_6 conc.(14%) (EHT = 20.00 Kv, WD = 9.0 mm, Signal = SE1).

Fig. 4. The scanning electron micrograph of silicon deposited at -1.25 V (vs. Pt), K_2SiF_6 conc.(14%) (EHT = 20.00 Kv, WD = 9.0 mm, Signal = SE1).

Fig. 5. The scanning electron micrograph of silicon deposited at -0.8 V (vs. Pt), K_2SiF_6 10% (EHT = 20.00 Kv, WD = 9.0 mm, Signal = SE1).

the entrapped melt since LiF, a major component of melt, is highly insoluble in water or acids, and is therefore not easily removed from deposit during cleaning. The purity of electrodeposits, greater than 99.94%, must be compared with a purity of only 99.25% for starting material employed in the melt preparation. Therefore it is recommended to operate the system at cathode potential more positive than or equal -0.8 V (vs. Pt) to reduce the contaminants by ion metals present in the melt.

3.3. Effect of K_2SiF_6 concentration on the purity of silicon

Table 4 shows the effect of potassium fluorosilicate concentration on the purity of silicon prepared for 6 hr potentiostatic operation at cathode potential (-0.8 V vs. Pt). The results indicate a higher purity of silicon obtained with decreasing K_2SiF_6 concentration. Concentrations lower than 10% are not recommended because the current decreased rapidly. The purity was improved at 10% but the grain size of deposit was lowered as shown in Figs. 3 and 5 where a higher grain size ($70\ \mu\text{m}$) obtained at concentration equal to (14%) in comparison with ($63\ \mu\text{m}$) for (10%) concentration.

The aim of the present work as mentioned previously was to electrodeposition of high purity silicon on to a low cost graphite substrate in bulk form with large grain

size using K_2SiF_6 prepared from H_2SiF_6 . Therefore, an experiment where achieved at -0.8 V vs. Pt and 14% K_2SiF_6 for 48 hr. Spongy compact deposits were obtained with net amount (2 g). Figs. 6 and 7 show the EDX, and scanning electron micrograph of the prepared sample.

The sample has a purity of 99.97% with impurities analysis as shown in Table 5. Grain size of ($130\ \mu\text{m}$)

Fig. 6. The EDX of silicon deposited at -0.8 V (vs. Pt), K_2SiF_6 14%.

Fig. 7. The scanning electron micrograph of silicon deposited at -0.8 V (vs. Pt), 14% K_2SiF_6 (EHT = 20.00 Kv, WD = 9.0 mm, Signal = SE1)

Table 4. The effect of potassium fluorosilicate concentration on the purity of silicon

K_2SiF_6 Conc.(%)*	14	12	10
Purity(%)	99.67	99.96	99.99

*Temperature (750°C), KF/LiF(58 g/26 g), cathode potential(-0.8 V vs. Pt)

Table 5. Impurities Analysis of the prepared silicon

Element	Li	Fe	Cu	Ni	Pb
Conc. (%)	0.009	0.007	0.008	0.004	0.003

was detected, larger grain size were common in deposits produced over several days of the electrolysis involving large charge densities or high potential. The iron content in prepared silicon is (0.007%) and would not seriously degrade the solar cell performance.

4. Conclusions

Potassium fluorosilicate were obtained from H_2SiF_6 produced as a by - product in Iraqi phosphate fertilizer plant with purity 99.25% at 60°C with maximum conversion (71% of theory), the impurities analysis showed Fe content 0.02% which makes the prepared material more suitable to use as a raw material for silicon electrodeposition. High purity deposits of silicon onto graphite have been obtained by the electrolysis of K_2SiF_6 -KF/LiF system at 750°C and condition have been determined for the deposition of spongy compact deposits for two days of electrolysis. The characteristics required of a polycrystalline silicon for use in photovoltaic are individual grains of at least (100 μm) to yield an efficiency photovoltaic greater than 10% and relative absence of impurities that would give rise to deep-level recombination centers. The silicon electrodeposited onto graphite in the present work has a grain size of (130 μm) and total impurities level of 0.02% for Cu, Fe and Ni. The electrodeposition technique in the present research has the potential to yield solar grade silicon at lower cost by using graphite as cathode material which appears highly promising as an inexpensive substrate for the deposition of silicon and using low cost high purity K_2SiF_6 prepared from fluorosilicic acid produced in Iraqi phosphate fertilizer plants.

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