

Influence of Different Electrolysis Parameters on Silicon Thin Film Electrodeposition

Lord Famiyeh¹, Prof. Geir Maartin Haarberg²

^{1,2}Department of Material Science and Engineering, Norwegian University of Science and Technology, NO-7491, Trondheim, Norway

Abstract: Preparation of silicon thin films by electrodeposition using an inexpensive raw material potassium fluorosilicate (K_2SiF_6) has proven to be low cost method compared to the tradition way of manufacturing silicon wafers for solar cell applications. The purpose of this work is to study the effect of electrolysis parameters such as temperature of the melt ($LiF-KF-K_2SiF_6$) (450 to 800°C), concentration of potassium fluorosilicate (5 to 30 mol%), and current density (17.5 to 122.5 mAcm⁻²) on morphology and purity level of silicon films prepared on silver substrate. The current efficiency (CE) of the electrolytic process was determined in three replicate experiments and the average found in the range from 53 to 92%. At 800°C, the films prepared were dense with coherent layer and had good adhesion properties with fewer impurities and inclusion free whiles at low temperatures in the range from 450 to 550°C the films were found containing only few traces of silicon and several salt inclusions. Despite acceptable quality deposits were obtained at high temperatures the current efficiency was found decreasing as temperature increases with maximum current efficiency obtained at 650°C. At low concentrations (5 to 10 mol%) the deposits prepared had uniform surfaces and contain only few impurities and salt inclusions. Silicon films with columnar structure and fewer impurities were obtained at current densities in the range from 17.5 to 52.6 mAcm⁻². The morphology and impurities was determined using SEM with EDS system.

Keywords: Electrodeposition, silicon wafers, electrolysis, morphology, current efficiency current density, columnar, SEM/EDS.

I. INTRODUCTION

Development of clean energy sources as an alternative to fossil fuel has become a major concern in the world today because burning of fossil fuel pollute our environment and cause global warming by emission of greenhouse gases such as carbon dioxide (CO₂), nitrogen oxides (NO_x), sulphur oxides (SO_x), and particulate matter (PM). It has been predicted that fossil fuel for electricity generation will be extremely scarce and expensive in the future as it becomes depleted. Renewable energy has the advantage of being constantly replenished and therefore provides a sustainable clean energy supply compared to fossil fuel. Solar power is an ideal energy solution, which theoretically has the capacity to meet the world's energy demand. The major drawback with the use of solar energy is the high price of solar-cells in the world today. Even though prices of solar-cells keep on decreasing, it is still not cheaper in comparison to the conventional methods of generating electricity. The high price of solar-cells in the world today is due to the high cost contribution from the production of polysilicon by Siemens process [1]. In order to make solar cells more accessible and cheaper it is important that production costs reduced and efficiency improved significantly [2].

Silicon thin films can be obtained on surfaces of substrates by electrodeposition for it to be used directly as wafers for solar cell applications. Electrodeposition of silicon has relatively recent history dating back only to the 1970s [3]. Electrodeposition 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. Electrodeposition of silicon 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 means of conveniently producing large area samples at low cost by making use of a technique which is readily adapted to industrial production.

In electrodeposition of silicon using high temperature furnace electric current is usually applied between the electrodes immersed in the electrolyte. For example when current is applied between a dissolving silicon anode, cathode materials such as silver, graphite, tungsten, and niobium and reference electrode such as coiled platinum wire silicon is electrodeposited. In this work silicon is electrodeposited on Ag substrate using alkali metal fluoride (LiF-KF) (m.p. 492°C) as the electrolyte and potassium fluorosilicate (K_2SiF_6) as electroactive source of silicon. The electrolyte LiF-KF was selected for this work because of its 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 decreases the diffusion controlled effect responsible for porous, dendritic and powdery growth of silicon films [2], [4]. Potassium fluorosilicate appears very promising electroactive source of silicon for this type of work because of its low cost and availability, and low volatility [5]. Silver was used as the cathode material because of its very low reactivity with silicon in comparison with other materials such as graphite, nickel, niobium, and tungsten [2].

II. MATERIALS AND METHODS

A. Chemical preparation:

The alkali metal fluorides lithium fluoride (LiF) and potassium fluoride (KF), and source of silicon potassium fluorosilicate (K_2SiF_6) were heated to dry and stored at 250°C. This is to ensure that moisture and other volatile impurities are removed before used for this work. The chemicals were usually grounded into fine powder to ensure complete mixing. The KF becomes difficult to ground because the individual particles coagulates during heating whiles LiF and K_2SiF_6 still remains dry and separate after heated at 250°C.

B. Electrochemical cell and analysis of deposits:

The electrochemical cell consists of the following: dissolving silicon anode (5cm long and 1x1cm cross section), cathode materials (silver (1mm thick (99.9% pure)), and reference electrode (0.5mm in diameter coiled platinum wire). The schematic diagram of the electrochemical cell used in this study is similar to that presented by Abbar et. al [2]. During electrodeposition the electrodes are usually immersed in a glassy carbon crucible container containing the electrolyte LiF-KF and silicon source K_2SiF_6 . The electrochemical cell is covered by a dense graphite cap with alumina tubes that allow loading of potassium fluorosilicate, and has holes for the cathode and reference electrode. There are three sintered alumina cemented radiation shield that support the electrodes and the alumina tubes. Before the start of each electrodeposition, pre-electrolysis was usually carried out at either 800°C or 750°C for 5 hours to remove moisture and reduce the level of impurities in the fluoride melt LiF-KF- K_2SiF_6 using silicon plate as cathode material. The silicon films deposited on Ag substrate were cleaned in ultrasonic bath to remove salt inclusions. The morphology and impurities was determined using SEM with EDS system. The current efficiency of the electrolytic process was determined by weighing the amount of silicon deposited and compared to the theoretical weight of silicon calculated using Faraday's laws of electrolysis.

III. RESULTS AND DISCUSSIONS

The influence of temperature of the melt (LiF-KF- K_2SiF_6), concentration of K_2SiF_6 , and current density on silicon thin film electrodeposition was successfully studied. This work focuses mainly on the impact of these parameters on the morphology, purity level, and current efficiency of the electrolytic process.

The temperature of the melt was varied in the range from 450 to 800°C whiles other parameters were kept constant (Table 1). The slight difference in the current densities is due to the slight differences in the electrode area.

TABLE 1: Effect of temperature on electrodeposition of silicon from LiF-KF-K₂SiF₆

Exp	T(°C)	Substrate	j [mA/cm ²]	t[hrs]	Conc. K ₂ SiF ₆ [mol%]	M _{act} [g]	M _{theo} [g]	CE
1	800	Ag	42.8	3	5	0.059	0.079	75
2	750	Ag	42.5	3	5	0.062	0.079	78
3	650	Ag	43.1	3	5	0.070	0.079	89
4	550	Ag	42.8	3	5	0.060	0.079	76
5	500	Ag	42.9	3	5	0.058	0.079	74
6	450	Ag	42.6	3	5	0.051	0.079	65

1, 2, 3, 4, 5, and 6 represents silicon electrodeposition on Ag substrate, pre-electrolysis carried out in 5 hours on Si substrate before the start of each electrodeposition experiment, j = current density, t = duration of electrodeposition, M_{act} = actual weight of silicon deposited, M_{theo} = theoretical weight of silicon calculated using Faraday's laws of electrolysis, CE = average current efficiency calculated as $[(M_{act}/M_{theo}) \times 100]/3$. Each electrodeposition experiment was carried out in three replicates. All parameters were kept constant as temperature varied in the range from 450 to 800°C.

It was observed that at high temperatures 750°C and 800°C the films formed were dense with coherent layers, good uniformity and compact deposits, and contains less impurities and salt inclusions. This is in accordance with the results reported by Boen *et. al* [4] and Sende *et. al* [6]. The high purity, the nodular structure, and homogeneous distribution of silicon deposits makes these films favourable for direct use in solar cell applications because of their increase surface area for sunlight absorption and less impurities trapping at the recombination centres which could enhance the solar cell efficiency. The films obtained at low temperatures (450-550°C) were found containing low content of silicon (Fig. 1) and brownish powdered in nature with high content of salt inclusion (fluoride ions) and calcium ions impurities. The Fig. 2 shown below is a photograph of deposits obtained on Ag substrate at a high temperature (800°C) and a low temperature (550 °C).

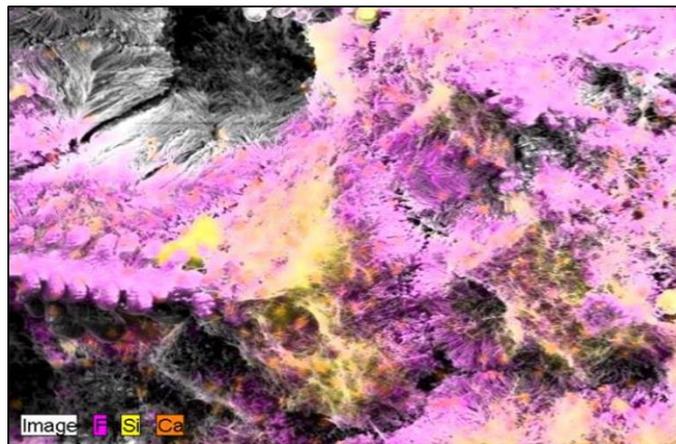


Fig 1: EDS mapping of major elements (F, Si, and Ca) obtained on silver substrate at 550 °C. Purple: F, Yellow: Si, Orange: Ca

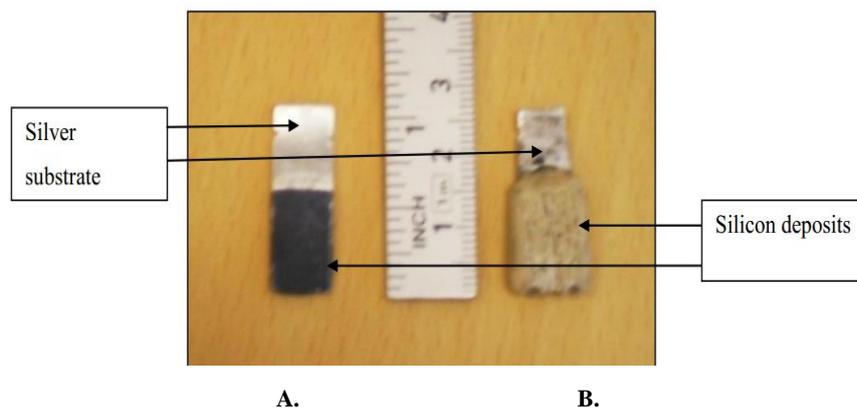


Fig 2: Photographs of deposits obtained at high and low temperatures: (A) 800°C, and (B) 550 °C

As temperature of the melt increases the current efficiency also increases reaching maximum at 650°C and decreases as temperature increases to beyond this temperature (Fig. 3). Shama *et. al* reported similar observation when studying the influence of temperature on electrodeposition of silicon in LiF-KF-K₂SiF₆ (15 mol %) on graphite electrode [7]. The low current efficiency obtained at high temperatures 750 °C and 800°C could be due to lowering of the concentration of K₂SiF₆ by volatilization, and also the potential drop that persisted in few minutes during the electrolysis. A large quantity of condensate of fluoride melt was observed beneath the radiation shield of the electrolytic cell which is an indication that at very high temperatures volatilization of the melt occurs and therefore electrodeposition of silicon in fluoride melts should not be carried out at very high temperatures, and also at very low temperatures which gives powdery and dendrite deposits. Rao *et. al* reported weight loss of LiF-KF containing 13.7 mol% K₂SiF₆ at working temperature of 745°C and also suggested that the weight loss is as a result of volatilization of K₂SiF₆ [8].

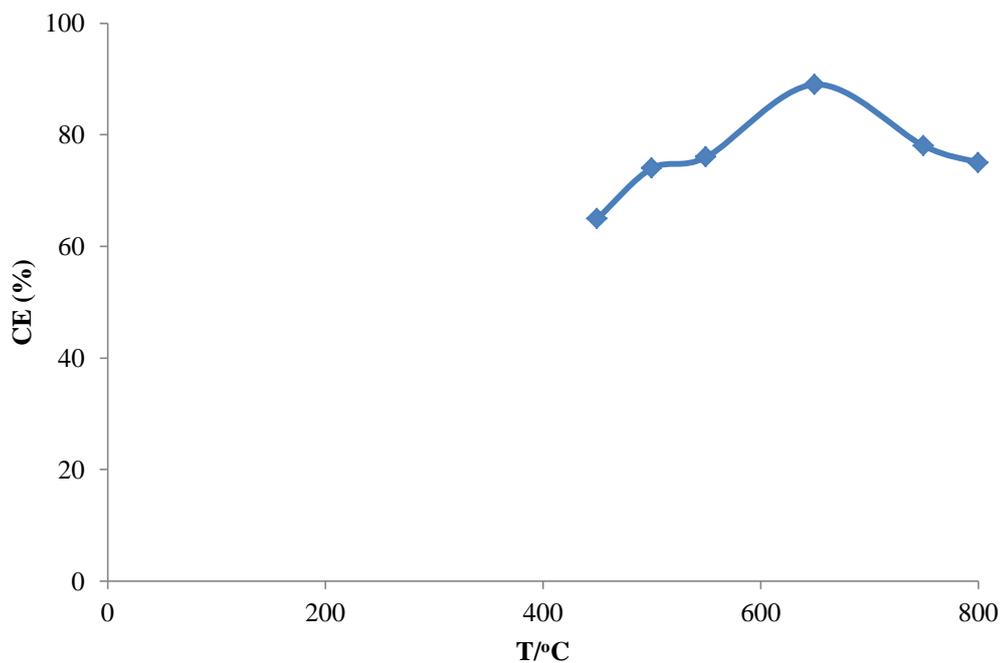


Fig 3: Current efficiency variations as a function of the temperature of the fluoride melt.

The concentration of potassium fluorosilicate was varied in the range from 5 to 30 mol% whiles temperature, and current density were kept constant (Table 2). At high concentrations (15 to 30 mol%), the films formed consists of elongated grains, high content of impurities and salt inclusions and also found weakly adhered on silver substrate whiles at low concentrations (5 to 10 mol%) the deposits prepared were found to contain only few impurities and salt content, and with good uniformity and adherence.

TABLE 2: Effect of concentration of potassium fluorosilicate on silicon electrodeposition from fluoride melt

Exp	T(°C)	Substrate	j[mA/cm ²]	t[hrs]	Conc. K ₂ SiF ₆ [mol%]	M _{act} [g]	M _{theo} [g]	CE
7	750	Ag	42.8	3	5	0.062	0.079	78
8	750	Ag	42.5	3	10	0.073	0.079	92
9	750	Ag	43.5	3	15	0.069	0.079	87
10	750	Ag	42.8	3	20	0.059	0.079	75
11	750	Ag	42.9	3	25	0.057	0.079	72
12	750	Ag	42.8	3	30	0.055	0.079	70

7, 8, 9, 10, 11, and 12 represents silicon electrodeposition on Ag substrate, pre-electrolysis carried out in 5 hours on Si substrate before the start of each electrodeposition, j = current density, t = duration of electrodeposition, M_{act} = actual weight of silicon deposited, M_{theo} = theoretical weight of silicon calculated using Faraday's laws of electrolysis, CE =

average current efficiency calculated as $[(M_{act}/M_{theo}) \times 100]/3$. Each electrodeposition experiment was carried out in three replicates. The concentrations of K_2SiF_6 varied in the range from 5 to 30 mol % while other parameters were kept constant.

The weakly adhered deposits obtained in the concentration range from 15 to 30 mol% could be due to a secondary reaction that usually occurs between silicon deposits and silicon ions in the fluoride melt as proposed by Rao *et. al* [8]. The secondary reaction can be written as: $Si + Si(IV) \leftrightarrow Si(II)$.

A high current efficiency of 92% was obtained at 10 mole percent concentration of K_2SiF_6 (Fig. 4) and decreases continuously as potassium fluorosilicate concentrations increases in the concentration range from 15 to 30 mol%. The possible reason for the decline in the current efficiency at these high concentrations could be due to chemical dissolution of silicon deposits in fluoride melt as predicted by Shama *et. al* [7].

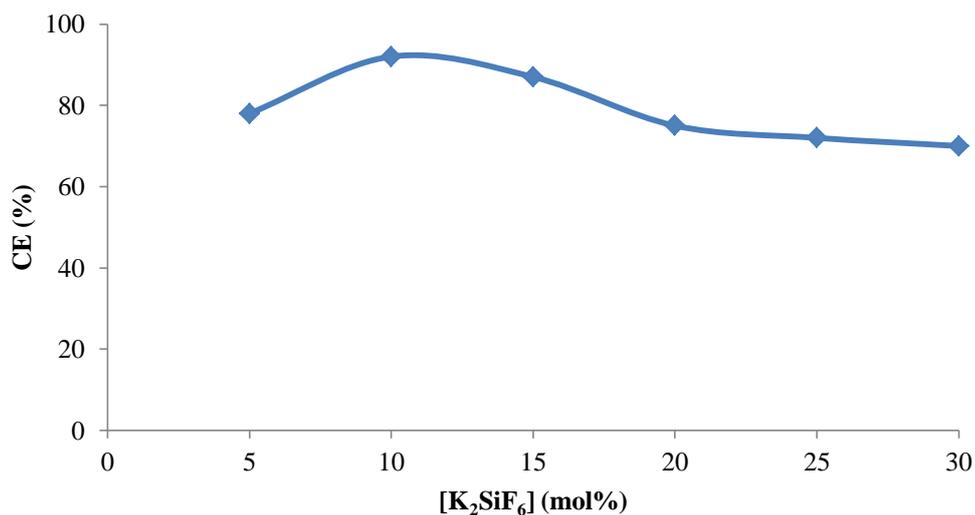


Fig 4: Current efficiency variations as a function of the concentration of potassium fluorosilicate.

The effect of current density in the range from 17.5 to 122.5 $mAcm^{-2}$ on silicon electrodeposition from $LiF-KF-K_2SiF_6$ was successfully studied, other parameters were kept constant (Table 3). At current densities in the range from 17.5 to 52.6 $mAcm^{-2}$, silicon films with columnar structure and high purity were prepared. The columnar structure has the tendency to enhance sunlight absorption capacity of the films and therefore seems to be good for solar cell applications.

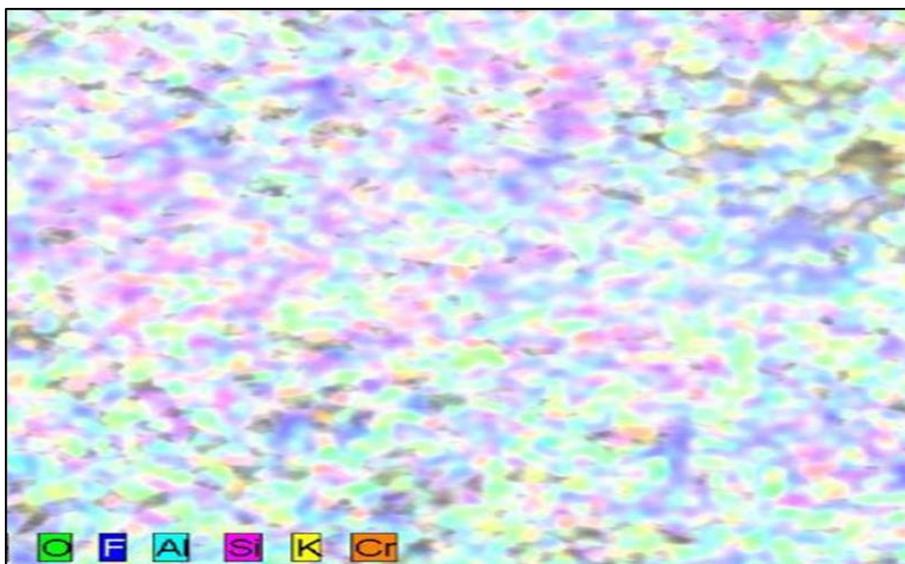


Fig 5: EDS mapping of major elements (O, F, Al, Si, K, and Cr) obtained at 90.5 $mAcm^{-2}$. Green: O, Deep blue: F, Light blue: Al, Pink: Si, Yellow: K, Orange: Cr

At high current densities in the range from 70.8 to 122.5 mAcm⁻² the deposits formed were powdered and dendritic in nature with only few traces of silicon deposits and high content of impurities (Fig. 5). The high current density might have caused the alumina tubes to melt or dissolve increasing the level of Al impurities detected. The powdered deposits formed could be due to a secondary reaction that usually occurs between alkali metal deposited via primary deposition and silicon ions in the electrolyte [8]. The secondary reaction can be represented by the equation: $4K + Si(IV) \leftrightarrow Si + 4K(I)$.

TABLE 3: Effect of current density on silicon electrodeposition from fluoride melt

Exp	T(°C)	Substrate	j[mA/cm ²]	t[hrs]	Conc. K ₂ SiF ₆ [mol%]	M act[g]	M theo[g]	CE
13	750	Ag	17.5	3	5	0.025	0.033	75
14	750	Ag	35.8	3	5	0.059	0.066	90
15	750	Ag	52.6	3	5	0.071	0.098	72
16	750	Ag	70.8	3	5	0.088	0.132	67
17	750	Ag	90.5	3	5	0.108	0.168	64
18	750	Ag	122.5	3	5	0.121	0.228	53

13, 14, 15, 16, 17, and 18 represents silicon electrodeposition experiment, pre-electrolysis carried out in 5 hours on Si substrate before the start of each electrodeposition experiment, j = current density, t = duration of electrodeposition, M_{act} = actual weight of silicon deposited, M_{theo} = theoretical weight of silicon calculated using Faraday's laws of electrolysis, CE = average current efficiency calculated as $[(M_{act}/M_{theo}) \times 100]$. Each electrodeposition experiment was carried out in three replicates. All parameters were kept constant while current density varied in the range from 17.5 to 122.5 mAcm⁻².

A maximum current efficiency of 90% was obtained at 35.8 mAcm⁻² and decreases continuously as current density increases (Fig. 6). The decrease in current efficiency at high current density could be due to the powdered nature and weakly adherent of the deposits to substrates. This might have caused part of the deposits to be lost during ultrasonic cleaning in hot water bath affecting the weight of silicon deposited. The low current efficiency at high current densities could also be associated to the significant potential drop that occurred during the electrolysis.

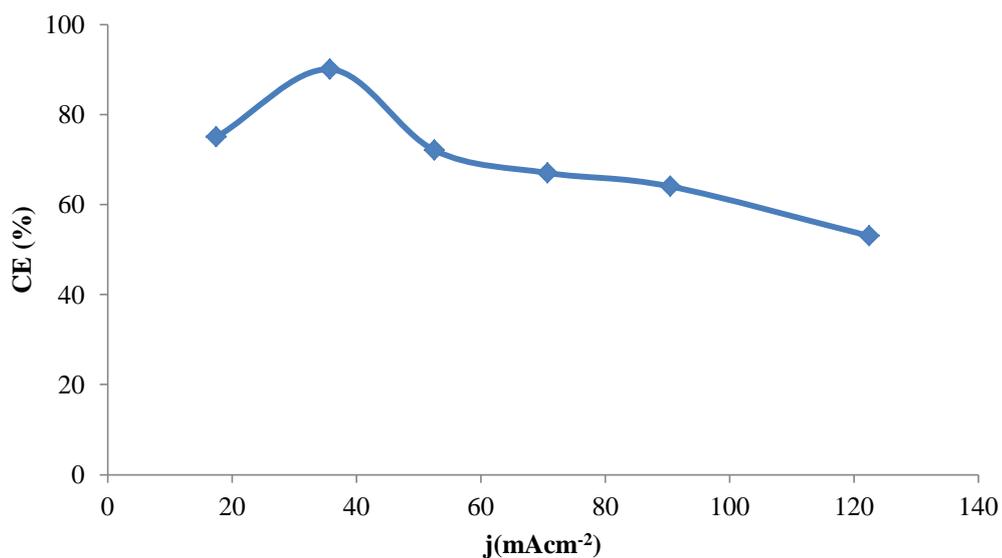


Fig 6: Current efficiency variations as function of current density.

Fig. 7 and Fig. 8 are typical SEM microphotographs and EDS analysis results respectively of a deposit obtained at 750°C, 35.5 mAcm⁻², and 5 mol% K₂SiF₆. The film formed at these conditions has a high content of silicon with less salt inclusions with only few impurities such as indium (In) and selenium (Sn) were found present. Generally, the presence of oxygen content in the silicon films is an indication of porosity as shown in the EDS analysis as dark spots (Fig. 8). The porosity in the films makes these deposits not good for solar cell applications because the pores could act as recombination centres to trap impurities resulting in the reduction of solar cell efficiency.

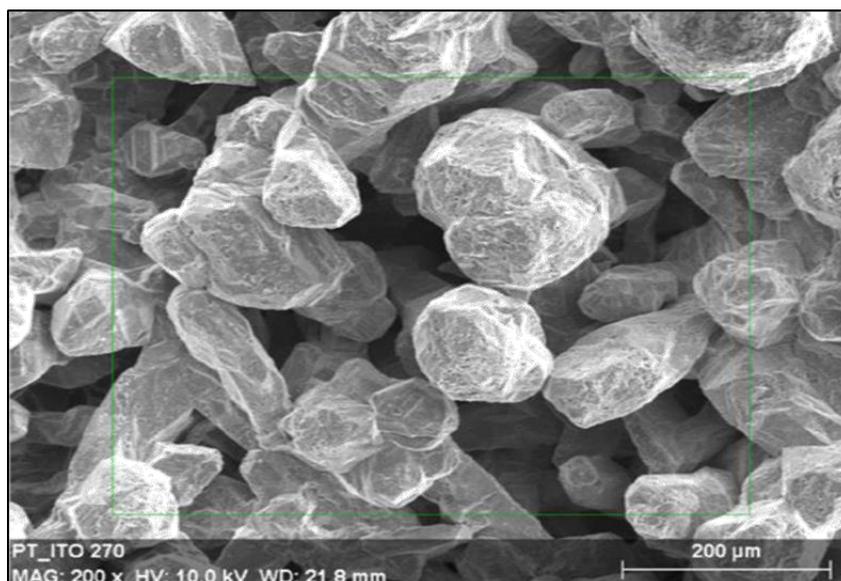


Fig 7: SEM photo of deposits obtained on Ag substrate at 750°C, 35.5 mAcm⁻², and 5 mol% K₂SiF₆

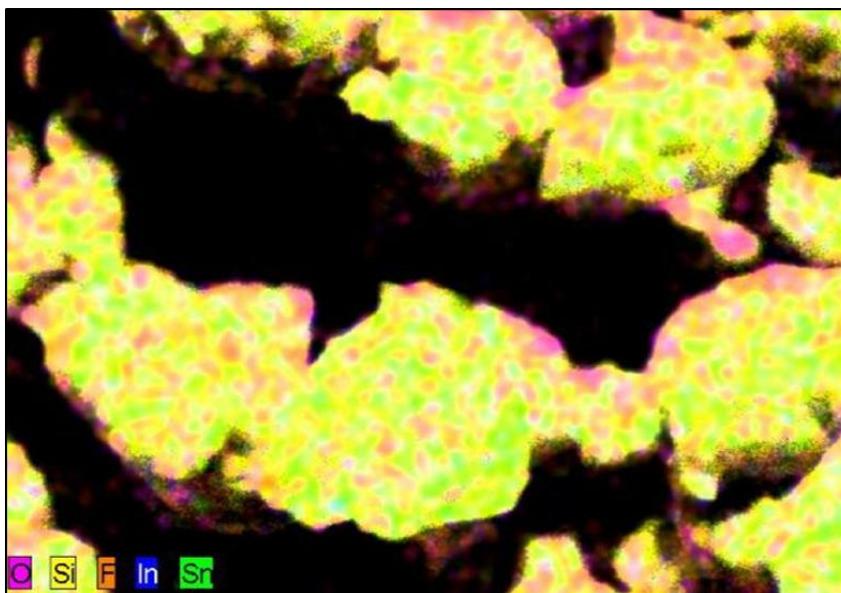


Fig 8: EDS mapping of major elements (O, Si, F, In, Sn) obtained on silver substrate, 35.5 mAcm⁻², and 5 mol% K₂SiF₆. Purple: O, Yellow: Si, Orange: F, Blue: In, Green: Sn. The porosity indicated as black spots.

IV. CONCLUSION

Silicon was successfully electrodeposited on silver substrate at different electrolytic parameters such as temperature of the electrolyte LiF-KF-K₂SiF₆ (450 to 800°C), concentration of K₂SiF₆ (5 to 30 mol%), and current density (17.5 to 122.5 mAcm⁻²). At a high temperature (800°C), low concentration of K₂SiF₆ (10 mol%), and moderate current density (35.5 mAcm⁻²) acceptable quality deposits were formed via electrodeposition in a high temperature furnace. At high temperatures compact deposits with good uniformity, and less impurities and salt inclusions were obtained. High purity and inclusion free deposits with minimal impurities and salt content were obtained at 10 mol% concentration of K₂SiF₆, and 35.5 mAcm⁻² current density. In high concentrations of K₂SiF₆ in the range of 15 to 30 mol%, and high current densities in the range from 70.8 to 122.5 mAcm⁻² powdered films with high content of impurities and salt were formed. Deposits with columnar and nodular structures have the potential to be used directly as silicon wafers for solar cell applications because of their increase surface area for sunlight absorption. In electrodeposition of silicon from LiF-KF-K₂SiF₆ an approximate current efficiency of 90% is possible.

REFERENCES

- [1] H. Flynn and T. Bradford, "Polysilicon supply, demand and implications for the PV industry" 2006, pp.14
- [2] A.H. Abbar, S.H. Kareemb, Fouad A.ALSaadyc, "Electrodeposition of Silicon from Fluorosilicic Acid Produced in Iraqi Phosphate Fertilizer Plant", *JEST*, 2011, 2(3), pp.168-173.
- [3] J.S. Wellings "Electrodeposition of semiconductors for applications in thin film solar cells", 2009, pp.18.
- [4] R. Boen, J. Bouteillon, "The electrodeposition of silicon in fluoride melts", *Journal of applied electrochemistry*, 13, 1983, pp.277-288.
- [5] K.S. Osen, A.M. Martinez, S. Rolseth, "Electrodeposition of Silicon from molten salts", Literature review SINTEF Internal report, 2010, pp.3
- [6] K.S. Osen, A.M. Martinez, S. Rolseth, H. Gudbrandsen, M. Juel and G. M. Haarberg, "Electrodeposition of crystalline Silicon Films from Alkali Fluoride Mixtures", *Electrochemical Society Transactions*, 33, 2010, PP.429-438
- [7] I.G. Shama and T.K. Mukherjee, "A study on purification of metallurgical grade silicon by electrorefining", 1986, pp.395-396.
- [8] G.M. Rao, D. Elwell and R. S. Feilgelson, "Characterization of electrodeposited silicon on graphite", *J. Electrochem. Soc: Electrochemistry and Technology* 1981, pp. 15-17.