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Electrowinning of Silicon from K_2SiF_6-Molten Fluoride Systems

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ABSTRACT

The electrowinning of silicon from solutions of K_2SiF_6 in fluoride melts at 745°C has been achieved. Electrolysis close to the deposition potential gave dense, coherent, and well-adherent deposits. Up to 3 mm thick films were grown using a K_2SiF_6 concentration of 4-6 m/o. The polycrystalline silicon has a columnar structure with grain size up to 100 μm. The morphology of the electrodeposited silicon onto silver substrates and its dependence on the deposition parameters is discussed. The purity of the deposits is substantially higher than that previously reported for electrodeposited silicon.

The availability, low toxicity, and high degree of technological development make silicon the most likely material to be used in terrestrial solar cells. The cost of silicon solar cells is still too high, however, for economic energy production, and the cost of pure elemental silicon is itself a major problem in achieving the cost objective of \$100-300 per peak kW by 2000 (1). Electrowinning is, in principle, a very attractive process for production of elemental silicon since it allows direct, single-stage production from some source material. The process can be operated at relatively low temperatures in comparison with those which involve molten silicon, and can yield a product which is substantially lower in impurity concentration than the source material.

The electrodeposition of silicon was first reported in 1854 (2) but there have been relatively few systematic studies reported in the literature. The most detailed investigation to date has probably been that of Monnier *et al.* (3, 4), who showed that silicon of 99.99% purity could be produced in a two-stage winning and refining process. Their deposits were, however, apparently powdery and incoherent and required subsequent separation from entrapped solvent. Cohen *et al.* (5-7) in our laboratory showed that single crystal epitaxial layers could be electrodeposited from solutions of K_2SiF_6 in a KF/LiF eutectic and that continuous films could be produced by electrorefining using a dissolving silicon anode.

The objective of the present study was to electrowin high purity silicon, in bulk form or as films with large grain size, from an inexpensive source. The morphology of the polycrystalline silicon films produced and their dependence on the electrodeposition conditions is discussed. A preliminary report of this investigation has been presented previously (8).

Experimental

The apparatus used in this investigation was similar to that reported by De Mattei *et al.* (9), except that silica tubes were used to electrically insulate the electrode leads from the top flange. The nickel leads were fixed into the silica tubes using a low vapor pressure epoxy cement. The tubes were replaced after several experiments when devitrification was evident.

Potassium fluorosilicate was chosen as the source of silicon because of the large number of successful silicon and silicide depositions using this material (2-8). Fluorosilicic acid is a by-product of phosphate fertilizer manufacture and has at present no useful application, so that fluorosilicates are an inexpensive source of silicon. The potassium salt has the lowest volatility and material of 99% purity was obtained commercially (Alfa Ventron).

The solvent used was the ternary LiF/NaF/KF eutectic "Flinak" (mp 459°C) or the binary LiF/KF eutectic (mp 492°C). These solvents have the advantages of high conductivity, low viscosity, high decomposition voltage, and high solubility for oxides which tend to form on the electrode surfaces. LiF of 99.5% purity, NaF of 99% purity, and 99-99.5% KF were used in this investigation. These anhydrous materials were mixed and dried first under vacuum at 200°C and then under flowing argon for several hours prior to fusion. The argon was purified by passing it over titanium chips at 650°C. After cooling the fused solvent, K_2SiF_6 was added and the resulting solution was purified by pre-electrolysis for 12-24 hr under conditions similar to those used for deposition but at a substantially higher potential and current density.

Electrodeposition of silicon was performed at 745° ± 10°C in a two- or three-electrode configuration with the melt contained in a vitreous carbon crucible. After graphite, niobium, and nickel had been tried

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Key words: polycrystalline silicon, electrocrystallization, semiconductor, solar cell.

in preliminary experiments, silver was selected as the cathode material because of its low reactivity with silicon. Graphite was found to be unsuitable as an anode material because it reacts and tends to disintegrate. Platinum was therefore used both as anode and reference electrode. Electrodes were ultrasonically cleaned in ethanol prior to use. Voltammetry and electrolysis at constant current or potential were carried out using a potentiostat/programmer and the charge passed was measured with a coulometer.

Salts adhering to the deposit were removed by digesting in hot distilled water for about 12 hr followed by ultrasonic cleaning in water, then ethanol, for about 15 min.

The morphology of the deposits was investigated by scanning electron microscopy and optical microscopy. The samples were analyzed for impurities by x-ray, electron microprobe, and emission spectrographic analysis.

Results

Morphology.—A major aim of this investigation was to determine the conditions for the deposition of inclusion-free, coherent layers of uniform thickness. Initial studies were made using K_2SiF_6 concentrations from 0.5 to 2.5 mole percent (m/o) in the two-electrode configuration and a typical cyclic voltammogram for a 1 m/o solution at 750°C is shown in Fig. 1. Deposition potentials extrapolated from linear regions of current-voltage plots for graphite, nickel, niobium, and silver are listed in Table I. Silicon is highly reactive at 750°C and only in the case of silver was the reaction between the deposit and the substrate found to be negligible.

Table I. Deposition potentials extrapolated from linear regions of current-voltage plots

Substrate	Deposition potential (V)	Remarks
Graphite	-0.75 ± 0.1 (*vs.* graphite)	No identifiable deposit
Nickel	-1.26 ± 0.01 (*vs.* graphite)	Powdery deposit—mainly nickel silicides
Niobium	-1.45 ± 0.05 (*vs.* graphite)	Powdery deposit—mainly niobium silicides
Silver	-1.96 ± 0.03 (*vs.* platinum)	Dense, coherent, and well-adherent silicon

Cell voltages above -2V *vs.* Pt and corresponding current densities above 20 mA cm^{-2} were found to result in very nonuniform powdery or dendritic deposits on top of a thin, coherent layer about 2 μm thick. Reducing the deposition potential to -1.9V was found to give coherent and strongly adherent deposits. Figure 2 shows a typical sample of about 20 μm thickness which was deposited at a constant potential and the current density was 3.9 mA cm^{-2} with a total charge passed of 208 C cm^{-2}. The average grain size is about 16 μm. A similar deposit at a constant current of 3.2 mA cm^{-2} is shown in Fig. 3 and 4. The measured potential was about -1.95V *vs.* Pt and the total charge passed was 514 C cm^{-2}. The cross section demonstrates that the deposit is free from inclusions but also shows the irregularity in the thickness.

It was found possible to deposit reproducibly coherent, well-adherent films of about 50 μm average thickness using a cell potential of -1.88 ± 0.02V *vs.* Pt with current densities of 2-13 mA cm^{-2} depending on the solute concentration. The current efficiency

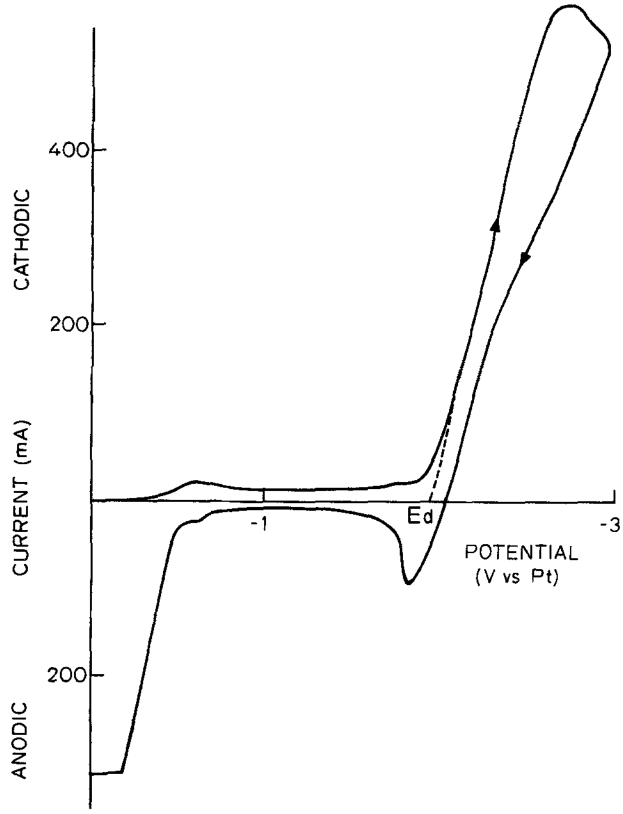

Fig. 1. Cyclic voltammogram of 1 m/o solution of K_2SiF_6 in Flinak eutectic at 750°C, v = 1 V/sec, silver cathode area ~1.56 cm^2.

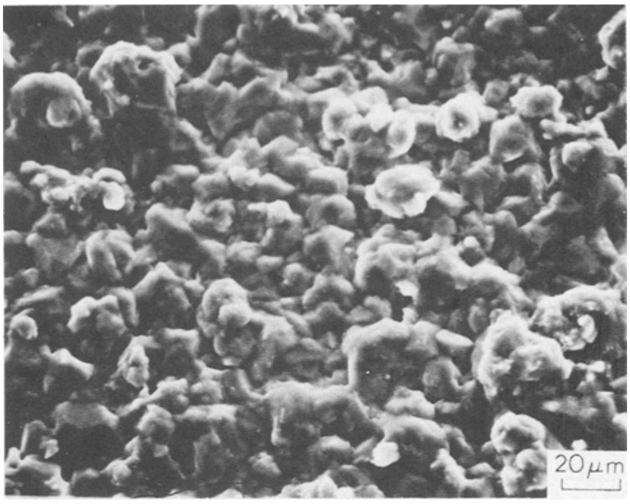

Fig. 2. Scanning electron micrograph of a deposit plated at constant cell potential of -1.9V vs. Pt at 750°C, the K_2SiF_6 concentration ~1 m/o.

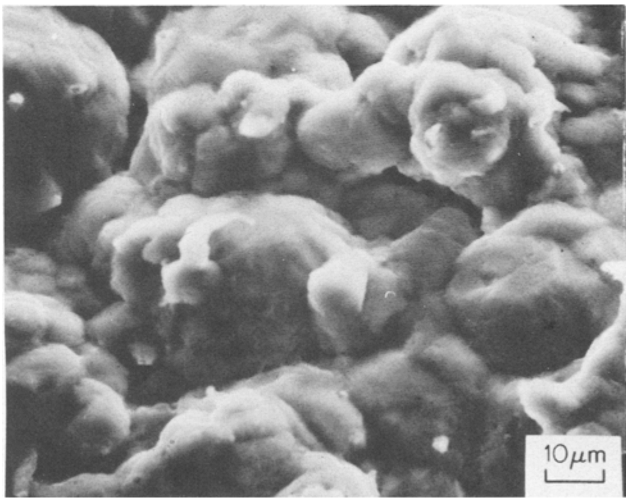

Fig. 3. Scanning electron micrograph of a deposit plated at constant current density of 3.2 mA cm^{-2} at 735°C, the K_2SiF_6 concentration ~1.5 m/o.

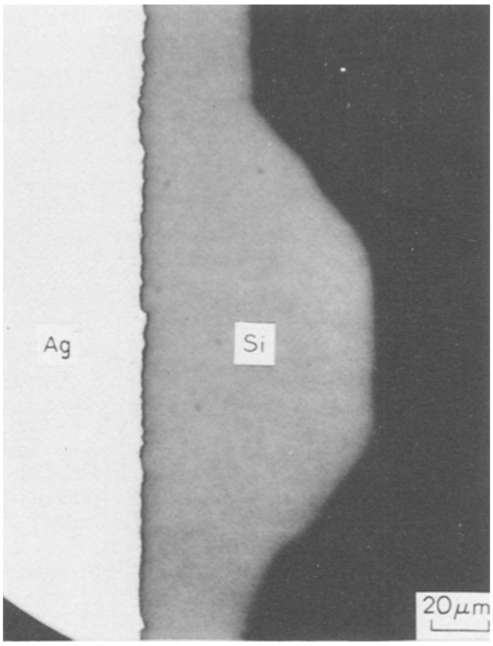

Fig. 4. Cross-sectional view of silicon, electrodepositing conditions same as in Fig. 3.

was normally 35-50% and the grain size up to 60 μm on top of an initial layer of 8-14 μm average grain size.

Attempts were made to deposit relatively thick layers at these low current densities. Figure 5 shows the result of prolonged electrolysis at −1.90 ± 0.02V *vs.* Pt over two days (2945 C cm^{-2} charge), at current densities in the range from 4 to 12 mA cm^{-2}. The deposit was 2 mm in thickness but a cross section (Fig. 6) shows that there was a very high concentration of fluoride inclusions trapped between grains. A surprising feature of this experiment is that the inclusion concentration is rather high even during the early stages of growth, but the deterioration in the later stages is severe.

Since thick, inclusion-free layers could not be electrodeposited from the dilute solutions used, the K_2SiF_6 solute concentration was increased to 4-6 m/o in subsequent investigations. In addition, a three-electrode arrangement was introduced since in principle this gives better control over the deposition rate. Although boron nitride compartmented metal/metal ion (*e.g.,* Ni/Ni^{2+}) and the hazardous fluorine reference cells have been used (10), a platinum foil pseudo-reference electrode was preferred in this study because of its simplicity. The measured deposition potential against a Pt reference electrode was found to be −0.74 ± 0.03V. However, variations by as much as 0.10V were observed in a few experiments. These variations may be due to changes in electrode separation or to small changes in electrode surface structure, or to the inherent uncertainties in the determination of deposition potential (11). The deposition potential was therefore determined prior to each electrodeposition experiment.

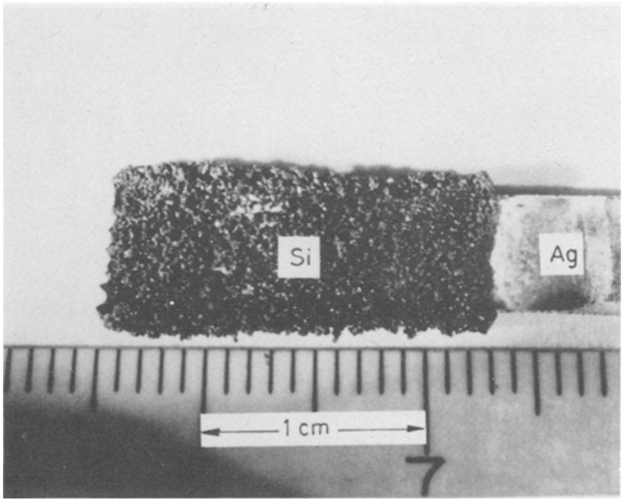

Fig. 5. General view of thick deposit plated at constant cell potential of −1.9V vs. Pt at 750°C, the K_2SiF_6 concentration ~2.5 m/o.

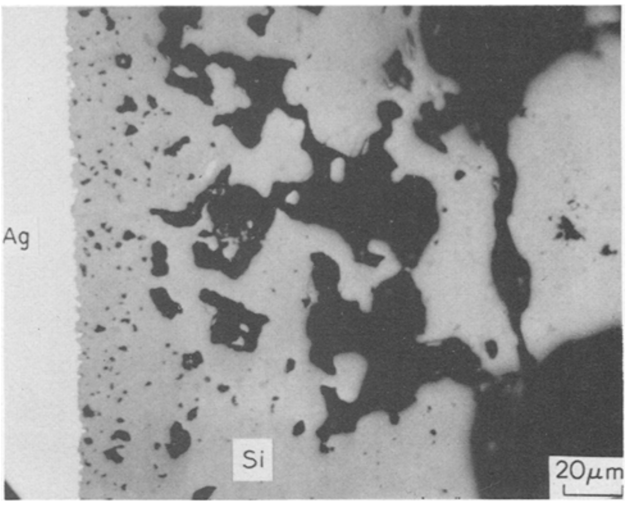

Fig. 6. Cross-sectional view of silicon, electrodepositing conditions same as in Fig. 5.

Well-adherent, inclusion-free deposits up to 3 mm in thickness were found possible using applied potentials in the vicinity of the deposition potential (Table II). The corresponding current density was from 10 to 60 mA cm^{-2} and the efficiency was from 35 to 70%. Figure 7 shows a typical example of a deposit plated at −0.75V *vs.* Pt for about four days (total charge 12,890 C cm^{-2}). The cross section of this deposit at the silver-silicon interface is shown in Fig. 8. With the exception of a few cracks introduced either during cooling or mounting, the deposits are substantially coherent; the wedge shape of Fig. 7 is an end effect and is characteristic of the small samples currently prepared.

Figure 9 shows the grain structure of a typical deposit as revealed by an HNO_3/HF etch. Growth is columnar with a grain size up to 100 μm, the grain size increasing with increasing thickness of the deposit as is usual for electrodeposits from aqueous solutions without complexing agents (12). Grain orientation has not yet been studied in detail but a columnar structure might be advantageous for the direct use of polycrystalline films in solar cells.

Purity.—As mentioned earlier, starting materials were of 99-99.5% purity and were not given any purification treatment apart from pre-electrolysis. This latter procedure is expected to remove from the

Table II. Experimental parameters and results for thicker deposits in three-electrode configuration

Experiment No.	Cathode potential *vs.* Pt (V)	Approximate current density (mA cm^{-2})	Total charge (C cm^{-2})	Thickness of the deposit (mm)	Efficiency
1	−0.74	44	2450	0.9	50
2	−0.75	33	12,889	2.5	44
3	−0.74	19	6884	1	34
4	−0.75	10	6822	2	41
5	−0.85	60	4100	1.2	69
6	−0.86	50	1749	0.4	49
7	−0.64	20	4015	1.1	38

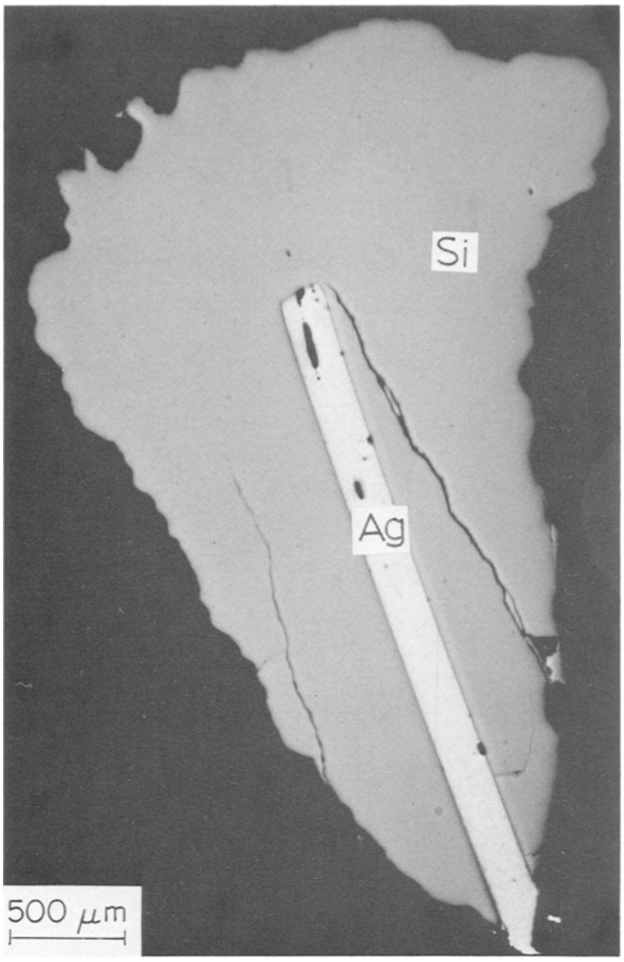

Fig. 7. Micrograph of silicon, deposited at constant cathodic potential of -0.75V vs. Pt at 746°C, the K_2SiF_6 concentration $\sim$5 m/o.

solution those impurities which deposit at lower potentials than silicon. Impurities with a higher deposition potential than that used for subsequent electrodeposits should remain in solution. This idealized situation rarely occurs in practice since co-deposition tends effectively to reduce differences in deposition potentials between individual elements. An additional factor to be considered is that normal segregation of impurities is expected to depend upon the morphology of the deposit, and also on the grain size.

The increase in impurity concentration in irregular deposits at higher potentials was confirmed by analysis of highly dendritic films. These showed 2-20% of Li, presumably as inclusions of LiF, together with about 2% of other impurities, mainly Al, Cr, and Fe with traces of B, Cu, Mg, and Ni.

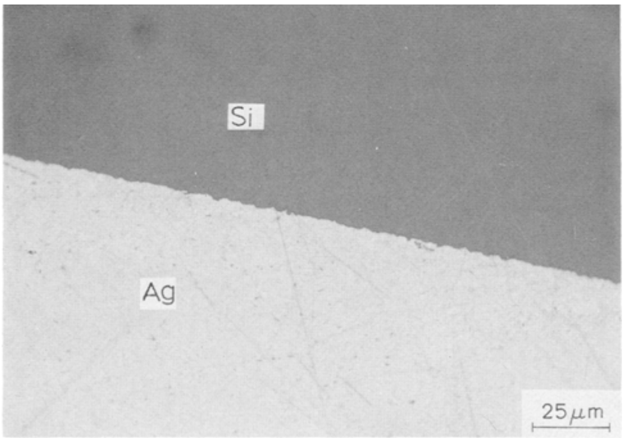

Fig. 8. Micrograph of silicon-silver interface of the deposit in Fig. 7.

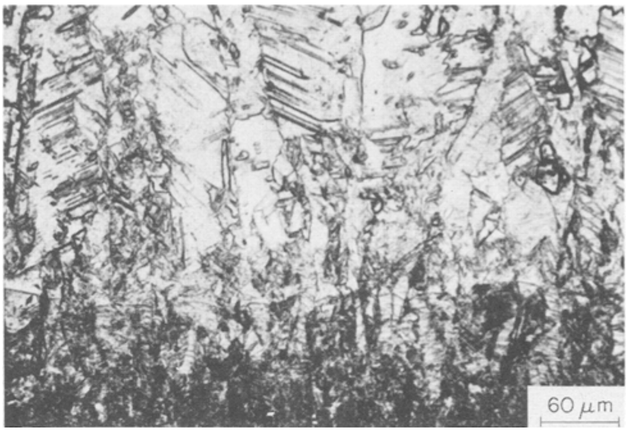

Fig. 9. Micrograph of etched silicon surface of the deposit plated at constant cathodic potential of -0.74V vs. Pt at 747°C, the K_2SiF_6 concentration $\sim$4 m/o.

When deposits were made at potential close to the deposition potential, the impurity concentration was reduced to typically about 200 ppm of Al, B, Cr, Fe, Mg, and Ni. The best electrodeposits, however, showed only 10 ppm of total impurity (2 ppm B, 5 ppm Cr, 0.6 ppm Cu, 0.3 ppm Pt, and 1 ppm Ag). This material appears to be the highest purity silicon to be prepared by electrodeposition to date, since the best material previously reported is that of Monnier *et al.* (3, 4) with 99.99% purity.

The thicker inclusion-free deposits were sometimes found to contain 0.01-0.1% of Cr and Fe. These deposits require a period of several days of electrolysis during which fluoride vapor or anodically liberated fluorine can attack the Inconel atmosphere tube and produce transition metal fluorides. These may be transported to the melt via the vapor phase and result in the transition metal contamination. Microprobe analysis of the reacted scales on the furnace wall indicated a Cr-rich phase instead of normal Ni-rich Inconel 600. Such a Cr-rich surface film formation upon aqueous oxidation of Inconel 600 even at 300°C was demonstrated recently by McIntyre *et al.* (13). This source of contamination can clearly be eliminated by the use of an alternative furnace design with an internal graphite element and water-cooled stainless steel jacket. However the 99.999% pure material was produced as thick deposits.

Discussion and Conclusions

Reproducible deposits of silicon onto silver have been obtained by the electrolysis of K_2SiF_6-fluoride systems at 745°C and conditions have been determined for the deposition of inclusion-free and well-adherent layers. Although silicon has been deposited previously from fluoride melts, the present experiments appear to be the first in which electrowinning of silicon gave coherent deposits up to 3 mm in thickness.

The powdery deposits at high potentials and the spongy or dendritic deposits on prolonged electrolysis of dilute K_2SiF_6 solutions at the deposition potential could be explained in terms of a secondary reaction between alkali metal deposited by the primary deposition as observed by Dodero (14)

$$4K + Si^{4+} \rightleftarrows Si + 4K^+$$

No evidence for electrodeposition of potassium was observed in our system and this is considered unlikely in view of the large difference in deposition potential between alkali metals and silicon. Dodero used very high depositional potentials and so the primary electrodeposition of alkali metals was to be expected in his experiments.

The noncoherent deposits may also be explained in terms of a secondary reaction between the deposited silicon and the melt

$$Si + Si^{4+} \rightleftarrows 2Si^{2+}$$

Dissolution of silicon has been observed when wafers were held in contact with the melt in the absence of an applied potential. However this does not necessarily imply that disproportionation occurs under the conditions of deposition, and it is difficult to understand how this effect can explain the major improvement in morphology on increasing the solute concentration.

It appears likely that polynuclear complexes are present in the solution and that these may have a strong influence on the deposition process. Complexes such as $Mo_2Cl_9^{3-}$ (15) in alkali chloride melts and $U_2O_4^{3-}$ in perchlorate solutions (16) are formed when the concentrations of $MoCl_3$ and uranyl ions, respectively, are increased. Compounds of structure Si_nF_{2n+2} are known to exist, and both Si_3F_8 and Si_4F_8 have been isolated (17). It is suggested that a slow chemical step involving dissociation of a polynuclear complex precedes the electron-transfer reaction and that this dissociation step is rate controlling and favors the deposition of coherent films. Further study is required before this postulate can be confirmed, but we believe that it is important to determine the rate-controlling step in the silicon deposition reaction.

The purity of the best deposits is good in comparison with the starting materials and indicates that the single stage electropurification process is effective. Since the solvent phase is reusable, high purity alkali metal fluorides can be used reducing the initial impurity content in the melt. Improved furnace design to eliminate high temperature reactions between fluoride vapors and Inconel 600 should lead to the deposition of "solar cell" grade material as either thin or thick films in a single step.

Thick films have a columnar structure of relatively large grain size as is required of the deposited material is to be used directly for solar cell fabrication. The power required to deposit 1 kg of silicon is about 16 kW-hr plus the cost of maintaining the melt at 745°C. In large scale plants, joule heating from the deposition current is adequate to maintain temperatures of this order, so that we believe that electrodeposition has the potential to yield silicon of adequate purity for solar cells at about $1 per kg. Silver is clearly too expensive a material for use on a large scale but the substrates could be reused if bulk silicon were stripped from the cathode after deposition. Alternatively a 20-100 μm coating on a cheap substrate would be sufficient in a process to produce thin film solar cells directly using this method.

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