

The electrodeposition of silicon in fluoride melts

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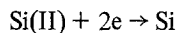
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A fused LiF-NaF-KF mixture was selected as a solvent for the preparation of electrolytic silicon, since they are the best alkali halides mixtures for the stabilization of the fluorosilicates. The solvent was purified by pre-electrolysis and treatment with HF.

Consistent with the thermodynamical data, the reduction of the fluorosilicate ion was easier than those of the alkali metal halides. The product formed with a silver or graphite cathode was insoluble and these materials could therefore be used as substrate for electrolytic deposit of silicon.

The mechanism for the reduction of fluorosilicate is:



Pulsed current electrolysis yielded regular and uniform silicon layers up to 1 mm thickness. The amount of impurities of deposited Si could be controlled.

The deposited material was a semi-conductor of resistivity $0.1 < \rho < 1 \Omega \text{ cm}$ and the life-time of the free carriers was about $30 \mu\text{s}$.

1. Introduction

Several groups [1], including the LEP in France [2] have attempted to prepare thin layers of polycrystalline silicon (for use in a photovoltaic cell) from electronic quality silicon to avoid the energy intensive processes of drawing and cutting of monocrystals. Some projects [3-5] have aimed at lowering the cost of production of electronic quality silicon, while others [6-9] are related to the production of silicon with ppm level impurities. These methods involve one or more steps at a temperature higher than the melting point of silicon 1410°C ; the electrolytic process should yield silicon of similar quality at lower temperatures.

We have focused attention on the electrolytic preparation of thin layers of silicon for the direct manufacture of photovoltaic cells. In this paper, the experimental technique, the choice and the preparation of the solvent electrolyte and results of a study of the reduction of the fluorosilicate ions on silicon, platinum, silver and graphite electrodes and a mechanism for the reduction process

are presented. The influence of the electrolytic parameters on the purity of silicon is described. Finally, based on this work, we comment on the chemical purity, structure and electrical properties of electrolytic silicon for applications as photovoltaic cells.

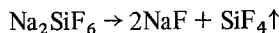
2. Experimental procedure

2.1. Solutions

In the electrolytic preparation of silicon, several workers [10-38], particularly Dodero [10-11] used either silica or fluorosilicates as the solute. They generally obtained either amorphous silicon or metallic silicides. Cohen and Huggins (26-28) were the first to prepare both mono and polycrystalline silicon by electrolysis of the alkaline fluorosilicates in LiF-KF eutectic. One year later, we also succeeded in the electrolytic preparation of polycrystalline silicon from the same melts [34]; afterwards several electrolytic silicon preparations were reported by R. S. Feigelson *et al.* using

fluoride [35, 36] or silicate melts [37] and D. Elwell *et al.* [38].

We have chosen alkali fluorosilicates as the solute; to suppress the decomposition reaction



the complexing nature of the eutectic mixtures LiCl-KCl ($T_f = 352^\circ\text{C}$), NaCl-KCl ($T_f = 654^\circ\text{C}$), LiF-KF ($T_f = 492^\circ\text{C}$), NaF-KF ($T_f = 710^\circ\text{C}$), LiF-NaF-KF ($T_f = 454^\circ\text{C}$) were examined; LiF-KF and LiF-KF-NaF stabilized the fluorosilicate most. The electrolysis was carried out at 750°C .

For most studies, the eutectic LiF-KF (Merck 'pr. Anal') was used as the solvent and Na_2SiF_6 (Carlo Erba 'RPE') as the solute.

The solutions were heated and fused under an argon (Air Liquide 'U') flow; the residual water and oxygen of the gas having been removed by successive passage through a silica gel column at room temperature and copper gauze at 180°C .

2.2. Electrolysis cell

The electrolysis cell (Fig. 1) was composed of two parts:

- (a) the body which contained the electrolysis graphite crucible,
- (b) the head which accommodated two to six holders for various electrodes, a thermocouple, a sheath micrometer screw, an argon inlet and outlet and a lock-chamber for salt additions.

The body was made in monel which was protected from the corrosive atmosphere by a graphite envelope; a clamp ensured an air tight seal with the head.

The head was fitted with seven air-tight joints, their cylinder piston arrangements allowing rotational and translational motions of the electrodes.

The head was fastened to the cell with O-ring teflon 'gyrolock' joints.

2.3. Electrodes

The working electrodes for the voltammetric studies were graphite or silver wire (diameter, one mm; length, 10 mm).

The counter electrode was the graphite crucible (diameter, 70 mm; height, 100 mm). In the absence of a suitable reference electrode, we used a plati-

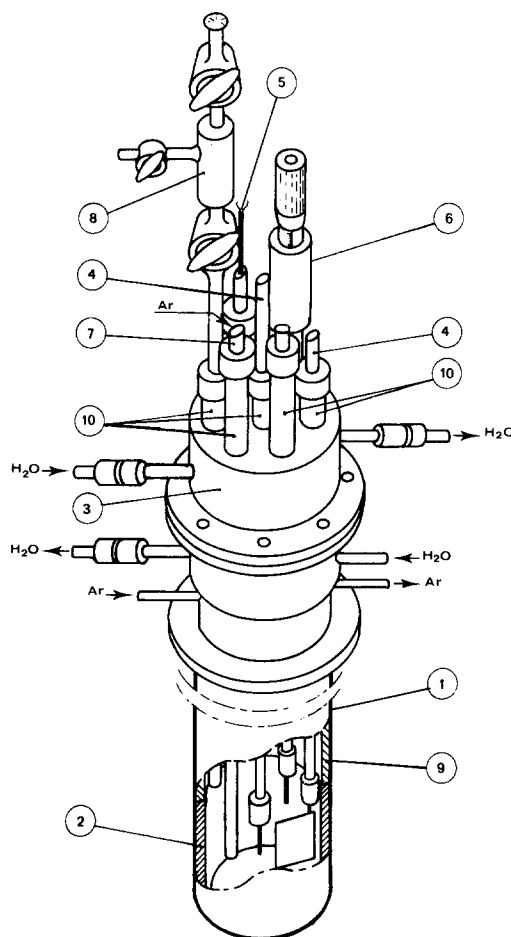


Fig. 1. Electrolysis cell; 1. Body-cell. 2. Graphite crucible. 3. Head cell. 4. Holders. 5. Thermocouple. 6. Micrometer screw. 7. Argon entrance. 8. Lock-chamber for the additions. 9. Graphite envelope. 10. Airtight passages.

num foil as a quasi-reference [39-42]; its potential was stable and reproducible within $\pm 20\text{ mV}$ over a one day period during the experiments. Unless otherwise stated, all potentials are referred to this reference electrode.

2.4. Limiting electrode processes and solvent impurities

The voltammogram shown in Fig. 2 was obtained on a graphite electrode. The reduction peak, A, could be assigned to the potassium ion reduction [43]. In the anodic potential range, the fluoride ion oxidation is observed. The experimental potential range available is thus less than 2 V. This low value is in accordance with those of

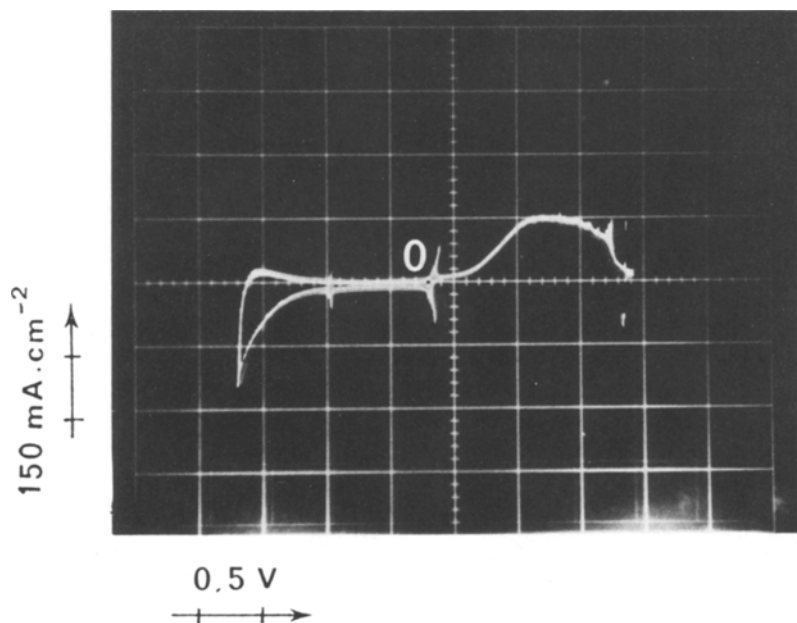


Fig. 2. Voltammogram of the solvent LiF-KF with a graphite electrode; potential scan rate, 1 V s^{-1} .

Delimarskii [44] and can be explained by the depolarization of the alkali metal ion reduction due to the insertion of the alkali metals in graphite [45–47]. Also with a silver microelectrode, the available potential span was 2.6 V, but this was still lower than the thermodynamic value (4.8 V) for LiF-KF. This was ascribed to the presence of impurities of base metal ions and oxygenated species (molar fraction $< 10^{-4}$), and a further purification was performed using the two common purification methods, namely, preelectrolysis, and treatment with hydrogen fluoride. We have subsequently tried to treat the electrolyte by a cementation with metallurgical silicon pieces.

The efficiency of the purification was monitored by the magnitude of the cathodic current at a silver microelectrode; typically this was three times lower after the Si-pretreatment. Although the fluorosilicate solute also possibly contained the same impurities as the solvent, no special purification was considered necessary because of the low solute concentration (molar fraction < 0.05).

3. Electrochemistry of the fluorosilicates

3.1. Study of the fluorosilicate reduction on silver, graphite and platinum electrodes

The partial pressure of SiF_4 above a fluorosilicate

solution ($X_{\text{Na}_2\text{SiF}_6} = 0.05$), at 750°C , was 0.16 atmosphere from which the calculated thermodynamical decomposition potential (E_{th}) of Na_2SiF_6 is 3.75 V.

The experimental study of the reduction of the fluorosilicates was performed using cyclic voltammetry. The voltammograms (Fig. 3) on a silver electrode show a cathodic peak distinctly separated (0.8 V) from that of the reduction of the alkali metal ions. This peak definitely corresponded to the reduction of the silicate ions since its height increased with the concentration of the dissolved fluorosilicates. The shape of this peak and the corresponding sharp anodic stripping peak are typical of the formation of an insoluble product. Similar results were obtained in the electrode reaction involving the reduction of fluorosilicate on a graphite electrode.

3.2. Study of the reversibility of the silicon ion reduction

The use of a monocrystalline silicon electrode was not convenient because of high ohmic drop. This difficulty was overcome by preparing a silicon electrode *in situ*, by forming an electrolytic thin layer on a silver wire (diameter, 1 mm) by constant current electrolysis at a low current density ($i_c = -10 \text{ mA cm}^{-2}$). Typical voltammograms on this

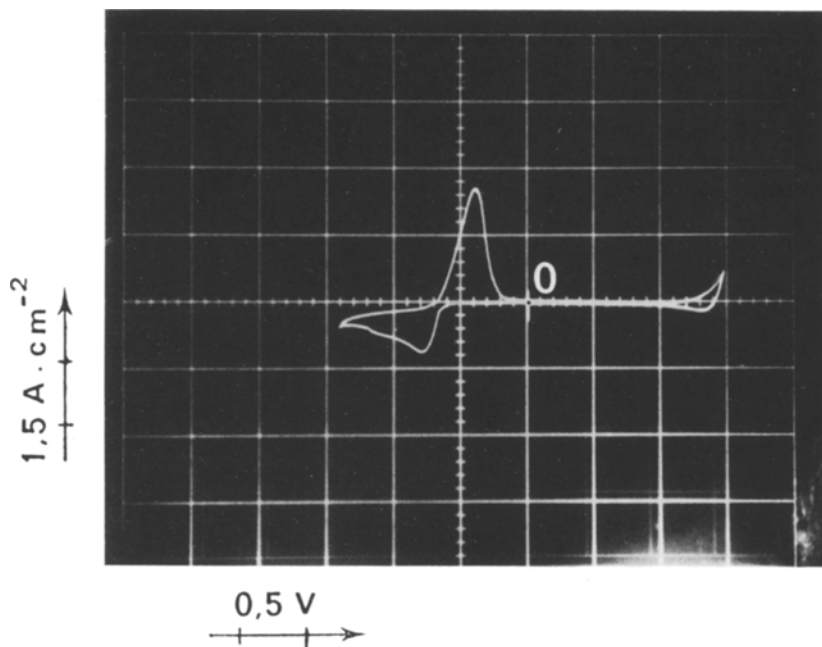


Fig. 3. Voltammetric study of the reduction of the fluorosilicates with a silver electrode, $X_{\text{Na}_2\text{SiF}_6} = 0.005$; potential scan rate, 1 V s^{-1} .

latter electrode with varying potential sweep rates are shown on Fig. 4. The silicon ions concentration in the solution was kept as low as possible; that present was formed by the reaction of the solvent with silicon metal. The shape of the cathodic peak obtained is typical of a reversible reaction with formation of an insoluble deposit. The poten-

tials are reported versus the potential of a silicon electrode dipped in the solution. The variation of the cathodic current peak height is linear with the square root of the sweep rate.

The initial slope of the curves at the foot of the peak is characteristic of an ohmic control. The variation of the peak and half peak potentials.

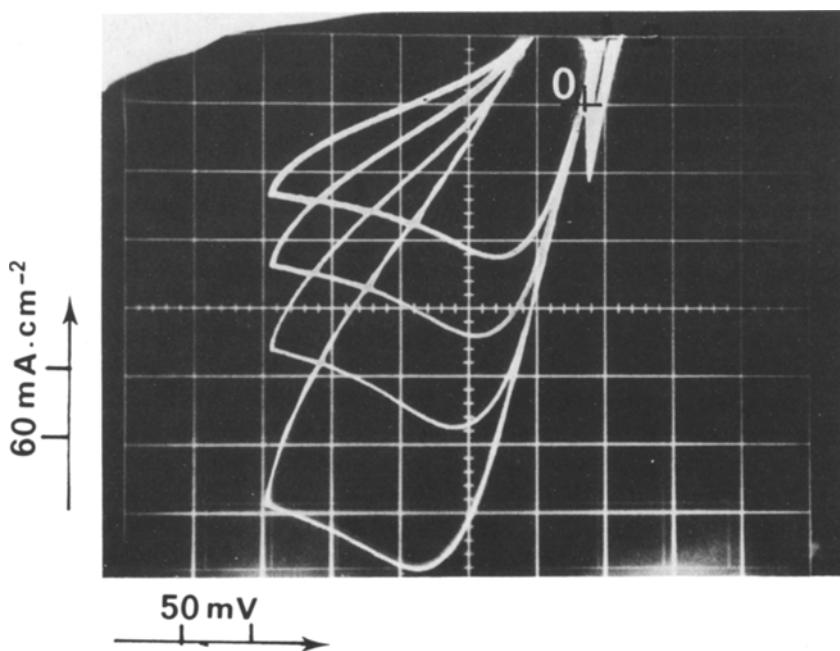


Fig. 4. Voltammetric study of the reduction of the fluorosilicates with a silicon electrode, $X_{\text{Na}_2\text{SiF}_6} = 0.002$; potential scan rates, $0.5, 1, 2$ and 4 V s^{-1} .

versus their corresponding current intensity (Fig. 5) are straight lines, parallel to the linear variation of electrode potential with current recorded at the beginning of the cathodic peak. Assuming that the displacements of the peak and half-peak potentials with the sweep arise essentially from the ohmic drop, the difference between the peak potential e_p with the half peak, $e_{p/2}$, and with the equilibrium potential of the silicon electrode $e_{i=0}$ are:

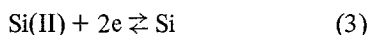
$$e_p - e_{p/2} = -0.032 \text{ V} \pm 0.003 \text{ V} \quad (1)$$

$$e_p - e_{i=0} = -0.038 \text{ V} \pm 0.003 \text{ V} \quad (2)$$

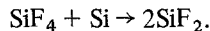
These experimental values when compared with the theoretical values [8] for reversible reduction, enables calculation of the number of electrons involved in the electrode process. These from Equations 1 and 2 are:

$$2.1 \pm 0.15 \quad \text{and} \quad 1.96 \pm 0.15 \quad \text{respectively.}$$

Thus the reduction of the fluorosilicates on a silicon electrode corresponds to:

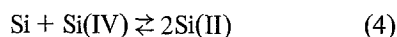


Although Si(II) compounds are usually unstable, some such as SiF_2 , SiO , SiS , SiH_2 , SiCl_2 have been reported. In this solution, these are assumed to be formed by a reverse disproportionation reaction as:



Cohen and Huggins [26–28] also suggested that the silicon was obtained from the reduction of the Si(II) species in alkali fluoride melts.

Fiegelson *et al.* [35, 36] concluded that a slow chemical step involving the dissociation of a polynuclear complex preceded the electron transfer step at the electrode, the chemical step being the rate controlling step and favouring the deposition of adherent films. The powdery and dendritic or spongy deposits obtained by them under different conditions were ascribed to the reaction:



Besides, it was noticed that the equilibrium potential of a silicon electrode dropped in the fluorosilicate solution was stabilized quickly, so the Reaction 4 should be fast enough.

Another experiment also supports this concept. A thin layer of silicon ($e = 0.5 \mu\text{m}$) was deposited *in situ* on a graphite electrode. After electrolysis the potential of this electrode versus another silicon electrode Fig. 6, was, first constant and equal to that of the other silicon electrode; progressively it took the value it had before the electrolysis, i.e., the layer of silicon was completely dissolved from the electrode.

It may be concluded that both silver and graphite electrodes are suitable substrates for the deposit of thin layers of silicon.

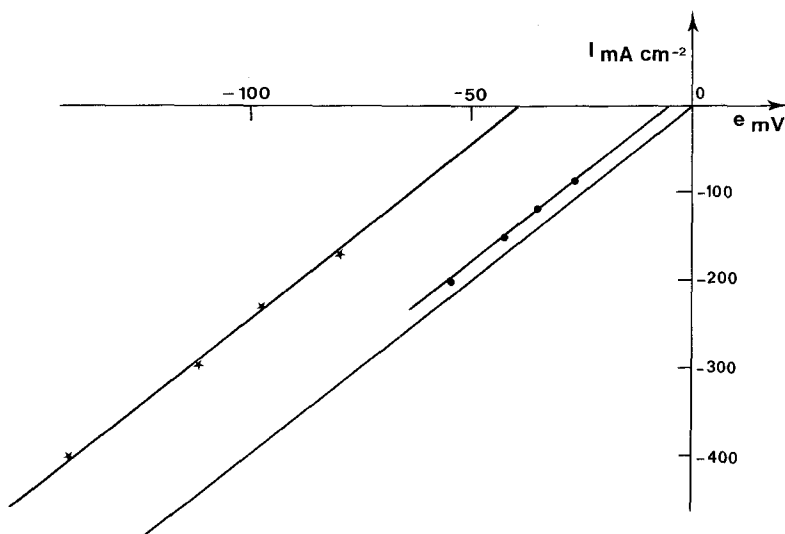


Fig. 5. Voltammetric study of the reduction of the fluorosilicates with a silicon electrode. The potentials are reported versus the equilibrium potential of a silicon electrode.
* $e_p - e_{i=0} = f(I)$; \bullet $e_p - e_{p/2} = f(I)$ $X_{\text{Na}_2\text{SiF}_6} \leq 0.002$; potential scan rates, 0.5, 1, 2 and 4 V s^{-1} .

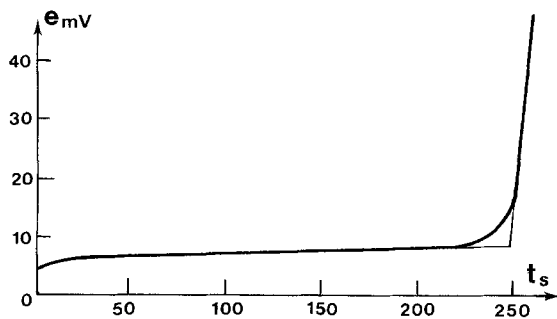


Fig. 6. Potential of a graphite electrode, first covered by a thin silicon layer, versus the equilibrium potential of a silicon electrode electrolyte $\text{LiF-KF-Na}_2\text{SiF}_6$, $X_{\text{Na}_2\text{SiF}_6} = 0.05$; $t = 0$, the end of the electrolysis.

4. Analysis of the influence of electrolysis parameters

4.1. Electrolyte purity

It was found that it was impossible to obtain electrolytic silicon on graphite or silver electrodes using a non purified solvent. With a partially purified solvent, i.e. for example when the cementation time was not sufficient, only discrete silicon nuclei were obtained on the electrode surface as can be observed on a scanning electron micrograph (Fig. 7). X-ray analyses have indicated that other parts of the electrode surface were covered by an iron deposit. The presence of iron seems to inhibit silicon nucleation. When the purification of the solvent was adequate, the silicon deposit covered all the electrode surface as can be observed on the corresponding X-ray micrograph (Fig. 8).

4.2. Form of the electrolysis current

4.2.1. Use of direct current. Electrolytic deposition of Si using direct current lead to dendritic growth (Fig. 9); the texture irregularity increased with increased current density. Some of the dendrites were monocrystalline in character. Direct current electrolysis does not allow the deposition of thin silicon layers nor high purity silicon.

4.2.2. Use of pulsed current. The use of the pulsed current technique [44–53] enables control of the parameters which influence the chemical purity and the structure of the deposits. It was employed

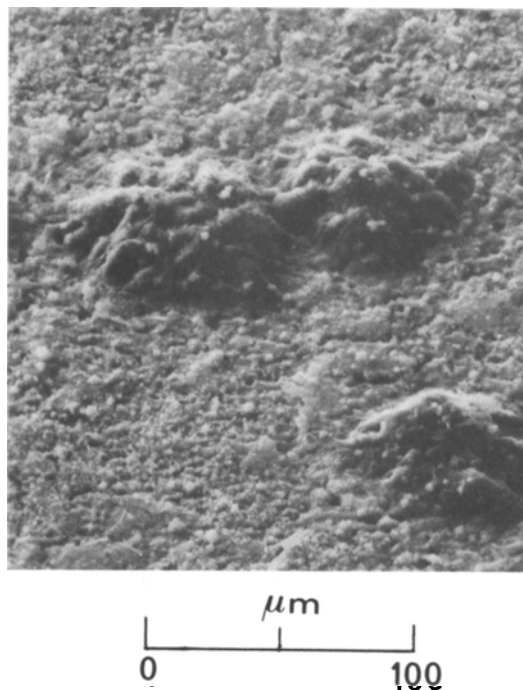


Fig. 7. Scanning electron micrograph of a deposit obtained in a partially purified solvent; $X_{\text{Na}_2\text{SiF}_6} = 0.05$; $i_c = -5 \text{ mA cm}^{-2}$.

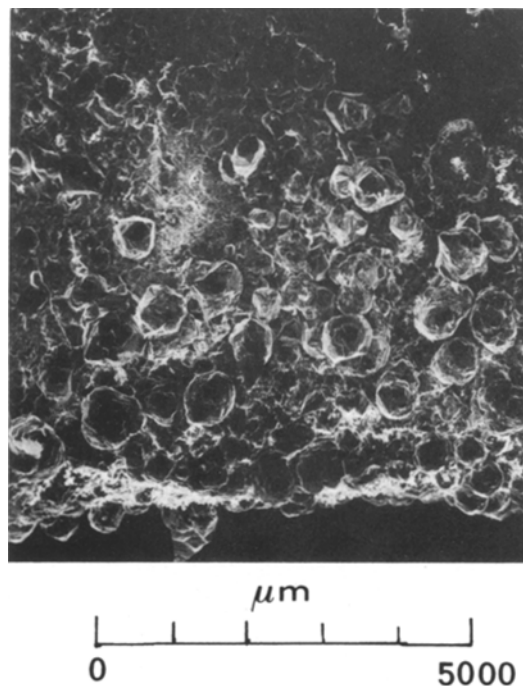


Fig. 8. Scanning electron micrograph of a deposit obtained in a purified solvent, $X_{\text{Na}_2\text{SiF}_6} = 0.05$, $i_c = -5 \text{ mA cm}^{-2}$.

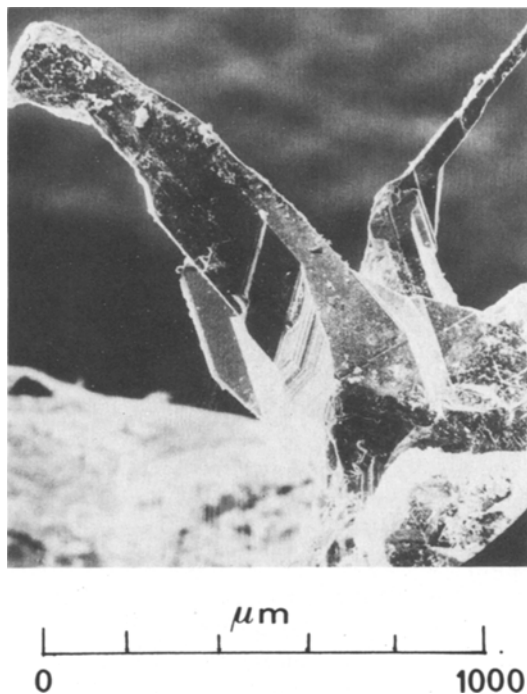


Fig. 9. Scanning electron micrograph of monocrystalline dendrites, $X_{\text{Na}_2\text{SiF}_6} = 0.05$, $i_c = -20 \text{ mA cm}^{-2}$.

to adjust the electrolysis conditions consistent with the mechanism proposed for the reduction of the silicon ions: it was necessary for the concentration of the Si(II) species to be as uniform as possible in the solution layer near the electrode.

The current profile shown in Fig. 10 enables us to maintain a constant Si(II) species concentration inside the electrolyte during the electrolysis; the species reduced by the electrode reaction

were compensated when the current was interrupted.

While the dissolved species, more easily reducible than the silicon ions, were simultaneously reduced during the cathodic pulse, they alone were reduced when the current was equal to zero. It was observed that the transition time corresponding to these impurities was short compared with the duration of the cathodic pulse. Their quantities in the electrolytic silicon were therefore proportional to their equilibrium concentration C_0 and inversely proportional to the current density and also to the ratio of the total sequence duration to the cathodic part.

Writing the Nernst equation for the electrode reaction and the solution of the Fick's equation ($n = 2$), we obtain:

$$E(t) = E_0 + \frac{RT}{2F} \ln \left[1 - \frac{1}{C_0 F (\pi D)^{1/2}} \frac{i_c (t_c)^{1/2}}{F} \right] \quad (5)$$

and for $t_c \ll \tau$, where τ is the transition time corresponding to the silicon ions reduction, Equation 5 becomes:

$$E(t) = E_0 - \frac{RT}{2F} \frac{i_c (t_c)^{1/2}}{C_0 F (\pi D)^{1/2}} \quad (6)$$

Finally the use of a short anodic impulse increased the purity of the deposit since a proportion of the impurities contained in the deposit, were dissolved again.

The deposits on silver and graphite using pulsed current were without dendrites (Figs. 11 and 12).

The crystal growth could reach several $\mu\text{m h}^{-1}$ and the thickness of the layers obtained varied from 10^{-4} to 10^{-1} cm.

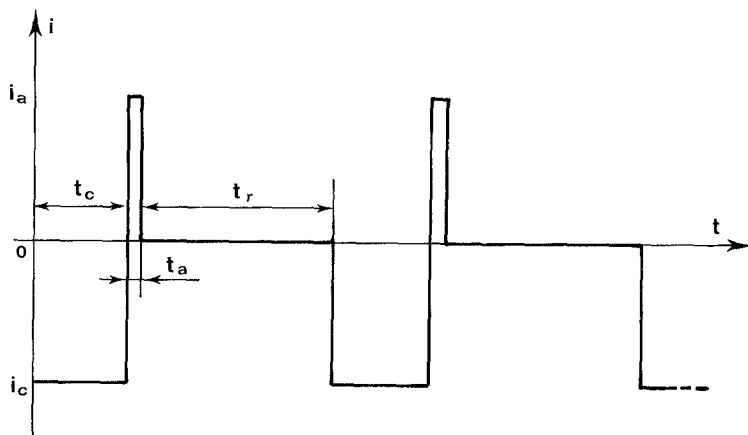


Fig. 10. The form of the pulsed

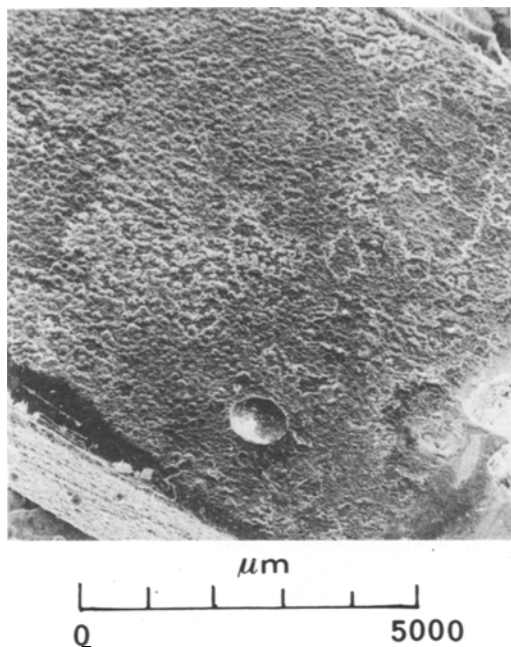


Fig. 11. Scanning electron micrograph of a deposit obtained using a pulsed electrolysis current with a silver electrode, $t_c = 30$ s, $t_a = 1$ s, $t_r = 60$ s, $X_{\text{Na}_2\text{SiF}_6} = 0.05$, $i_c = -40$ mA cm $^{-2}$.

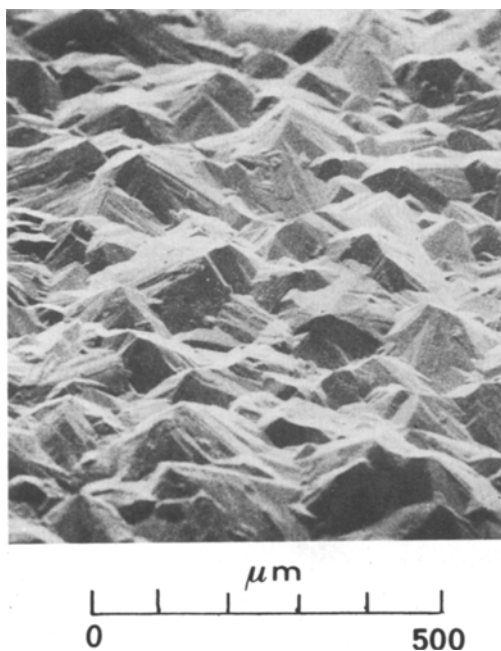


Fig. 12. Scanning electron micrograph of a deposit obtained using a pulsed electrolysis current with a silver electrode, $t_c = 30$ s, $t_a = 1$ s, $t_r = 60$ s, $X_{\text{Na}_2\text{SiF}_6} = 0.05$, $i_c = -40$ mA cm $^{-2}$.

5. Properties of thin silicon layers prepared

5.1. Structure

With a platinum wire, a layer of silicide was formed first. This was followed by the deposition of pure silicon and the deposit was nodular and dispersed all over the electrode surface. On a silver electrode regular layers of thickness up to 1 mm could be plated, the rate of crystal growth could be ≈ 30 $\mu\text{m h}^{-1}$. X-ray probes showed that the silicon was polycrystalline, with preferred orientations $\langle 111 \rangle$, $\langle 311 \rangle$ or $\langle 220 \rangle$ appearing on the electrolyte side.

The size of the grains were fixed by the electrolysis parameters. In the Figs. 13 and 14 are shown sections of the electrode parallel to its surface and a cross section perpendicular to the surface. The width of the grains was from 20 to 60 μm . The grains formed at the surface of the electrode did not increase and those which were growing tended, on the solution side, to a columnar structure, as was observed by Baraboshkin [54, 55] who has reported similar finding for electrolytic deposits from fused salts baths. The fact can probably be correlated with the preferential orientation of the deposits.

In this study we used four kinds of graphite:



Fig. 13. Scanning electron micrograph of a section of a deposit parallel to the electrode surface.

'TFA' (Vicarb), 'nuclear' with large grains, polished sheets of papyex (Carbone lorraine), and ribbon of payex (Carbone lorraine). Two kinds of deposits were obtained. On the TFA quality of graphite and the papyex ribbon, the deposits were nodular. The nodules, whose size could reach up to 200 μm (Fig. 15) coalesced (Fig. 16) on growing. Deposits on the 'nuclear' quality of graphite and on polished papyex sheets were similar to those obtained with a silver electrode.

5.2. Analysis of the deposits

The thin silicon layers obtained on a silver or graphite electrode were examined using emission spectroscopy. The results are reported in Table 1. The major impurities were alkali metals and iron. The amount of alkali was smaller when the solvent was purified by using cementation (analysis c).

The sparked mass spectrophotometry (Leti-Ceng) as used in the case of the electronic silicon analysis could not be used since we had difficulties in obtaining samples with the required dimensions. The neutron activation analysis proposed by Revel and Fedoroff [56] was better since the sensitivity of this method depends only on the mass of the sample. About fifty elements could be detected. We have prepared samples of electrolytic silicon

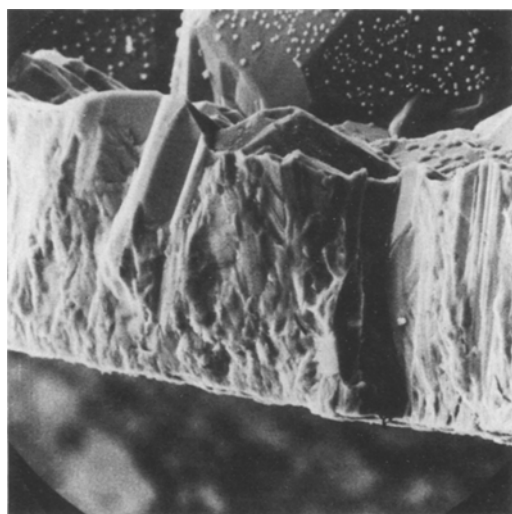


Fig. 14. Scanning electron micrograph of a cross section of a deposit obtained on a silver electrode.

Table 1. Qualitative analysis of emission spectroscopy

	Ag	Al	B	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Ti
a	0	F	ff	0	m	F ⁺	0	f	f ⁺	0	0	f ⁺	F
b	m	0	0	ff	f ⁺	ff	ff	fff	ff	f ⁺	ff	0	0
c	F ⁺	0	fff	0	fff	fff	0	ff	0	0	0	0	0

a Analysis of the metallurgical silicon used as anode.

b Typical analysis of the electrolytic silicon prepared when the solvent was purified by preelectrolysis.

c Typical analysis of the electrolytic silicon prepared when the solvent was purified by cementation.

Concentration in decreasing order are indicated by: F⁺, F, m, f⁺, f, ff, fff, 0 (not measurable).

using an insoluble anode of graphite or an anode of silicon. The typical results are given in Table 2.

The amounts of manganese (0.4 ppm and 0.1 ppm), magnesium (< 3.5 ppm and 0), vanadium (0.8 ppm and 1.1 ppm) were about the same for the two deposits.

On the other hand, the amounts of iron, copper and aluminium were lowered when a graphite anode was used (Fe < 5 ppm, Cu: 0.3 ppm, Al < 1 ppm) instead of metallurgical silicon (Fe: 60 ppm, Cu: 2.2 ppm, Al: 6 ppm). To lower the amount of

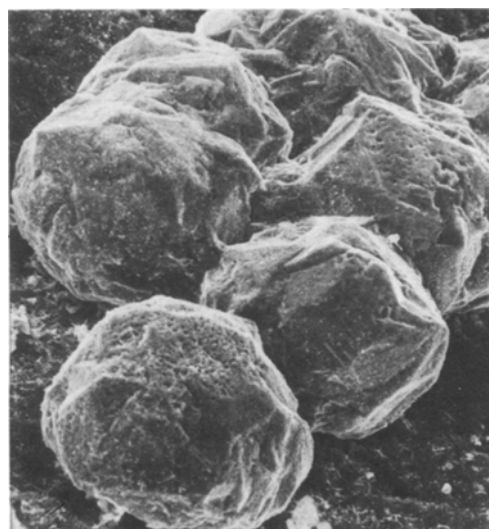


Fig. 15. Scanning electron micrograph of a deposit obtained on a papyex electrode.

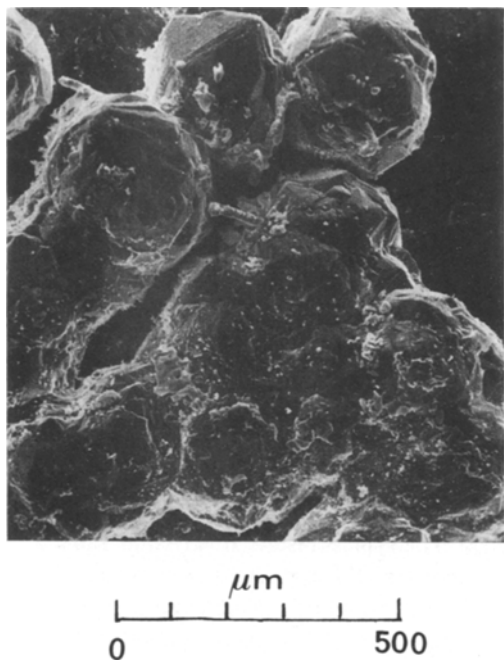


Fig. 16. Scanning electron micrograph of a deposit obtained on a papyex electrode.

Fe, Cu and Al, it was necessary to control the profile of the pulsed electrolysis current.

The other impurities resulted from the electrolyte and the materials used as the electrodes or the cell. These can be reduced by increasing the purification of the electrolyte or adjusting the pulsed electrolysis current parameters.

In conclusion, it is possible to obtain high purity electrolytic silicon, using a graphite or a metallurgical silicon anode; yet the choice of the electrolysis parameters must be specified.

5.3. The effect of the current parameters upon the chemical purity of deposits

As the amount of impurities from the solute was of the same order as those remaining in the purified solvent, no special chemical purification of the solute was carried out. But we tried to increase the purity of the electrolytic silicon by making the proper choice of the parameters of the current.

Thus the electrolysis of 0.05 mol dm^{-3} fluoro-silicate solutions were carried out varying the characteristic parameter $i_c t_c^{1/2}$ of the pulsed current between 6.3 and $118 \text{ mA cm}^{-2} \text{ s}^{1/2}$. We

Table 2. Results from the neutron activation analysis of the electrolytic silicon

Elements	ppm of impurities	
	Sample (d) 10 mg	Sample (e) 19.5 mg
Ag	0.4	1.7
Al	< 1	6
As	0.3	160
Au	0.006	0.006
Ba	< 1.2	< 5
Ce	< 0.02	< 0.02
Cl	< 6	—
Co	0.05	0.05
Cr	1.6	1.0
Cs	< 0.1	< 0.2
Cu	0.3	2.2
Eu	< 0.001	< 0.001
Fe	< 5	60
Ga	0.02	0.4
Hf	< 0.01	< 0.02
In	< 0.07	< 0.2
Mg	< 3.5	—
Mn	0.4	0.1
Mo	< 0.1	< 0.1
Na	11	14.5
Rb	< 0.2	< 0.2
Sb	0.08	0.3
Sc	0.0004	0.001
Sm	< 0.0002	< 0.0002
Th	< 0.003	< 0.004
U	< 0.005	< 0.005
V	0.8	1.1
W	< 0.002	< 0.003
Zn	< 0.8	1.9
Zr	< 11	< 3.7

obtained about the same results with silver or graphite electrodes, the purity of the prepared silicon was increased when the value chosen for $i_c t_c^{1/2}$ was lowered.

Looking at the quality of the different samples, it was observed that:

The amount of iron is very important for a possible photovoltaic use of the silicon and depended on the value $i_c t_c^{1/2}$, but not on i_c and t_c . It decreased six fold when $i_c t_c^{1/2}$ was varied from 118 to $6.3 \text{ mA cm}^{-2} \text{ s}^{1/2}$. The percentage of iron in the electrolytic silicon could be reduced to less than five ppm.

The nickel, which cannot be analysed by neutron activation, was tested by emission spectroscopic analysis; a verification by sparked mass

spectrophotometry showed that its amount was lower than three ppm.

The amount of other impurities e.g. cobalt, chromium, copper and antimony was between 0.05 to 2 ppm by using a pulsed current with $i_c t_c^{1/2} = 118 \text{ mA cm}^{-2} \text{ s}^{1/2}$; no better results were obtained for lower values of the quantity $i_c t_c^{1/2}$.

5.4. Physical properties of the material

This study was limited to the measurement of some electrical parameters. The conductivity of the silicon layers was always of the p-type. The resistivity by the four points method on a sample of thin layer, electrolytic silicon with thickness between 150 and 300 μm , varied between 0.1 and 1 $\Omega \text{ cm}$. The life time of the free carriers, obtained by the decrease of the photoconductivity using an electronic flash was around 30 μs . The mobility of the major carriers concerned, measured by the Hall effect, is of the order of magnitude for the crystals ($0.05 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} < \mu < 0.1 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$).

Acknowledgement

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References

- [1] C. Belouet, Réunion DGRST-CNRS Conversion Photovoltaïque, Limeil-Brevannes, Octobre 1978.
- [2] C. Belouet, J. J. Brissot, R. Martres and Ngo Tichphoc, 'Proceeding of the photovoltaic Solar Energy Conference', Luxembourg September 1977.
- [3] L. P. Hunt, V. D. Dosaj, T. R. McCormick and A. W. Rauchmolz, Dow Corning Corporation, Solid-state Research and Development Hemlock, Michigan 48626 CH 1319-3/78/0000-0333500 75 (C) (1978).
- [4] W. C. Breneman, E. G. Farrier and M. Morihara, Union Carbide Corporation CH 1319-3/78/0000-0339500 75 (C) (1978).
- [5] W. H. Reed, T. N. Meyer, M. G. Fey, F. J. Harvey and F. G. Arcella, Westinghouse CH 1319-3/78/0000-0370500-75 (C) (1978).
- [6] T. L. Chu, S. S. Chu, R. W. Kelm and G. W. Wakerfield, *J. Electrochem. Soc.* **125** (1978) 595.
- [7] T. L. Chu, G. A. Vander Leeden and M. I. Yoo, *J. Electrochem. Soc.* **125** (1978) 661.
- [8] R. Gauthier, Réunion DGRST-CNRS Conversion photovoltaïque, Limeil-Brevannes, Octobre 1978.
- [9] J. Amouroux, P. Fauchais, D. Morvan and D. Rocher, *Annales de chimie*, **4** (1979) 231/255.
- [10] M. Dodero, Thèse de Doctorat, Grenoble, (1937).
- [11] *Idem*, Abstracts de IUUPAC, Műwster, September (1954).
- [12] R. Monnier and D. Barakat, *Helv. Chem. Acta* **40** (1957) 2041.
- [13] G. Boe, K. Grojtheim, K. Matiasovsky and P. Fellner, *Canad. met. quart.* **10** (1971) 79.
- [14] *Idem, ibid.* **10** (1971) 179.
- [15] Yu. K. Delimarskii, R. V. Chernov and I. G. Kovzum, *Ukrain. Khim. Zhur.* **33** (1967) 675.
- [16] Yu. K. Delimarskii, R. V. Chernov and A. G. Golov, *ibid.* **34** (1968) 880.
- [17] *Idem, ibid.* **35** (1969) 792.
- [18] *Idem, ibid.* **35** (1969) 903.
- [19] Yu. K. Delimarskii, A. G. Golov, A. P. Nizov and R. V. Chernov, *ibid.* **34** (1968) 1227.
- [20] Yu. K. Delimarskii, R. V. Chernov and A. P. Nizov, *ibid.* **37** (1971) 422.
- [21] Yu. K. Delimarskii, N. N. Storchak and R. V. Chernov, *Electrokhimiya*, **9** (1973) 1443.
- [22] G. W. Mellors and S. Senderoff, *J. Electrochem. Soc.* **112** (1965) 266.
- [23] A. J. Gay and J. Quarkernaat, *J. Less Common Met.*, **40** (1975) 21.
- [24] *Idem, ibid.* **50** (1976) 189.
- [25] F. Olstovski, U.S. Patent 3022 233 (1962).
- [26] U. Cohen and R. A. Huggins, *J. Electrochem. Soc.* **123** (1976) 381.
- [27] U. Cohen, U.S. Patent 3 983 012 (1976).
- [28] *Idem, J. Electron. Mater.* **6** (1977) 607.
- [29] Y. A. Zyzhev and A. I. Ezrielev, *Sb. Tr. Agron. Fiz.* **13** (1966) 32.
- [30] P. J. Jorgensen, *J. Chem. Phys.* **49** (1968) 1594.
- [31] P. Blum, Thèse de Doctorat, Grenoble (1952).
- [32] P. Feliner and K. Matiasovski, *Electrodeposition and Surf. Treat.* **3** (1975) 235.
- [33] E. J. Frazer and B. J. Welch, *Electrochim. Acta* **22** (1977) 1179.
- [34] R. Boen, J. Bouteillon and M. J. Barbier, 'Proceeding of the second photovoltaic energy conference', Reidel Publishing, Luxembourg (1977) p. 860.
- [35] G. M. Rao, D. Elwell and R. S. Feigelson, *J. Electrochem. Soc.* **127** (1980) 1940.
- [36] *Idem, ibid.* **128** (1981) 1708.
- [37] R. C. De Mattei, D. Elwell and R. S. Feigelson, *ibid.* **128** (1981) 1712.
- [38] D. Elwell and G. M. Rao, *Electrochim. Acta* **27** (1982) 676.
- [39] D. L. Manning, *J. Electroanal. Chem.* **6** (1963) 227.
- [40] *Idem, ibid.* **7** (1964) 303.
- [41] D. L. Manning and G. Mamantov, *J. Electrochem. Soc.* **6** (1963) 328.
- [42] *Idem, ibid.* **7** (1964) 102.
- [43] J.A.N.A.F. Thermodynamical Tables (3rd edition) Nat. Stand. Ref. Data Ser., NBS (1976).
- [44] Yu. K. Delimarskii and B. F. Markov, 'Electrochemistry of fused Salts', The Sigma Press, Washington (1961).
- [45] A. Herold, *Bull. Soc. Chim. France* (1965) 999.
- [46] R. Setton, 'Les carbonés (II)', (edited by Masson), Ph. Touzain, Regards sur l'électrochimie et
- [47]

- l'électrometallurgie, OPE ed. Paris (1978).
- [48] P. Delahay, 'New instrumental methods in electrochemistry', Interscience, New York (1954).
- [49] J. W. Diggle, A. R. Despic and J. O'M. Bockris, *J. Electrochem. Soc.* **116** (1969) 1503.
- [50] J. N. Jovicevic, D. M. Drazic and A. R. Despic, *Electrochim. Acta* **22** (1977) 589.
- [51] N. Ibi. J. Cl. Puipe and H. Angerer, *Surf. Technol.* **6** (1978) 287.
- [52] M. Yokoi and T. Hayashi, *Denki Kagaku*, **46** (1978) 195.
- [53] D. L. Rehrig, H. Leidheiser and M. R. Notis, *Flu-ting and Surf. Fin.* **12** (1977) 40.
- [54] A. N. Baraboshkin, Z. S. Marten'yanova, S. V. Plaskin and N. O. Eisina, *Elektrokhim.* **13** (1977) 1807.
- [55] *Idem, ibid.* **14**, (1978) 9.
- [56] G. Revel and M. Fedoroff, *Nucl. Instrum. and methods*, **143** (1977) 277.