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Electrolytic production of silicon

D. ELWELL*

Diamond Cubic Corp, 4039 Avenida de la Plata, Oceanside, CA 92056, U.S.A.

GOPALAKRISHNA M. RAO

Chemistry Department, Rice University, Houston, TX 77251, U.S.A.

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A critical survey is given of the research and development studies on the electrodeposition of silicon. Among several systems, three are given particular attention, using inorganic baths with SiO_2 or K_2SiF_6 as the source of silicon respectively, or organic baths. The former two appear capable of development to commercial production. Conceptual designs of a commercial-scale cell for silicon production at temperatures above its melting point, and of a pilot plant for plating silicon from an all-fluoride bath are presented.

1. Introduction

Silicon is the Earth's second most abundant element and finds important applications in electronics and as an alloying component in the metals industry. It occurs primarily in the form of silicate rocks but the most important source mineral for silicon production is its oxide, SiO_2, which is the main constituent of sand. Silicon may also occur in a wide variety of forms from large quartz crystals to amorphous deposits, which are the skeletal remains of small marine creatures. The free element does not occur naturally, and most of the material used in the metals and electronics industries is obtained by carbothermic reduction of SiO_2. The purpose of this review is to explore the question of a possible role in industry for the electrolytic production of silicon. A critical survey will be given of the research done on the electrodeposition of silicon, and suggestions will be made of techniques which appear particularly promising in development for commercial application.

2. Relation to other elements

The argument that silicon should have a place in the electrochemical industry can be made by analogy with related elements in the periodic table. When those elements, for which an electrolytic process is of practical importance are surveyed [1–5], there is a strikingly high concentration to the left of silicon in the second row of the periodic table of metals which are produced on a large scale by electrowinning: Na, Mg and Al. Interestingly, these are all commercially produced in liquid form by molten salt electrolysis. Of course, the higher melting point (1412° C) and the higher charge on the Group IV element are disadvantageous for electrolytic processing of silicon. However, it is of interest to note that a Japanese group has been seriously considering the extraction of titanium as a liquid metal [6] and the Group IV elements; lead, titanium and tin (which also has a stable valence of 2) have already received commercial attention for electrowinning or electrorefining [1, 7–10].

3. Comparison with aluminium

The Hall–Heroult process for electrowinning of aluminium is now over 100 years old and is the industry standard for Al production. In terms of scale of production, aluminium electrolysis is second in importance only to the chlor-alkali industry. The source material is bauxite, Al_2O_3, which is mined with a purity of around 40%, so that extensive pre-treatment is required prior to its decomposition in the electrolytic bath. The bath is a solution of 2–6 wt % Al_2O_3 in molten cryolite ($3NaF \cdot AlF_3$) with small additions of CaF_2 and AlF_3 at 940–980° C, well above the melting point of aluminium. At this temperature the density of molten aluminium is higher than that of the bath, so the aluminium sinks and can be retrieved from the electrolytic cell by suction. The main advantage of the density difference is that the molten metal is protected by the bath from atmospheric oxidation, so the smelters do not require a protective atmosphere.

From Faraday's law, the energy required to produce 1 kg of aluminium is given by

$$W = \frac{FV_c z}{A\eta} \qquad (1)$$

where F is Faraday's constant, V_c the cell voltage, z the valence of Al and A its atomic weight, η the cell efficiency. Substituting $z = 3$ and $A = 27.0$ gives

$$W = 10.73\, V_c/\eta \,\mathrm{MJ\,kg^{-1}} \qquad (2)$$

For a typical cell voltage in modern plants of around

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* *Present address*: Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, CA 90265.

0021-891X/88 $03.00 + .12

4 V, with $\eta = 0.9$, the power requirement is around $47\,\mathrm{MJ\,kg^{-1}}$, a value which would be considered satisfactory [11]. The total cell voltage V_c is made up of a decomposition voltage of 1.75 V, a voltage drop V_b across the bath of around 1.5 V, with the remainder the ohmic drop across the anode, connectors, lining etc. The producer list price of aluminium in 1986 was #1.78 $\mathrm{kg^{-1}}$, spot price about \$1.2 $\mathrm{kg^{-1}}$, and world production was in the region of 18 million metric tons [12].

In the case of silicon, $z = 4$ in Equation 1 and $A = 28.0$, so that Equation 2 becomes

$$W = 13.79 V_c/\eta\,\mathrm{MJ\,kg^{-1}} \qquad (3)$$

an increase of 28.5% over aluminium, assuming the same values of V_c and η in a commercial silicon cell. The higher energy requirement is, however, offset by the widespread availability of silica in relatively high purity and at a low price. The cost of alumina, including purification, accounts for about 30% of the cost of production of aluminium. Electricity accounts for about 23%, labour 16%, anodes and other materials about 14% and the remaining 17% is capital.

4. Source materials

Silica occurs extensively as quartzite, a rocky crystalline variety with typically less than 1% of metallic impurities and often occurring in very high purity. Dosaj *et al.* [13] carried out a survey to find the purest naturally-occurring deposits of silica and some typical analyses for the most significant impurities (Al, Fe, Ti) are shown in Table 1. These materials have been used in processes aimed at producing 'solar grade' silicon (SGSi) with a purity substantially higher than that of the metallurgical grade (MGSi). The relatively pure lump sources cost around \$0.50 $\mathrm{kg^{-1}}$ while the less pure Illinois material costs around \$0.10 $\mathrm{kg^{-1}}$ in bulk.

Another important source of silicon is fluorosilicic acid which is a by-product of phosphate fertilizer production. Silicates occur together with phosphates in the rocks from which the fertilizer is extracted, and the extraction process yields fluorosilicic acid of 98–99% purity and at low cost. The silicon costs less than \$1 $\mathrm{kg^{-1}}$. The acid may be neutralized to form the sodium or potassium salt:

$$H_2SiF_6 + 2KOH = K_2SiF_6 + 2H_2O \qquad (4)$$

or the dilute acid is reacted with NaF to give hydrofluoric acid as a by-product:

$$H_2SiF_6 + 2NaF = Na_2SiF_6 + 2HF \qquad (5)$$

Table 1. Impurity analysis of high purity natural silica (p.p.m.w.) [13]

Impurity	*Mt. Rose Lump*^{a}	*Malvern Lump*^{b}	*Manville*^{c}	*Illinois powder*^{d}	*Ottawa silica*^{e}
Al	30	60	35	1300	430
Fe	20	30	63	250	160
Ti	1	< 1	< 10	300	150

Sources: (a) Mount Rose Mining Co, Armstrong, BC, Canada; (b) Malvern Minerals Co, Hot Springs, Arkansas; (c) Manville Corp, Lompoc, California; (d) Illinois Mineral Co, Cairo, Illinois; (e) Ottawa Silica, Ottawa, Illinois.

Table 2. Impurity analysis of fluorosilicic acid [14] and rice hulls [15] (p.p.m.w.)

Element	*Fluorosilicic acid*	*Rice hulls*
Al	8	10
As	9	–
B	1	2
Ca	110	1000
Fe	13	20
K	9	3800
Mg	55	500
Mn	0.2	350
Mo	11	–
Na	460	25
P	33	130
Pb	15	–
S	–	40
Ti	–	3

Another potential source of silicon which has not been exploited commercially is rice hulls. It is the silica particles in the rice hulls which gives them their stiffness, and US production alone could yield 100 000 tons of silicon annually if an extraction process could be developed. The hulls can be bought for about \$0.20 $\mathrm{kg^{-1}}$ and the metallic impurities are comparable with those in a high purity mineral silica. Carbon is, of course, a major constituent and the C : Si ratio in rice hulls is about 4 : 1. Analytical data for rice hulls and fluorosilicic acid are given in Table 2.

MGSi, for comparison, contains typically 0.1–0.4% Al, 0.1–0.6% Fe, 0.1–0.3% C and smaller quantities of transition metals and other metallic impurities. The price of MGSi is in the range \$1–2 $\mathrm{kg^{-1}}$ depending on purity and market conditions.

5. Electrodeposition of silicon

5.1. *Introduction*

Progress in silicon electrodeposition and the possible applications of electrolytic silicon have been reviewed by a number of authors. Elwell [16] and Fulop and Taylor [17] surveyed the whole field of electrodeposition of semiconductors. Elwell and Feigelson [18] discussed the possible application of electrolysis to produce SGSi, while Rao and Elwell [19] briefly considered the prospects for economic electrowinning of silicon for more general applications. A general review of silicon electrowinning and refining was given by Monnier [20], with particular emphasis on the SiO_2/cryolite system.

5.2. *History*

Shortly after the invention of the first battery, the Volta piles, electrolysis was used to produce light metals and it is not surprising that attempts to electrodeposit silicon date back to the mid-19th century. The first attempt on record is that of St. Claire DeVille, who claimed that silicon was produced by electrolysing an impure melt of $NaAlCl_4$, but his material did not oxidize at white heat [21]. However, Monnier [20] reports that DeVille later electrolysed a solution of SiO_2 in a KF/NaF melt and deposited silicon on a platinum cathode where it reacted to form a Pt silicide. Gore [22] claimed to have deposited silicon from an aqueous solution of potassium monosilicate, but there has been no subsequent confirmation that silicon can be electrodeposited from any aqueous system. It is possible that the first electrodeposition of elemental silicon can be credited to Ullik [23] who in 1865 electrolysed a solution of K_2SiF_6 in KF. Before the end of the century, Minet [24] made Fe–Si and Al–Si alloys from the solutions of SiO_2 with iron and aluminium oxides in NaCl + $NaAlF_4$, and Warren [25] made a silicon amalgam by electrolysis of SiF_4 dissolved in alcohol, with a mercury cathode. Already by 1900, therefore, SiO_2 and fluorosilicates had been established as possible solutes for Si electrodeposition, alkali halides as possible solvents, and both organic solutions and liquid cathodes had been tried.

Systematic study of Si electrodeposition did not begin until the 1930's when Dodero [26, 27] electrolysed various molten silicates in the temperature range 800–1250° C. Fluoride additions were used to lower the melt viscosity and melting temperature. Dodero used very high deposition potentials which might be expected to liberate alkali or alkaline earth metals in addition to silicon, and the maximum Si in any deposit was 72%. This best result was obtained from a melt of composition $5SiO_2 \cdot 1Na_2O \cdot 0.2NaF$, electrolysed at 1150° C. His experiments did not offer conclusive proof that the silicon was a primary product of electrolysis, rather than being produced by a secondary reaction between electrodeposited alkali or alkaline earth metal and silicon-containing species in the melt.

5.3. *Silica-based electrolytes*

In considering more recent work, we examine the promise of electrolysis in electrorefining, electrodeposition of various coatings, and particularly in electrowinning. An attempt is made to identify broad trends and to focus on promising developments.

In general, studies aimed at the development of a commercial process for electrowinning have focussed on SiO_2 as the source of silicon. The melt compositions most likely to serve as electrolytic baths in a commercial process are molten silicates or solutions of SiO_2 in cryolite.

Cryolite Na_3AlF_6 is appealing as a solvent for SiO_2 because of its availability and its success in the Hall–Heroult process. The SiO_2/Na_3AlF_6 system has been extensively investigated in both laboratory experiments and pilot scale trials, particularly by Monnier and co-workers [20, 28, 29] and by Grjotheim and co-workers [30–33] who were mainly concerned with the deposition of Al–Si alloys. Studies of the solution interactions reveal a two-stage reaction when the constituents are first heated. Over the first 30 minutes, simple oxides are formed:

$$\begin{aligned} &4Na_3AlF_6 + (x+3)SiO_2 \\ &= 3SiF_4 + 2Al_2O_3xSiO_2 + 12NaF \qquad (6) \end{aligned}$$

As the reacion proceeds, complex oxides such as albite $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ and nepheline $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ can be seen in quenched solutions [20].

Monnier and co-workers were able to obtain 99.9 to 99.99% pure silicon from SiO_2-cryolite even at fairly high current densities. The measured deposition potentials (at zero current) could be explained by thermodynamic data. A graphite anode was used, and the gases generated by the anode reaction were mixtures of CO and CO_2. The higher purity silicon required the use of a two-stage cell. Electrowinning occurred in the first stage, the cathode of which was a molten Cu–Si alloy which formed the anode of the second stage.

The only pilot plant study of Si electrodeposition reported in the literature involves the electrolysis of the SiO_2-cryolite system. Monnier [20,34] reports that his studies of this system began in 1957 and that a pilot plant was built and operated between 1960 and 1966. Two types of furnace were used, one with carbon electrodes heated by 3-phase AC, with some heating provided by the electrolytic current. The highest deposition current in this case was 300 A. In the second version, currents up to 3000 A were used and the entire heating was provided by the electrolytic current. The crucible was protected by a coating of solidified electrolyte, so the bath was effectively contained in a solid of the same composition (Fig. 1). Current densities as high as 800 mA cm^{-2} were used. The deposits were in the form of crystals 1–3 mm in size, which were separated from the solidified bath by vacuum evaporation or selective dissolution. After purification by zone refining, the silicon was stated to be of semiconductor quality.

The failure of this project to reach commercial development is probably due to the slow rate of deposition which is inevitable in any process where the deposit is a solid. This limitation has been discussed

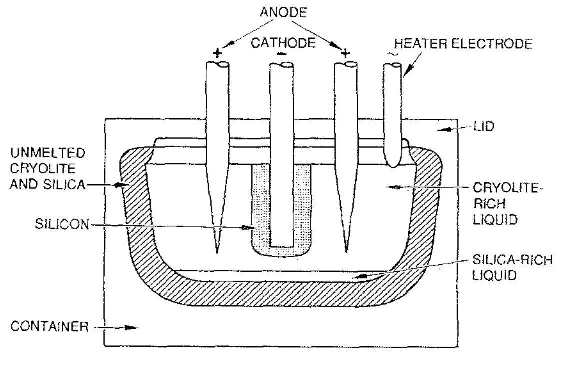

Fig. 1. Cell for silicon production in which the electrolyte is contained in an unmelted solid of the same composition [20, 28].

by Huggins and Elwell [35], who derived an expression for the limiting rate of advance of a plane surface growing by electrodeposition if solvent inclusions are to be avoided. The limitation does not apply if deposition occurs in the liquid phase, since the surface tension of the liquid acts to exclude solvent globules that would be trapped between adjacent protrusions in the growth of a solid at high rates.

The attempt to develop a viable process for deposition of silicon above its melting point was the focus of a 3-year program at Stanford during 1978–81. This program was limited to studies in a small experimental chamber with crucibles typically 6 cm in diameter and 8 cm tall. These appeared to be the first electrodeposition studies at temperatures well in excess of 1200° C. The relatively high melting point of silicon, 1412° C, is a handicap in attempts to develop a 'Hall–Heroult' process for silicon, and the choice of construction materials is restricted.

Since SiO_2 melts at temperatures above 1700° C, a binary or ternary melt composition is required for deposition at about 1450° C and the simplest choice appears to be an alkali- or alkaline earth-silicate system. Electrolysis of molten silicates may produce silicon, silicon monoxide or the metal as the cathodic product. The respective reactions may be represented schematically by the equations:

$$3\,MSiO_3 = 3MO + [Si] + 2SiO_2 + O_2 \qquad (7a)$$

$$4\,MSiO_3 = 4.MO + [2SiO] + 2SiO_2 + O_2 \qquad (7b)$$

$$2\,MSiO_3 = [2\,M] + 2SiO_2 + O_2 \qquad (7c)$$

where the cathodic product is shown in square brackets. Thermodynamic data is in general not available for calculations of the likely reactions in systems of interest. Johnson [36] calculated that the theoretical product of electrolysis of calcium silicate should be silicon throughout the range 1200–2000 K and Poris and Huggins [37] extended these calculations. They found that Ca and Mg silicates appeared particularly favourable for Si deposition; Li silicate less promising; while K and Na silicates should yield the alkali metal on electrolysis. It was confirmed experimentally that potassium was liberated on electrolysis of K_2O/SiO_2 melts at 1450° C. Electrolysis of Li silicate melts gave silicon, but not at temperatures above its melting point. Mg and Ca silicates did not yield silicon, and the best results were obtained using the BaO/SiO_2 eutectic [38]. BaF_2 was added to facilitate the reaction between $BaCO_3$ and SiO_2 to form the melt, and to lower the melt viscosity. Silicon was also deposited by electrolysis of baths in the $SrO/SiO_2/SrF_2$ system.

The BaO/SiO_2 system has a single eutectic of composition 53% SiO_2/47% BaO by weight and melting at 1370° C. About 15% of BaF_2 was added to this composition and purified melts were electrolysed at about 1450° C in graphite crucibles and using graphite electrodes. Applied potentials were normally in the range 1–8 V with curents of 0.1–2.0 A on an immersed area of about 2 cm^2. Silicon has a lower density than the bath, and the molten Si deposits floated around the cathode and gathered into roughly spherical drops, in a horizontal layer near the surface. The largest lump obtained by cooling a melt and dissolving the solidified silicate weighed over 1.6 g and contained over $\frac{1}{3}$ of the total silicon deposited from a 125 g bath. The Faradaic efficiency of deposition was typically 20%, although values as high as 40% were observed. The efficiency tended to decrease with applied potential difference, possibly because of increasing liberation of SiO. This correlation was not firmly established, however, and the SiO could have been evolved because of a slow reaction between the electrodeposited silicon and the silicate bath. Clearly an efficiency in the range 20–40% would not be acceptable for a commercial process but the main limitation could be associated with the small size of the apparatus used. A reverse reaction between anodic and cathodic products is to be expected in a small system, and is known to be significant in Hall–Heroult systems when the anode–cathode separation is less than about 2 cm.

The purity of Si electrowon from the barium silicate melts was about 99.98% by weight, the main impurities being 60 p.p.m. of Ti and 20 p.p.m. each of Al and Fe. Silicon of this purity is close to the quality required to produce 10% efficient solar cells by a single stage of directional solidification [39]. The major impurities originate in the SiO_2 and can be reduced by purification of the silica in HCl gas at about 800° C, or by the use of a purer starting material. The SiO_2 used in this investigation [38] was Illinois Mineral material of 99.5–99.8% purity.

Since electrolytically produced silicon is of lower density than the bath, a modified magnesium [40] or Down's cell for sodium [2] might be suitable. A possible design for a commercial cell for silicon electrodeposition is given in Fig. 2. The cell is of steel construction with the cathode supports welded to the

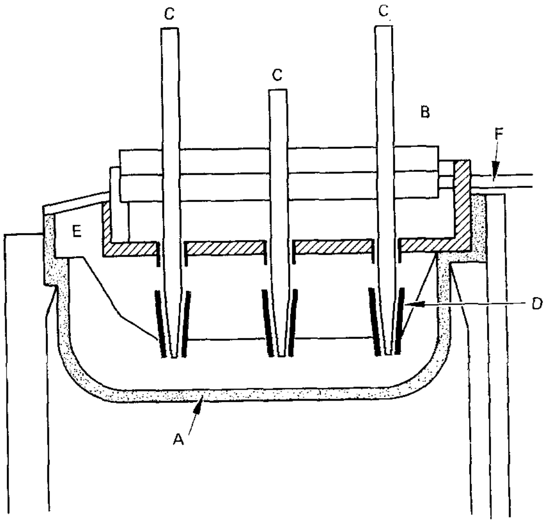

Fig. 2. Schematic of a commercial scale cell for depositing silicon above its melting point, adapted from [40]. The steel container (A) is fitted with a ceramic cover (B) through which pass the graphite anodes (C). The silicon is deposited on the cathodes (D) and rises into a collection area (E). Gaseous anodic products are withdrawn through a vent (F).

tub-like container that holds the melt. These are fitted with refractory covers, which act as ports for the graphite anodes, metal suction system and solute feed. The anodes are suspended in a manner that permits them to be adjusted independently as the graphite is consumed during electrolysis, to maintain the proper spacing and centering with respect to the cathode. The outside area of the steel container is surrounded by a refractory chamber with arrangements for gas or electric heating. This allows flexibility in adjusting to various electrical loads, especially as the cells are restarted after a complete shutdown. Since a similar system, oxide/cryolite, is used in aluminium electrolysis the cell construction materials used in aluminium cells are generally an appropriate choice. There is, however, the requirement that any materials used must be stable and inert up to 1500° C. Without a protective coat on the steel cathode support, the initial product deposited at the cathode is likely to be iron silicide. If this silicide formation ceased on continued electrolysis, steel would be an inexpensive choice for the silicon production. Otherwise, a suitable coating material on the steel would certainly be required. This coat would also have the role of minimizing the iron contamination of the silicon. Our laboratory experiments [38] suggest graphite as a suitable coating material and inner liner for the steel container. Alternatively TiB_2, TiC or TiB_2–TiC mixtures, which have been successfully tested in aluminium pilot scale cells [11, 41], could be tried as possible coating materials. Although consumable graphite anodes are the initial choice, the inert anodes in development for aluminium cells [41] should also be tested in this system. The silicon produced at the cathode rises into the collection chamber in front of the cell. Molten silicon can be periodically pumped out and cast into ingots. Alternatively, the silicon could be pulled directly from the collection chamber as relatively pure boules because of the additional purification inherent in controlled solidification. Although not shown in Fig. 2, it is desirable to use a diaphragm either to separate the anode and cathode or to act as a hood surrounding the upper region of the anode but immersed 2–3 cm into the melt. The purpose of this arrangement is to minimize the back reaction. To maintain the heat balance in the cell and to control the mass balance in the bath, the cells should be fed semicontinuously through a screw-type feeder, not shown in Fig. 2.

An inert gas atmosphere is required to protect the graphite and to prevent oxidation of the floating silicon. This requirement would add to construction and operating costs but the argon would be recirculated after passing through scrubbers to remove fluoride traces.

The cost of power is an important factor affecting the commercial viability of a silicon plant. Commercial plants could be designed in which most or all of the heat required to maintain the bath at about 1450° C would originate from Joule heating by the deposition current. In a plant with a current 10^5 A at 6 V, a Joule component of 20% would provide 150 kW of 'waste' heat which should be ample to compensate for heat losses from a well-insulated container. Plants used for aluminium production normally require active (i.e. forced) cooling. In general, the cost of silicon produced by this method should be comparable with that of aluminium from the Hall–Heroult process.

An alternative technique which avoids 1400° C+ temperatures involves the use of liquid cathodes as pioneered by the Monnier group [20]. Olson and Kibbler [42] introduced a molten tin cathode which is preferable to Al or Cu used earlier since it does not lead to shallow levels or to deep-level recombination centres in semiconductor silicon. Using a bath of SiO_2 dissolved in Na_3AlF_6/LiF, crystallites in the size range 1–10 mm were produced on solidification of the Sn–Si solution. The silicon contained about 10 p.p.m. of transition metals and had a resistivity of 0.05–0.1 Ω cm. The major disadvantage associated with the use of the alloy cathode is the slower deposition rate combined with the increased complexity of extracting the silicon from the solidified tin. In the opinion of the reviewers, it is the high temperature process which offers the best prospects for commercialization.

5.4. *Fluorosilicate-based electrolytes*

Fluorosilicates as source materials have been investigated intensively but their continued availability as an inexpensive source is dependent on the fertilizer industry. However, fluorosilicates can also be produced *in-situ* by the reaction of silica with alkali and alkaline-earth fluoride baths at 1000–1100° C [43]. The commercial production of silicon using a fluorosilicate-fluoride system is analogous to the molten salt process for titanium. The latter process was tested successfully on a pilot plant scale [1, 7, 8] but did not proceed to full-scale development due to market conditions rather than to any technical problems, at least for the Dow-Howmet cell [44]. It is therefore clear that silicon produced from an analogous system would be attractive to industry only if the product had some special application. Film deposits have shown promise for direct application in low-cost solar cell fabrication and as a corrosion protection coating [19, 45], especially at elevated temperatures. Also, electrolytically produced silicon of 4N (99.99%) purity or better (as layer, dendrite, sponge or powder) has the potential to replace MGSi, which needs further purification, as a charge for directional solidification or distillation as a volatile species (e.g. trichlorosilane or tribromosilane) to produce electronic grade silicon.

The deposition of silicon films using K_2SiF_6 began at the Stanford University Center for Materials Research in the early seventies. Although several fluoride solvent systems were studied, only LiF–KF and LiF–KF–NaF melts gave acceptable quality deposits. In early work, Cohen [46] showed that single crystal epitaxial layers could be electrodeposited from solutions of K_2SiF_6 in a LiF–KF eutectic and that

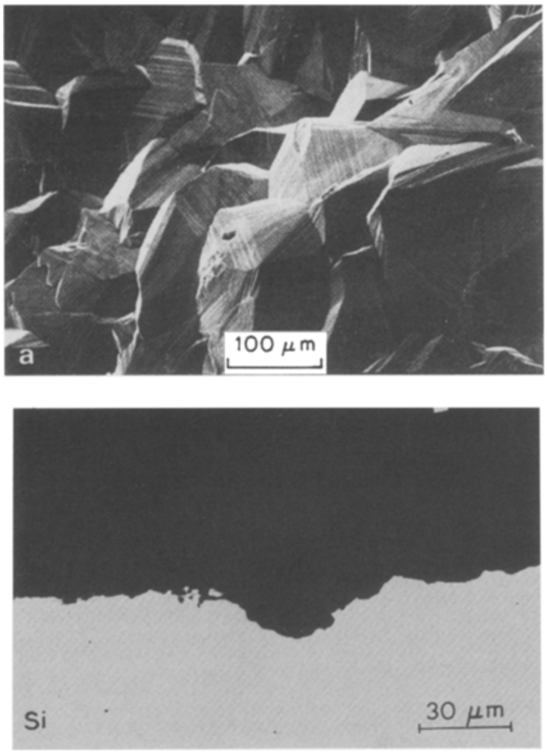

Fig. 3. (a) SEM photograph of the surface of an electrodeposited silicon layer on graphite [49]; (b) Polished cross-section through a boundary between the silicon electrodeposit and a porous graphite cathode. Note the low concentration of inclusions and voids in the silicon.

continuous films could be produced by electrorefining using a dissolving silicon anode. Later work shifted to electrowinning of silicon using an inexpensive graphite anode. The ternary LiF–KF–NaF eutectic or the binary LiF–KF eutectic at 750° C were used as solvents and had the advantage of a high solubility for K_2SiF_6. In the earlier experiments [45, 47], silver was chosen as cathode material because of easy nucleation of silicon. Relatively inexpensive graphite substrates, including low grade porous material, were used in later experiments [48, 49]. Since a low K_2SiF_6 concentration normally resulted in a non-uniform powdery or dendritic deposit on top of a thin, coherent layer about 2 μm thick [47], the K_2SiF_6 concentration was maintained between 4–20 m/o to grow thicker, continuous silicon deposits. The silicon was electrodeposited at a constant current (10–25 mA cm^{-2}) or at a constant potential (-0.74 ± 0.04 V against Pt) for 2–4 days. Well-adherent, coherent and continuous films (Fig. 3) up to 3–4 mm in thickness were prepared in this study. Growth was columnar with a normal grain size up to 250 μm. The current efficiency for silicon deposition was as high as 80%. The purity of electrodeposited silicon was normally 4 N, but the level of impurities in the best samples was less than 10 p.p.m. Undoped samples were normally *n*-type with resistivity up to 3 Ω cm, carrier mobility 100 cm^2 V^{-1} s^{-1} and carrier concentration 10^{17} cm^{-3} [50].

Other recently published studies [51–57] on this system have added additional complementary information. Olson and Carleton [51] used a silicon-copper anode to simulate the electrorefining of the metallurgical grade silicon, while Sharma and Mukerjee [56] demonstrated the semi-continuous production of 99.99% pure silicon powder from impure (2.5% impurity) MGSi. Bouteillon *et al.* [54, 57] showed that improvements in deposit morphology and the purity of the silicon (impurity levels less than 1 p.p.m.), both during electrowinning and electrorefining, could be achieved by pulsed electrolysis, which is currently practised in commercial copper electrolytic cells.

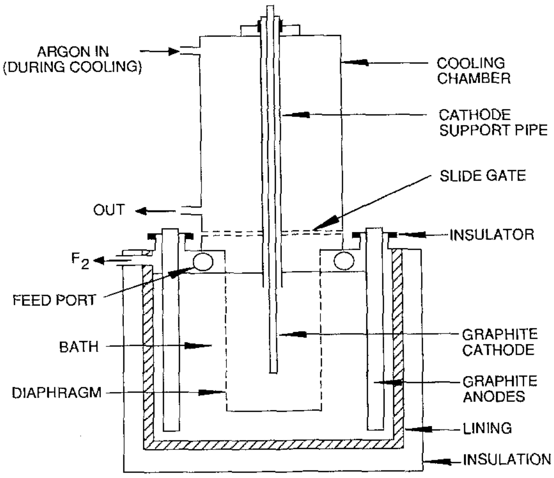

Fig. 4. Design for a pilot cell for electrodeposition of silicon from a fluorosilicate-fluoride bath (adapted from [8]).

The quality, purity and electronic properties of electrolytically produced silicon from the fluorosilicate-fluoride system show promise for commercial applications. However, all the experiments to date have been done on a small laboratory scale. Future study should include pilot plant investigations aimed at solving electrochemical engineering problems. A pilot scale design is shown in Fig. 4, which is adapted from the pilot scale cell for titanium electrowinning developed by NL Industries [8]. Both Si and Ti processes involve a molten salt medium and require four electrons for the reduction from M^{4+} to M, although the actual steps are more complex [57, 58]. The capital cost, the use of refractory metals and other working conditions are also comparable. The initial choice of electrode materials would be graphite. If it is economically possible, graphite- or silver-coated steel could replace graphite cathodes. The inert electrodes discussed in the preceding section and the new diaphragm materials must be tested thoroughly prior to use even in pilot production cells.

5.5. *Organic electrolytes*

The deposition of amorphous silicon (a-Si) films is of interest both for solar cells and for hard, protective coatings. Since a-Si can be deposited at temperatures close to ambient, the energy cost of a-Si deposition is very low in comparison with that possible using molten salts.

The first report of a-Si electrodeposition was by Austin [59], who investigated a number of organic systems at temperatures in the range 20–100° C. He preferred anhydrous aprotic organic solvents such as propylene carbonate or tetrahydrofuran, with silane or a simple silicon halide as solute. The silicon deposited had a resistivity of around 20 Ω cm, and contained a number of impurities in concentrations of less than 10 p.p.m.

Bucker and Amick [60] reported that their attempts to reproduce the earlier results led to films which were unstable against atmospheric attack. They recommended heat treatment of the films at about 350° C to remove excess hydrogen prior to exposure to the atmosphere. Preferred solvents were tetrahydrofuran/benzene, tetrahydrofuran/toluene, dioxolane/benzene and dioxolane/toluene. Silicon tetrachloride or trichlorosilane were used as solute. The films contained traces of chlorine and chromium.

In the most detailed studies to date, Kroger and co-workers [61, 62] included dopant studies in investigating the potential of a-Si for solar cells. Lee and Kroger [61] used solutions of SiF_4 in ethyl alcohol, dimethyl sulfoxide with HCl, and acetonitrile. In order to increase the conductivity, potassium fluoride was added to form solutions of K_2SiF_6, with additional HF added for further increase in conductivity. Their aim was to make fluorinated a-Si, which should have a higher stability than hydrogenated a-Si. Since fluorine is normally an anodic product, the cathodic deposition of fluorinated a-Si implies the incorporation of fluorine-containing complexes from the electrolytes. Deposition was performed in a Teflon vessel with argon gas as a protective atmosphere. Nickel or stainless steel was used as cathode, and platinum as the anode. The resistivity of the films was of the order of 10^{12} Ω cm and, although phosphorus doping could change the films from p- to n-type, the lowest resistivity was still 10^{11} Ω cm.

A parallel study by Rama Mohan and Kroger [62] included a-Si deposition using tetraethyl orthosilicate or silicic acid dissolved in ethylene glycol or formamide-ethylene glycol mixtures containing HF. The undoped films were p-type due to the presence of the fluorine, but in this system the resistivity could be reduced to $\sim 10^5$ Ω cm by phosphorus doping using triethyl phosphate. At this stage, therefore, the resistivity is still not low enough for the fabrication of useful solar cells, but the techniques for depositing films of a-Si at temperatures close to ambient have been well established. Future studies should be concentrated on the use of a-Si films as protective coatings.

6. Summary and conclusions

Silicon dioxide SiO_2 occurs in nature as pure deposits which can be mined inexpensively. Although carbothermic reduction is well established as a practical method of producing silicon of metallurgical grade, electodepositon offers a viable alternative of producing silicon of significantly higher purity at a cost comparable with that of aluminium. The relative absence of carbon in electrodeposited silicon should offer advantages for some high-grade metallurgical applications, and the electrodeposited silicon should be an attractive starting material for solar applications or as a feed material for the production of semiconductor or detector grade silicon.

The rate of production of silicon as a solid may be too low for commercial viability, and materials such as Na, Mg and Al in the same row of the periodic table are all produced at temperatures above their respective melting points. Designs have been presented for a plant for production of silicon as a liquid, by electrolysis of a barium silicate-fluoride bath. Its rather high melting point of 1412° C is clearly a disadvantage but should not be an impossible hurdle and is, for example, much lower than that of iron. The yield of silicon needs to be improved over that obtained in small-scale laboratory studies but an improvement is to be expected on scale-up. This challenge and that of developing a method for efficient collection of the electrolytically-produced silicon are reasonable and should not require a very high investment.

The alternative of using an all-fluoride bath, with K_2SiF_6 as the source of silicon, may also find a commercial role. The purity and morphology of the deposits from laboratory scale experiments show promise for the direct fabrication of solar cells. The most promising application of this technology is in producing hard, chemically stable coatings on metal surfaces. Also, silicon dendrites, sponge and powder of 4 N purity could replace MGSi as the charge to produce higher purity silicon by directional solidification. Amorphous silicon can be electrodeposited from organic baths but the material is a long way from reaching a stage where it could challenge deposition from the vapour phase for applications in solar calculators etc. Again there may be some potential as a chemically stable protective coating at moderate temperatures.

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