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## **Silicon Literature Review and Reaction Data**

This document is a collection of information that has been gathered related for purposes of the silicon electrochemistry project at San Juan College.

### **Silicon Literature Review**

#### **M. A. Green**

The University of New South Wales

Photovoltaics Special Research Centre at the University of New South Wales

<http://www.pv.unsw.edu.au/info/thininfo.html>

Home Page <http://www.pv.unsw.edu.au/>

Most commercially available solar cells are made from wafers of very pure monocrystalline or polycrystalline silicon. Such solar cells can attain efficiencies of up to 18% in commercial manufacture and over 20% in the laboratory. However, the silicon wafers used to make them are relatively expensive, making up 20-40% of the final module cost. Although silicon is highly abundant (comprising one quarter of the earth's crust), making a very pure wafer suitable for solar cell manufacture requires much energy and is therefore relatively costly. Moreover, a solar cell made using a 300-400 micrometre thick wafer generates 90% of its energy from the top 15-20 micrometres. The rest of the wafer is required simply to hold the cell together.

The Center at UNSW continues to develop buried contact multiple junction solar cells.

#### **T. Matsuda, S. Nakamura, K. Ide, K. Nyodo, S. Yae, and Y. Nakato, "Oscillatory Behavior in Electrochemical Deposition Reaction of Polycrystalline Silicon Thin Films Through Reduction of Silicon Tetrachloride in a Molten Salt Electrolyte", *Chemistry Letters*, no 7, p569 (1996)**

A new electrochemical oscillation is found for the reduction reaction of silicon tetrachloride on a partially immersed single crystal n Si electrode in a lithium chloride potassium chloride eutectic melt electrolyte. The reduction of  $\text{SiCl}_4$ , which is almost insoluble in the electrolyte, occurs mainly near the upper edge of an electrolyte meniscus on the electrode, and it is discussed that the oscillation is caused by a change in the height of the meniscus due to a change in the chemical structure and hence the interfacial tension of the electrode surface with progress of the silicon deposition reaction.

#### **K. Agrawal and A. E. Austin, "Electrodeposition of Silicon from Solutions of Silicon Halides in Aprotic Solvents", *J. Electrochem. Soc.* Vol 128, no 11, p2292 (1981)**

Amorphous silicon has been electrodeposited from nonaqueous baths using  $\text{SiHCl}_3$  as the silicon source. A typical bath composition was 1 M  $\text{SiHCl}_3$  in propylene carbonate containing .1M tetrabutyl ammonium chloride as the supporting electrolyte. Deposits were made potentiostatically at around  $-2.5\text{N}$  vs Pt reference at temperatures 35 to 145 C under and argon atmosphere. A variety of materials including Pt, Ti, Ti 6Al 4V alloy, nSi and indium tin oxide

coated fused silica were used for the substrate. The as deposited silicon contains some hydrogen bonded as SiH<sub>2</sub> or Si H. The quality and hydrogen content of the deposits are controllable by selecting the proper bath composition and operating temperature. The electrodeposition process offers an inexpensive route for producing a Si films for possible solar cell applications.

**G. M. Rao, D. Elwell, and R. S. Feigelson, "Electrowinning of Silicon from K<sub>2</sub>SiF<sub>6</sub> Molten Fluoride Systems", J. Electrochem. Soc., vol 127, no 9, p 1940 (1980)**

The electrowinning of silicon from solutions of K<sub>2</sub>SiF<sub>6</sub> in fluoride melts at 745 C has been achieved. Electrolysis close to the deposition potential gave dense, coherent, and well adherent deposits. Up to 3mm thick films were grown using a K<sub>2</sub>SiF<sub>6</sub> concentration of 4-6 m/o. The polycrystalline silicon has a columnar structure with grain size up to 100 micrometers. 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.

**Y. Takeda, R. Kanno, O. Yamamoto, T. R. Rama Mohaan, C. H. Lee, and F. A. Kroger, "Cathodic Deposition of Amorphous Silicon from Tetraethylorthosilicate in Organic Solvents", J. Electrochem. Soc., vol 128, no 6, p 1221 (1981)**

A blue thin film of amorphous silicon has been deposited on a nickel cathode by the electrolysis of a solution of tetraethylorthosilicate in acetic acid. The maximum thickness of the film obtained was about .5 micrometers. The deposit was confirmed to be amorphous silicon by IR reflection spectra, RHEED, and nondispersive x ray analysis in the scanning electron microscope.

**J. Gobet and H. Tannenberger, "Electrodeposition of Silicon from a Nonaqueous Solvent", J. Electrochem. Soc., vol 135, no 1, p 109 (1988)**

Electroplating of silicon from solutions of SiHCl<sub>3</sub>, SiCl<sub>4</sub>, SiBr<sub>4</sub>, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>, Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>, Si(OOCCH<sub>3</sub>)<sub>4</sub>, and Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> in tetrahydrofuran, using LiClO<sub>4</sub>, TBAP, or TBAB as supporting electrolyte has been studied. Si-C, Si-O, and Si-N bonds are not reduced. Cyclic voltammetry shows a reduction peak, followed by passivation, for the halogenosilanes. Potentiostatic and galvanostatic deposition of Pt, Au, Ni, Cu, glassy carbon, or ITO glass yields smooth layers up to .25 micrometers. Thicker layers have cracks. Auger spectroscopy shows C (~8), O(~8), and Cl(~1.5) as impurities (atomic percent).

**"Lower Cost Route to High-Purity Silicon", Chem. and Eng. News, 3 Sept, p 8 (1979)**

Short Chemical and Engineering news article on electrowinning Silicon from Na<sub>2</sub>SiF<sub>6</sub>, a common by product of the phosphate fertilizer industry.

**H. Burger, R. Eugen, "Low Valent Silicon", Topics in Current Chemistry, Silicon Chemistry I, Vol 50, p 1, Springer-Verlag, New York (1974)**

Discusses the spectroscopy of Si under 4+. Slanted for Si organic polymer compounds.

**F. Hofler, "The Chemistry of Silicon-Transition-Metal Compounds", Topics in Current Chemistry, Silicon Chemistry I, Vol 50, p 129, Springer-Verlag, New York (1974)**

M-Si ligand Chemistry.

**E. Hengge, "Properties and Preparations of Si-Si Linkages", Topics in Current Chemistry, Silicon Chemistry II, Vol 51, p 1, Springer-Verlag, New York (1974)**  
Si polymer chemistry.

**R. A. Sharma, and R. N. Seefurth, J. Electrochem. Soc., vol 123, p 1763 (1976)**  
**"Thermodynamic Properties of the Lithium-Silicon System"**  
More about LiCl-KCl eutectics.

**H. A. Laitinen and C. H. Liu, J. Am. Chem. Soc., vol 80, p 1015 (1958) "An Electromotive Force Series in Molten Lithium Chloride-Potassium Chloride Eutectic"**  
Accurate evaluations of the oxidation reduction potentials of various electrode systems.  
Applicable to manufacture of glasses and the electrowinning and electro-refining of metals.

**C. H. Lee and F. A. Kroger, "Cathodic Deposition of Amorphous Alloys of Silicon, Carbon, and Fluorine", J. Electrochem. Soc. vol 129, p 936 (1982)**

Amorphous silicon containing fluorine and carbon, pure and doped with boron or phosphorus, was deposited cathodically from solutions of  $K_2SiF_6$  in acetone with HF. The conditions for optimum deposition were determined, and the deposits were characterized by electron microprobe x ray emission, electrical conductivity, and infrared absorption. Doping with phosphorus causes a change from p to n type semiconductor behavior, with a maximum of resistivity  $> 10^{13}$  ohm cm at the compensation point.

Covered teflon vessel under argon, Pt anode, nickel or stainless steel as cathode of  $1\text{cm}^2$ . Current density studies of  $K_2SiF_6$  in 100 ml of acetone with 0 to 6% vol of 48% HF. Changes in the electrolyte change the deposition process- growing film no effect. Carbon and fluorine seemed to be incorporated into the films. Triethyl Borate boron source triethyl phosphite phosphorous source.

**R. Boen and J. Bouteillon, J. Appl. Electrochem., vol 13, p 277 (1983) "The electrodeposition of Silicon in Fluoride Melts"**

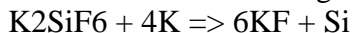
A fused LiF-NaF-KF mixture was selected as a solvent for the preparation of electrolytic silicon, since they are the best alkali halides mixtures for the stabilization of the fluorosilicates. The solvent was purified by the pre-electrolysis and treatment with HF. Consistent with the thermodynamic data, 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  $Si(IV) + Si = 2Si(II)$ ,  $Si(II) + 2e^- = Si$ . 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 semiconductor of resistivity  $.1 < \rho < 1$  ohm cm and the life time of the free carriers was about 30 microseconds.

**H. N. Warren, Chemical News, vol 67, p 303, June 30 (1893)**

First reported electrochemical deposition using  $SiF_4$  in alcohol on mercury

**Rochow, Eugene George, "The Chemistry of Silicon", Oxford ; New York : Pergamon, 1975 1973, Pergamon texts in inorganic chemistry ; v. 9 Pergamon international library of science, technology, engineering and social sciences ISBN: 0080187927**

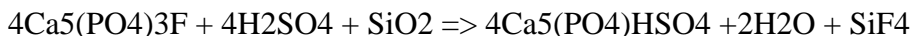
Silex, silicis, latin for flint. 1811 Gay Lussac and Thenard reduced silicon tetrafluoride with potassium but did not recognize as element. 1823 Berzelius reduced  $K_2SiF_6$  with potassium



Si can be determined in minerals and oxidized material by treatment with dil. HF, decanting the clear liquid, and adding a tiny crystal of NaCl to a drop of the liquid on a plexiglas microscope slide. Crystals of sodium fluorosilicate develop at the edges of the drop as the water evaporates hexagonal prisms, plates and pyramids.

Aluminum and silicon form a eutectic with 11.7% Si which melts at 577. The phase diagram contains no compounds and only a very narrow range of solid solution.

Silicon tetrafluoride in large quantity results from the treatment of phosphate rock with sulfuric acid in the manufacture of phosphate fertilizer. The rock contains apatite  $Ca_5(PO_4)_3OH$  and the isomorphous fluorapatite  $Ca_5(PO_4)_3F$  along with other calcium phosphates. When treated with the acid much HF is evolved, and it combines with the silicious matter present to form volatile  $SiF_4$



It can also be made in the lab by decomposition of the fluorosilicates or the addition of  $H_2SO_4$  and  $Na_2SiF_6$ . It is freed from HF and  $H_2O$  by passing it through hot glass wool and then through a trap cooled to  $-60$ . It can then be purified by sublimation in a metal vacuum system.  $SiF_4$  can form silicon polymer compounds.

**E. R. Corey, J. Y. Corey, P. P. Gaspar, "Silicon Chemistry" Ellis Horwood for the International Union of Pure and Applied Chemistry (1988) ISBN: 0745805280 : 0470210818 (Wiley)**

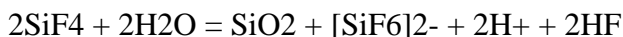
Collection of articles of wide range. Much organo-silicon chemistry. Some general articles on plasma deposition, plasma etching.

**E. Hengge, "Silicon Chemistry", Topics in Current Chemistry, Springer-Verlag, Berlin, New York, (1974) ISBN: 0387067140 (v. 1)**

Collection of articles related to organo-silicon chemistry (si polymer chemistry)

**Cotton, A. F., Wilkinson, G., Gaus, P., "Basic Inorganic Chemistry" 3d Ed., Wiley, ISBN 0-471-50532-3 (1995)**

Silicon Anionic Complexes: silicon forms only fluoroanions, normally  $[SiF_6]^{2-}$  whose high formation constant accounts for the incomplete hydrolysis of  $SiF_4$  in water, according to



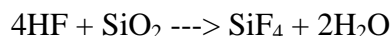
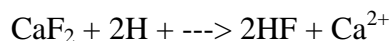
The ion is usually made by dissolving  $SiO_2$  in aqueous HF and is stable even in basic solution. Silicon will also form oxolato anions  $[Si(ox)_3]^{2-}$ .

**Michele Lavanga\*, Sergio Di Lena\*, Shane Sullivan\*\* and Alan Ingram\*\* \* Fluorid S.p.A, Italy, \*\* Svedala Ltd., Sweden**

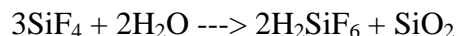
Recovery of Fluosilicic Acid and Fluoride Bearing Waters for the Production of a Mixture of Silica and Precipitated Calcium Fluoride Usable for the Production of Cement  
International Fertilizer Industry Association's 2000 Technical Conference in New Orleans  
(Read full paper at: <http://www.fertilizer.org/PUBLISH/tech0032.pdf>)

As fertilizer producers well know, the disposal of fluosilicic acid is a major environmental problem of phosphoric acid and phosphate fertilizer manufacture. Fluorides, such as silicon tetrafluoride and hydrogen fluoride, are among the main polluting streams resulting from phosphoric acid production. Phosphate rocks contain 2 to 4 percent fluorine. Part of the fluorine from the rock is precipitated with the gypsum, another part is leached out with the phosphoric acid product, and the remaining portion is vaporized in the reactor or evaporator. The relative distribution of fluorine among these three forms depends on the type of the rock, the plant configuration and the operating conditions.

From the reactor and the evaporator, fluorine is liberated initially in the form of hydrogen fluoride, but in the presence of silica it readily reacts to form silicon tetrafluoride



It is common practice to absorb this vapour by water scrubbing, to form fluosilicic acid



The quantity of fluosilicic acid obtained as a by-product in phosphoric acid production is normally in the range 20 to 40 Kg (as H<sub>2</sub>SiF<sub>6</sub> 100%) per ton of P<sub>2</sub>O<sub>5</sub> produced. At present, only a small portion of this acid is used. In most cases, the effluent is simply discharged to sea or to fresh water rivers. It is, therefore, evident that the disposal of these effluents is an ever more serious environmental problem for phosphoric acid manufacturers. According to Italian law, the concentration of F<sup>-</sup> ions in sea or fresh water discharges must be lower than 6 mg/liter.

### **Jons Jakob Berzelius**

A Swedish chemist Jons Jakob Berzelius (1779-1848) who accurately determined more than 2000 relative atomic and molecular masses. He devised (1813-14) the system of chemical symbols and formulae now in use and proposed oxygen as a reference standard for atomic masses. He was the first to prepare silicon.

Electrochemistry, Vol. 69. No. 11, 2001, p834

## Preparation of a Novel Fluorosilicate Salt for Electrodeposition of Silicon at Low Temperature

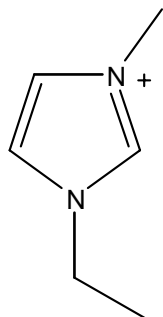
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A novel fluorosilicate salt, 1-ethyl-3-methylimidazolium hexafluorosilicate ((EMI)2SiF6), was prepared by the reaction of EMICl and hexafluorosilicate acid aqueous solution. A transparent thin film containing silicon was deposited on a silver electrode by potentiostatic electrolysis in molten (EMI)2SiF6 at 90 C. The film was reactive against water to form silicon dioxide.

(EMI)2SiF6 was found to dissolve in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfone)imide (EMITFSI) room temperature molten salt. The same thin film was also obtained on a silver electrode by potentiostatic electrolysis in EMITFSI containing (EMI)2SiF6 at room temperature.

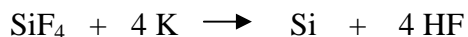
### Ethyl Methyl Imidazolium Organic Electrolytes (Eric Miller)



The above structure shows the ethyl-methyl-imidazolium ion (EMIZ). It can be purchased in many salt forms including the chloride and bromide. Our work with the bromide and chloride indicated it is hygroscopic (absorbing water). Whereas others have reported that they are hydrophobic. We had a difficult time using the bromide in metathesis to make EMIZ hexafluorosilicate due to the low vapor pressure of HBr in the solution. We also found Imidazolium chloride to be reactive to silicon tetrachloride typical for amines and hydroxides. Therefore, ethyl-methyl-imidazolium salts are unsuitable solvents for silicon tetrachloride.

### Silicon Reference Reactions

Amorphous Silicon can be prepared in the laboratory by heating potassium in an atmosphere of silicon tetrafluoride.



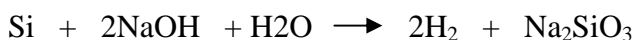
Silicon exists in different allotropic forms which differ in chemical and physical properties.

Amorphous Silicon is a dark brown powder which on heating in air forms a protective coating of silica which prevents further oxidation, is insoluble in water and most acids, and dissolves in hydrofluoric Acid forming fluorosilicic acid.

Unoxidized silicon can be dissolved by hydrofluoric acid



Silicon dissolves in sodium hydroxide forming sodium silicate.



Silica is attacked by hydrofluoric acid

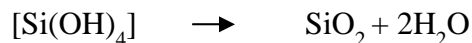
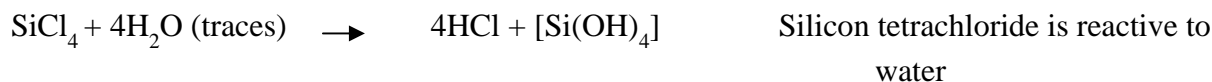
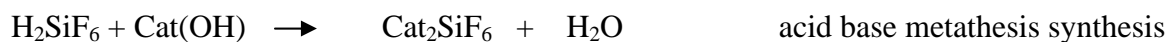


Crystalline Silicon resembles amorphous silicon in many of its chemical reactions but it is less reactive, consists of dark-gray needles or octahedral plates, which are hard enough to scratch glass.

Other Reactions of interest



The onset occurs at about 700C (Eric Miller, Sean Moffit)



Similarly, Silicon tetrachloride is also reactive to alcohols and amines.



Direct synthesis of alkyl silanes by grignard type reactions

