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# **Electrodeposition of Silicon from a Nonaqueous Solvent**

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# ABSTRACT

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 halogeno-silanes. Potentiostatic and galvanostatic deposition on Pt, Au, Ni, Cu glassy carbon, or ITO glass yields smooth layers up to 0.25  $\mu$ m. Thicker layers have cracks. Auger spectroscopy shows C (~8), O (~8), and Cl (~1.5) as impurities (atomic percent).

An electrochemical silicon coating process would find application in the field of corrosion protection and for the fabrication of low cost photovoltaic solar cells provided the necessary material characteristics could be met.

A nonaqueous medium must be used for the electrodeposition of silicon because of its very large negative reduction potential and the high reactivity of most of its compounds towards water. A few publications indicate the possibility of electrodepositing silicon from organic solutions. Best results were obtained from SiHCl<sub>3</sub> solutions in propylene carbonate (1-3). Electrodeposition from K<sub>2</sub>SiF<sub>6</sub> in acetone (4) and Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> in acetic acid (5) were also reported.

The present paper describes the results obtained for different silicon precursors. Tetrahydrofuran was chosen as the solvent because of its resistance to electrochemical reduction and the possibility of removing most of its water and dissolved oxygen by an appropriate purification procedure. Cyclic voltammetry, potentiostatic, and galvanostatic electrolysis were used to evaluate the characteristics of these systems. The current efficiency was measured and the morphology and composition of the silicon film were checked for different electrodeposition conditions.

#### Experimental

All experiments were done in a glove box (Mecaplex, Model GB 91) in a nitrogen atmosphere containing less than 10 ppm O<sub>2</sub> and 1 ppm H<sub>2</sub>O. Tetrahydrofuran, THF, (Fluka, puriss.) was purified by distillation over a solution of sodium biphenylide under N2. Its water content measured by Karl Fisher coulometric titration was 5 10<sup>-4</sup>M (10 ppm). Trichlorosilane (Fluka, purum or Alfa, 99.9%) tetrachlorosilane (Fluka, puriss. or Alfa, ultrapure) and the other silicon compounds (Alfa, highest available grade) were used without further purification. The supporting electrolytes were dried 48h under vacuum at 160°C for the lithium perchlorate (Fluka, purum) and 100°C for the tetrabutylammonium bromide. TBAB (Fluka, puriss.) and the tetrabutylammonium perchlorate. TBAP (Fluka, purum). The latter was recrystallized in acetone according to the procedure described by Mann (6).

The cyclic voltammetry and electrodeposition experiments were done at room temperature in a three-electrode glass and Teflon cell of 120 ml capacity. The platinum counterelectrode was separated from the remaining solution by a fine porosity glass. The cathode, an 8 mm diam disk of platinum, gold, or other material maintained in a Teflon holder was mechanically polished with fine grain alumina, then rinsed with deionized water and THF prior to each run. The distance between the center of the extremity of the Luggin capillary, parallel to the substrate, and the surface of the substrate was 2 mm. The ohmic drop resulting from the high resistivity of the solutions (LiClO<sub>4</sub> 0.3M:2.7  $\cdot$  10<sup>3</sup>  $\Omega$   $\cdot$  cm, TBAP 0.3M:1.1  $\cdot$  10<sup>3</sup>  $\Omega$ cm, TBAB 0.02M:3  $\cdot$  10<sup>4</sup>  $\Omega$   $\cdot$  cm) was compensated for by positive feed back in all cyclic voltammetry and potentiostatic electrolysis experiments, except when

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TBAB was the supporting electrolyte. Two reference electrodes were used, Ag/AgCl(s), LiCl(s),  $LiClO_4$   $(0.3M)//LiClO_4$   $(0.3M)//\dots$  and  $Ag/AgClO_4$  (0.02M),  $LiClO_4$   $(0.3M)//LiClO_4$   $(0.3M)//\dots$  both in THF. The saturated solution of the first reference electrode was prepared in the presence of an excess of AgCl. All the reported potentials here are relative to the Ag/AgClO\_4 electrode. They are 0.80 V more cathodic than the corresponding potential relative to the Ag/AgCl(s) electrode. An Amel potentiostat-galvanostat (Model 552), function generator (Model 567), and integrator (Model 721) were used.

The deposit's morphology was systematically observed by scanning electron microscopy and the relative content in Si, C, and O was measured by electron probe microanalysis (Camebax). The total amount of silicon electrodeposited was determined by colorimetric analysis of the silicomolybdic acid derivative (8) with an accuracy of  $\pm 0.5 \ \mu$ g in the range 2-50  $\ \mu$ g. The deposit thickness was calculated on the base of a deposit density of 2.2 g/cm<sup>3</sup>.

### **Results and Discussion**

Cyclic voltammetry.—Figure 1 shows typical voltammograms obtained from solutions of  $SiHCl_3$ ,  $SiCl_4$ , and  $SiBr_4$ . They share two common characteristics. First there appears only one reduction peak, and no corresponding oxidation peak is observed. Second the current density is much smaller in the second cycle (only a small further decrease was observed in a third and fourth



Fig. 1. Cyclic voltammograms of silicon halides in THF. Supporting electrolyte TBAP 0.3M, sweeping rate 80 mV/s, —— first, --- second, — - — third cycle.

Table I. Reduction peak potential of various halogenosilanes

Halogenosilane	SiHCl <sub>3</sub>	SiCl₄	SiBr <sub>4</sub>
Peak potential (V)	-2.7	-3.0	-2.2

cycle). The peak heights were roughly proportional to the silicon compound concentration (Fig. 1a and b). Gold and platinum electrodes gave identical results. Peak potentials are listed in Table I.

Modifications of the aspect of the voltammograms of SiBr<sub>4</sub> solutions were observed a short time after their preparation ( $\sim$ 30 min). However the addition of an organic base, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, resulted in stable solutions. The peak associated with the reduction of SiI<sub>4</sub> disappeared almost immediately after the preparation of the solution and attempts to stabilize it did not succeed.

This reactivity might be explained by unavoidable trace amounts of HX (X = Br, I) in the solution due to the reaction of residual water with the halogenosilanes. It is well known that HBr and HI are effective reagents for the scission of ether bonds. In THF the final decomposition product of SiBr<sub>4</sub> or SiI<sub>4</sub> will be Si[O(CH<sub>2</sub>)<sub>4</sub>X]<sub>4</sub>, where X = Br or I, due to the catalytic effect of HX.

No reduction peak could be observed by cyclic voltammetry up to the cathodic stability limit of the system (-3.6V), when 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>, or Si[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> were added to TBAP or LiClO<sub>4</sub> solutions in THF.

These results show that the reduction of the halogenosilanes is irreversible and that all electrons are transferred in a narrow potential range, probably in a multistep process. Intermediate oxidation states of Si were not detected, a fact not surprising in view of the instability of Si (II) compounds. Two distinct polarographic waves have, however, been reported for SiCl<sub>4</sub> in DMSO (8), and in fluoride melts both Si(IV)  $\rightarrow$  Si(O) and Si(IV)  $\rightarrow$  Si(O) mechanism were proposed (9, 10). The relatively anodic reduction potential of SiBr<sub>4</sub> compared with SiCl<sub>4</sub> or SiHCl<sub>3</sub> is advantageous, however, its lesser chemical stability is a major drawback.

Si—O, Si—C, and Si—N bonds appear to be too stable to be reduced in the potential range allowed by this system.

The silicon electrodeposited in the first cycle ( $\sim$ 50-200Å for a uniform layer) drastically modifies the characteristics of the working electrode. The rate of the reduction processes, not the diffusion, limits the current density in the following cycles. The reasons are not completely understood at this time, a strong adsorption of a bath constituent on the freshly deposited layer could produce this change. Moreover the SiCl<sub>4</sub>, and to a less extent SiHCl<sub>3</sub>, reduction in the second cycle starts at potentials more anodic. This fact indicates a complex behavior at the electrode surface.



Fig. 2. Galvanostatic electrolysis of SiHCl<sub>3</sub>. Variation of cathode potential with charge. Concentration and current density, respectively, 0.1M and 1 mA  $\cdot$  cm<sup>-2</sup>; curve a, 0.1M and 0.6 mA  $\cdot$  cm<sup>-2</sup>; curve b, 1M and 0.8 mA  $\cdot$  cm<sup>-2</sup>; curve c, supporting electrolyte TBAP 0.3M.



Fig. 3. Potentiostatic electrolysis of SiHCl<sub>3</sub>. Variation of current density with time. Potential -2.6V. Supporting electrolyte TBAP 0.3M. Curves a and b, concentration 0.1M and 1M, respectively.

*Electrodeposition.*—The chlorosilanes  $SiCl_4$  and  $SiHCl_3$ were chosen for most of the electrodeposition experiments. Reduction of the SiH bond is highly improbable and use of  $SiHCl_3$  should allow incorporation of hydrogen in the deposit. Platinum or gold substrates were used except where otherwise mentioned.

Figure 2 shows examples of the variation of the potential recorded during galvanostatic electrodeposition from SiHCl<sub>3</sub> solutions. They illustrate three types of behavior. A steep decrease in potential down to approximately -3.8V followed by a plateau (curve a), a regular but slower decrease in potential (curve b), and constant potential (curve c). The first two were measured for identical SiHCl<sub>3</sub> solutions under similar conditions, the trichlorosilane concentration in the last was ten times higher (1.0M). Galvanostatic electrodeposition from SiBr<sub>4</sub> (0.1M) gave systematically type a curves with little dependence on the current density from 0.2 and 1.4 mA/cm<sup>2</sup>. From SiCl<sub>4</sub> 0.1M solutions only type c curves were obtained. In potentiostatic deposition experiments current densities decreased or stayed constant accordingly (Fig. 3).

The cathodic current density was always smaller than the diffusion limited current. Furthermore there was no significant decrease of the halogenosilane concentration during an electrolysis experiment. The potential or the current density should therefore stay constant as curve c in Fig. 2 or curve b in Fig. 3. The fact that this is not always the case might be explained in two ways. First, passivation of the cathode, for example by strong adsorption on the freshly deposited silicon layer, or second, by a high resistivity of the film. Both hypotheses could be simultaneously true; the first is supported by cyclic voltammetry results, the second by the known properties of intrinsic amorphous silicon and by the actual resistivities measured for films deposited from SiHCl<sub>3</sub> in propylene carbonate solutions (1). Assuming the latter hypothesis only, resistivities calculated from the slope of the approximately linear part of curve a and b in Fig. 2 are  $1.5 \cdot 10^8$  and  $3 \cdot 10^7 \Omega \cdot cm$ , respectively (3 electrons, 100% current efficiency), in accordance with (1). The leveling of curve a is believed to be linked with the presence of defects in the deposited layers and the cathodic stability limit of the system  $\sim -3.6V$ 

The causes of the observed difference of resistivity and/or passivation behavior of silicon deposited from different solutions have not been identified.

The current efficiency has been calculated from the total amount of silicon deposited on the cathode. A threeand four-electron reduction process was assumed for SiHCl<sub>3</sub> and SiCl<sub>4</sub>, respectively. Results are reported in Tables II and III. For SiHCl<sub>3</sub> an average of 60% is obtained. For SiCl<sub>4</sub> the values are scattered around 35%, the differences are larger than experimental errors, but no clear correlation with the electrolyzed charge is observed.

Table II. Current efficiency for potentiostatic electrodeposition of silicon at -3.2V from a 0.2M solution of SiHCl<sub>3</sub>, supporting electrolyte TBAB

Charge (C · cm <sup>-2</sup> )	0.45	0.67	0.90	1.14	1.92
Efficiency (%)	50.7	61.5	60.0	64.4	57.9

Table III. Current efficiency for galvanostatic electrodeposition of silicon at 0.6 mA · cm<sup>-2</sup> from a 0.07M solution of SiCl<sub>4</sub>, supporting electrolyte TBAB 0.03M

Charge (C · cm <sup>-2</sup> )	0.32	0.64	0.96	1.28	1.62
Efficiency (%)	45.7	41.8	29.3	26.1	35.6

Reduction of HCl (produced by the reaction of traces of water with the chlorosilane) might be responsible for a loss of efficiency of about 15-25% estimated from the value of the residual current.



Fig. 4. Scanning electron micrographs of silicon electrodeposits. (a, b, c) Potentiostatic electrolysis at -3.2V of a 0.2M SiHCl<sub>3</sub> solution in THF. Supporting electrolyte TBAB 0.03M. Deposit thickness, 0.24; 0.32; 0.49  $\mu$ m, respectively. (d) Galvanostatic electrolysis at 0.6 mA  $\cdot$  cm<sup>-2</sup> of a 0.07M. SiCl<sub>4</sub> solution in THF. Supporting electrolyte TBAB 0.03M. Thickness, 0.15  $\mu$ m. (e) Galvanostatic electrolysis at 1.4 mA  $\cdot$  cm<sup>-2</sup> of a 0.1M. SiBr<sub>4</sub>, 0.3M triethylamine and 0.3M LiClO<sub>4</sub> solution in THF. Thickness, 0.1  $\mu$ m. (f) Potentiostatic electrolysis at -2.8V of a 0.08M SiHCl<sub>3</sub> solution in dimethoxyethane. Supporting electrolyte TBAP 0.25M. Thickness, 0.27  $\mu$ m.

Other competitive reduction processes should therefore take place but have not yet been identified. Simultaneous reduction of the supporting electrolyte can be excluded as the potentiostatic electrolysis of SiHCl<sub>3</sub> was done at -3.2V and the galvanostatic reduction of SiCl<sub>4</sub> occurred at a constant potential of approximately -3V, both well under the cathodic stability limit of -3.6V.

The morphology of silicon films electrodeposited from SiHCl<sub>3</sub> solutions appeared smooth and nodule-free up to a thickness of 0.20-0.25  $\mu$ m by SEM observation at 1000 times magnification (Fig. 4a). Above this limit a progressive development of cracks was observed (Fig. 4b, c). The morphology was found independent of the SiHCl<sub>3</sub> concentration in the range 0.1-1.0M, of the use of TBAP or TBAB as supporting electrolyte and of the cathode material Pt, Au, Ni, Cu, vitreous C, or ITO glass. Electrodeposition conditions had only a small effect. The same uniform deposits (up to 0.25  $\mu$ m thickness) were obtained in potentiostatic electrolysis at ~ -3V or galvanostatic electrolysis at ~ 0.5 mA/cm<sup>2</sup>. However higher current densities, 1 or 2 mA/cm<sup>2</sup>, resulted in films already cracked at 0.25  $\mu$ m thickness.

Similar results were obtained for films electrodeposited from SiCl<sub>4</sub> solutions, but cracks became already apparent in layers thicker than 0.12  $\mu$ m (Fig. 4d). Deposits obtained from SiBr<sub>4</sub> solutions in THF were slightly nodular (Fig. 4e). Dimethoxyethane was also tried as solvent instead of THF. Reduction of SiHCl<sub>3</sub> occurred at the same potential also resulting in cracked silicon layers but with a clearly nodular structure (Fig. 4f).

X-ray diffraction indicated an amorphous structure. The high intrinsic stress typical of amorphous silicon (11) could be the cause of these defects. The high impurity content (see below) is another likely explanation.

Results of a typical Auger electron spectroscopy analysis are shown in Fig. 5. The only detected elements were Si, O, C, Cl, and the substrate. Bulk concentration excluding H were Si  $\sim$  82, O  $\sim$ 8, C  $\sim$  8, Cl  $\sim$  1.5 atomic per cent. The signal of the substrate, here Pt, increased smoothly with the sputtering time indicating uneven sputtering or uneven thickness of the deposit. No significant difference between the composition of layers electrodeposited from SiCl4 or SiHCl3 could be observed (hydrogen is not detected by Auger spectroscopy). Hydrocarbon contamination and rapid oxidation during the transfer to the AES chamber can explain the high carbon and oxygen surface concentration. Further investigations will be needed to understand the mechanism of bulk C incorporation and to determine whether the bulk level of oxygen is caused by *in situ* oxidation during the deposition process or is a consequence of an open porosity in the film.



Fig. 5. Concentration profile by Auger spectroscopy. Silicon electrodeposited potentiostatically at -2.8V from a 0.13M SiHCl<sub>3</sub> solution in THF. Supporting electrolyte LiClO<sub>4</sub> 0.3M.

A preliminary estimation of the hydrogen content of hydrogenated silicon prepared with the SiHCl<sub>3</sub> precursor was obtained from the scattering of a proton beam by a 0.25 µm layer electrodeposited on a 6 µm nickel foil. It gave the expected high Si:H ratio of 1:0.9.

### Summary

Electrochemical reduction of SiHCl<sub>3</sub> in tetrahydrofuran gave smooth and uniform deposits of silicon up to a thickness of about 0.25 µm. Detected impurities were O, C, and Cl. For practical applications, morphology of thick deposits, stability in atmosphere, and impurity content have to be greatly improved. The influence of the chemical nature of the solvent, the hydrogen content of the film as well as other deposition parameters should be investigated in order to reach these goals.

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# **Electrochemical Pretreatment of Thin Film Platinum Electrodes**

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### ABSTRACT

Thin film noble metal electrodes and electrode arrays prepared by photolithographic process suffer from contamination of the surface by the traces of transition metals and their oxides which are used as adhesion promoters at the insulating substrates. This contamination is an ongoing process as the transition metals migrate continuously along the grain boundaries through the thin (1000-4000Å) layer of the noble metal. The transition metal oxide affects the electrochemical properties of the noble metal surface and also its electron work function. A simple electrochemical pretreatment has been developed which removes these contaminants from the surface and "anneals" the surface in such a way that acceptable electrochemical behavior identical with a thick noble metal electrode is obtained. It consists of electrochemical etching of the surface by pulsing it between 0 and +2V in solution containing 0.08M EDTA, 5.2% NH<sub>4</sub>OH, and  $2.7 \times 10^{-4}M$  H<sub>2</sub>O<sub>2</sub> for 5-10 min. It is then followed by cycling of the applied potential between 0.4 and -0.4V in 1M KNO<sub>3</sub> for 10 min. Surfaces prepared by this procedure have remained clean for a period of at least 24h.

Techniques for deposition and patterning of thin films (500-3000Å) of noble metals have been well developed for the purposes of fabrication of planar integrated circuits (1). The fundamental problem is the adhesion of these metals to the insulators, which are typically silicon dioxide, silicon nitride, or oxynitride, and to other insulating oxides. It has been solved by interposing so called "glue" metals, such as Ti,W, V, Nb, Zr, Cr, etc., between the insulator and the noble metal. The role of the transition metal is to react with the substrate containing oxygen and to form a covalently bonded mixed oxide at that interface (2, 3)

$$Ti + SiO_2 = TiO_{(2-x)} + SiO_x$$
[1]

At the other interface these metals form alloys with Pt or Au, thus assuring a good adhesion between the noble metal and the insulating substrate. Because of the small thicknesses involved, which are dictated to a large extent by the resolution of the patterning process and by economical reasons, the intermixing of these layers by

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diffusion (4-6) occurs and has to be taken into account. Various ways of controlling it have been developed which optimize the final structure from the point of view of electrical resistance, mechanical, and chemical stability. The most common combination of metals is chromium/gold (7). However, it suffers from relatively rapid migration of metallic Cr along the grain boundaries to the surface of Au with concomitant formation of Cr<sub>2</sub>O<sub>3</sub> at the metal surface which results, among others, in difficulties with wirebonding. Various diffusion barriers have been studied and Ti,W/Pt structure has been found to be optimal for this purpose. For some applications it is necessary to deposit Au on Al in which case a diffusional barrier to prevent intermixing of Al with the noble metal is required in addition to the formation of a good adhesive seal with the neighboring substrate. For this purpose again, Ti,W, and Ti,W/Pt diffusional barriers, containing a small amount of oxide, proved to be most effective (8-10). Many more different combinations, which have been dictated by the specific application, have been studied and the above references only serve to illustrate the general nature of this problem.