

Electropolishing Silicon in Hydrofluoric Acid Solutions

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Electropolishing Silicon in Hydrofluoric Acid Solutions

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ABSTRACT

Silicon is electropolished in hydrofluoric acid solutions if a critical current density is exceeded. Below the critical c.d., silicon dissolution is largely divalent, and a thick solid layer forms. This film is unstable and reacts slowly with the electrolyte to form tetravalent silicon and hydrogen gas. In the electropolishing region, silicon dissolution is mainly tetravalent with the formation of a very thin high resistance type of film.

Experimental results on the effect of HF concentration, viscosity, and temperature indicate that electropolishing begins when the HF concentration at the silicon becomes limited by the rate of "mass transfer" of HF from the solution bulk to the surface.

Silicon is a semiconductor material used in making solid-state electronic devices. In their manufacture, it is necessary to employ chemical and electrochemical techniques to remove damaged surface material and/or shape the silicon to a particular geometry. The principle advantage of electrochemical over chemical methods of removing silicon is that the amount and the place where the material is to be removed can be controlled more easily. It is usually desirable that the surface of the silicon be polished after processing.

The technique of electropolishing involves making the metal to be polished anode in a suitable electrolyte at a current density sufficient to produce a thin continuous anode film on the surface. The anode film must be soluble in the electrolyte, but not too soluble or no appreciable electropolishing film will be built up at a reasonable current density. The electropolishing anode film is described by various workers as either a solid or highly viscous liquid layer. Polishing requires both brightening and smoothing. Hoar and Mowat (1) have proposed that the brightening effect is due to a random transfer of metal atoms into vacant cation sites in the anode film. Smoothing is due to preferential

dissolution of the film at high points on the surface.

Previous work on electropolishing silicon is almost nonexistent. Uhler (2) was able to electropolish p-type silicon in a largely nonaqueous electrolyte of ethylene glycol containing some HF.

Electropolishing silicon appears practical only for p-type material at the present time since an internal voltage barrier is formed in n-type semiconductors (3) which causes excessive heating of the electrode before the required polishing current is attained. Methods of breaking down the voltage barrier by introducing hole-electron pairs with heat and/or light is effective with germanium, but this is difficult if not impossible with silicon because of its higher energy gap.

The experimental work was done in two parts. First, a number of exploratory experiments were performed to determine the best electrolyte and general conditions for electropolishing. This work was done with silicon electrodes held vertically in solution and without temperature control. The second part was done more carefully with the silicon positioned horizontally facing up and the temperature controlled.

Preliminary Experiments

Most of the preliminary experiments were carried out with 1 ohm cm single-crystal p-type silicon electrodes. A number of electrolytes were investigated to determine one suitable for electropolishing silicon.

Strong alkaline solutions chemically attack silicon, forming a soluble silicate and hydrogen gas. The rate of reaction increases rapidly with temperature. If a piece of silicon is made anodic in hot 1N KOH, however, the chemical attack stops above a critical anode potential. The surface is passivated. Furthermore, after the cell current is interrupted, the hot alkaline solution requires several minutes to break through the passive layer and resume chemical attack of the silicon. A brief cathodic treatment reactivates the silicon immediately. Alkaline solutions do not appear promising for electropolishing silicon. The passivating anodic film formed, however, may be of value in stabilizing the surface electronically (4).

Electrolytes containing the fluoride ion were considered since they can be made to form soluble fluosilicate complexes with silicon. The most successful electrolyte found for electropolishing silicon was hydrofluoric acid. For a given set of conditions of HF concentration, temperature, viscosity, and stirring, there is a critical current density which must be exceeded before electropolishing can take place. Below this critical current density, a thick solid anode film forms on the silicon. For example, Uhler (2) reported that silicon does not electropolish in 24 to 48% HF solutions up to 0.5 amp/cm² because of a thick anode deposit. As will be seen later, higher current densities are required to electropolish silicon at these HF concentrations.

The HF concentration range in which a vertical p-type silicon electrode is electropolished at 400 ma/cm² current density is shown in Fig. 1. There was no temperature control in this experiment. The effective resistance of the electrolytic cell and the power dissipated in the cell were measured at the same time. These data are included only to show the qualitative effect of HF concentration on the cell resistance and power dissipation. At low HF concentrations the cell resistance is high, the power

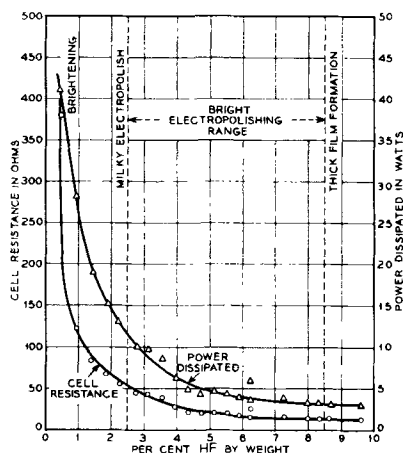


Fig. 1. Cell resistance and power dissipated in an electropolishing cell vs. HF concentration using a vertical p-type silicon anode at 400 ma/cm² density.

dissipated as heat is large, and the silicon is anodically etched but not electropolished. A clear polished silicon surface is not obtained until the HF concentration is at least 2.5%. More concentrated solutions of HF decrease the effective cell resistance and thus the power dissipated in the cell. The thick film begins to form at about 8.5% HF under the conditions of this experiment.¹ There is no discontinuity in the cell resistance with film formation which indicates that the thick film is probably porous.

Anode efficiency measurements were made during electropolishing in 5% HF using a vertical p-type silicon electrode. Since there was a tendency for the current to oscillate in the electropolishing range, it was necessary to employ a copper coulometer to integrate the current used. Assuming a silicon valence of 4, an anode efficiency of $105 \pm 2\%$ was obtained which indicates that about 5% of the current formed divalent silicon. The anode efficiency appears to be independent of current density over the range studied between 110 and 850 ma/cm². The rate of silicon dissolution by electropolishing in 5% HF calculated from the observed anode efficiency and the electrochemical equivalent for silicon is 3.3×10^{-5} cm²/coulomb. At 500 ma/cm², the etching rate is 1.7×10^{-5} cm/sec (0.0004 in./min).

A silicon electrode held vertically in the solution without temperature control requires a relatively high minimum current density of about 300 ma/cm² to start electropolishing in 5% HF. A high current density promotes rapid electropolishing which is often desirable. However, the I^2R heat generated in the silicon at these current densities can be excessive and cause the solution around the electrode to boil and even melt the soft solder connection made to a copper wire. It was of a practical interest, therefore, to investigate the various parameters of the silicon electropolishing process to determine how the minimum current density for electropolishing could be reduced.

Experimental Arrangements Using a Horizontal Electrode

A cross-section view of the electrolytic cell designed for these experiments is shown in Fig. 2. The silicon electrode was mounted horizontally facing up

¹ Since this paper was submitted for publication, P. Wang, of Sylvania, in an oral presentation at the Buffalo Meeting of the Society reported that p-type silicon could be electropolished in 1-10% aqueous HF solutions.

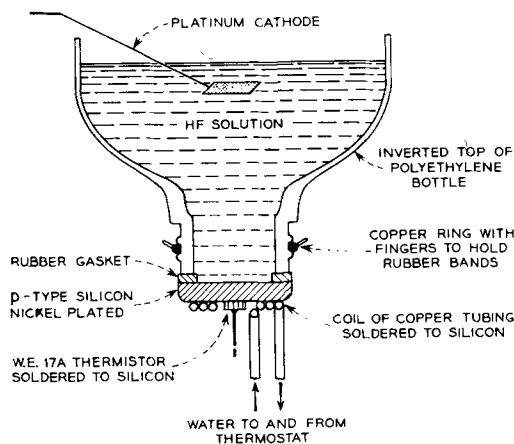


Fig. 2. Cross-section view of the electrolytic cell

to minimize stirring by convection. The arrangement also provides for a fairly uniform primary current distribution over the silicon and permits a visual examination of the surface at all times. A circular piece of single crystal 3.5 Ω cm p-type silicon about 2.5 cm in diameter and 0.5 cm thick was used in most of the experiments. After the silicon was nickel plated by the "electroless" process (5), a coil of 3-mm diameter copper tubing was soft soldered to the back side. This served the dual purpose of forming an ohmic contact to the silicon and a convenient means of controlling the silicon temperature. The temperature of the silicon during an electropolishing experiment was usually controlled to $\pm 0.3^\circ\text{C}$ by pumping water through the coil at the rate of about 400 cc/min from a 1-gal thermostat reservoir. A Western Electric thermistor type 17A was also soldered to the back side of the electrode to measure temperature. The thermistor was connected in series with a 5 ma milliammeter and a 1.5 v No. 6 dry cell and calibrated in terms of current as a function of temperature.

Prior to each experiment, the top surface of the silicon was lapped with No. 600 mesh silicon carbide. The electrode was held tightly against the rubber gasket by two rubber bands (not shown) attached to the fingers of the copper ring.

Also not shown is the polyethylene syphon used to make electrode potential measurements against a saturated calomel reference electrode. One end of the syphon was heated and drawn to a fine capillary tip. The syphon was filled with the HF solution and plugged at the large end with rolled-up filter paper. The plugged end of the syphon dipped into a saturated solution of KCl which contained the reference electrode, while the capillary tip end dipped into the electrolytic cell and was positioned so that only one corner touched the silicon. This arrangement produces a negligible amount of masking by the capillary tip and yet insures sufficient proximity to avoid including an appreciable solution IR drop in the potential measurement. An error of 10 or even 100 mv in the potential is not important in this study. Considerable difficulty was encountered in obtaining potential data when gas was being evolved at the electrode. Gas bubbles have a tendency to enter the capillary tip when close to a gassing electrode. This often produces an open circuit. The best procedure was to lower the tip to touch the silicon for each potential measurement and then withdraw it some distance away.

The cathode was a 1 cm square sheet of platinum welded to a platinum wire. All the HF solutions were made up using 48% by weight reagent grade hydrofluoric acid. About 100 cc of solution was used in each experiment as this was the cell capacity. The power supply consisted of one or two large 45-v dry batteries with two slide wire rheostats in series to adjust the current.

Anode Potential—Current Density Characteristic

A typical anode potential-current density curve for a horizontal p-type silicon electrode facing up is shown in Fig. 3. The curve was obtained by slowly decreasing the rheostat resistance while the anode

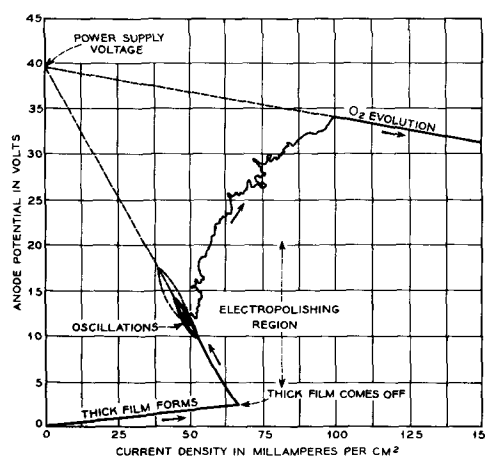


Fig. 3. Typical anode potential-current density curve for a horizontal p-type silicon anode facing up in 5% HF at 25°C .

potential and current were recorded on an L&N X-Y Recorder. In the initial portion of the curve, a thick film forms and there is considerable gassing. At a critical current density, the thick film suddenly starts coming off and floats to the surface. Gassing virtually ceases. If no change is made in the rheostat setting, the current slowly decreases while the anode potential increases. This is due to a high resistance film being formed on the silicon. The negative slope in the anode potential-current density curve above the critical c.d. is determined by the power supply voltage and the rheostat resistance. If the straight line sections are projected back to zero current, they intersect the potential axis at the power supply voltage as shown in Fig. 3. When the anode potential reaches about 10 v, oscillations in current and potential occur. It may take several minutes to reach this condition. The transition can be hastened by raising the voltage applied to the cell. If the transition stage in Fig. 3 had been allowed to continue, the current and potential would have changed further along the same straight line; however, the oscillations would have stopped at about 17 v. In one experiment, the transition stage was allowed to continue for about 1 hr and the anode potential rose to about 30 v while the current density dropped to 20 ma/cm. The anode potential-current density curve above the initial transition stage is erratic as seen in Fig. 3. It is interesting to note that above 20 v anode potential, if the current is interrupted, a burst of gas is given off the surface of the horizontal silicon electrode. At a second critical current density, continuous oxygen evolution begins and the anode potential decreases while the current increases in a runaway process.

The E-I curve for a vertical electrode (with convection stirring) differs from the curve shown in Fig. 3 in that there is no abrupt change in the current and potential when electropolishing starts. Perhaps this is due to electropolishing beginning at only some areas at first and gradually spreading to the entire surface with increasing current.

If a voltage is suddenly applied to the cell which is sufficient to pass more than the critical current density initially, the anode potential and current will pass quickly into the electropolishing region.

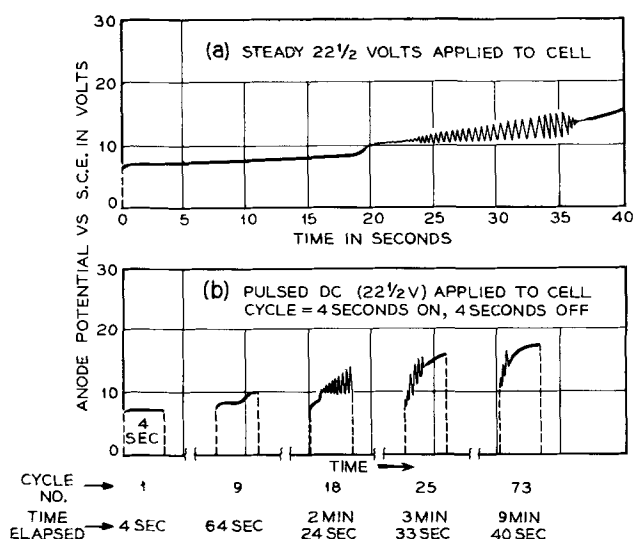


Fig. 4. Anode potential-time curves for p-type silicon in 5% HF at 30°C: (a) steady 22½ v applied to cell; (b) pulsed D.C. (22½ v) applied to cell cycle: 4 sec on, 4 sec off.

A short induction period is required before the transition takes place, however, as shown in Fig. 4a which is a record of the anode potential change with time. A 22½-v battery was connected directly across the cell with no external resistance. Electropolishing does not begin until after 20 sec, at which time there is a step in the curve. Oscillations also begin and tend to increase in amplitude with time. Eventually the oscillations stop and the anode potential rises to a fairly steady value approaching the supply voltage.

Another technique employed was to apply a pulsed d-c voltage to the cell. The anode potential-time curves obtained under these conditions are shown in Fig. 4b. A cycle of 4 sec on and 4 sec off was used. The first appearance of the step in potential comes during the ninth cycle or about 1 min after the start. In successive pulses, the E-t curve changes so that a greater portion of the pulse time is occupied in the electropolishing region.

The simplest means of electropolishing silicon in aqueous hydrofluoric acid solutions is to apply a constant voltage between 10 and 20 v directly across the cell. Initially the current is large and is limited mainly by the electrolyte resistance. As the high resistance electropolishing film forms, the current drops and an increasing amount of the applied voltage appears across the electropolishing film. The potential between the silicon and the electrolyte thus automatically stays in the electropolishing region.

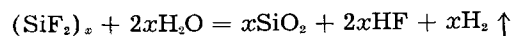
Nature of Thick Anode Film Prior to Electropolishing

The most reproducible and stable part of the E-I curve for silicon in HF solutions is the initial section where a thick, solid film forms. The film is removed easily for study by briefly raising the current above the critical value. It comes off in large flakes and floats to the surface. The film is a brown color when formed on a surface lapped with No. 600 mesh silicon carbide. If the silicon is electropolished beforehand, several orders of interference colors can be seen as the film thickens. Thick pieces grown on

an electropolished surface are an orange-red color and glassy in appearance. Electron and x-ray diffraction studies show the film to be amorphous. This is characteristic of anodically grown films. The film appears to be a good insulator since it holds a static charge well. Pieces of the film react with explosive violence when put in contact with a strong oxidizing agent such as nitric acid. This result and the fact that Uhler (2) obtained an effective valence of about two for the dissolution of silicon with the thick anode film being formed means that the film contains divalent silicon. Brouillet and co-workers (6) also found that in perchloric acid solutions, if a metal has several valence states, the anodic dissolution process favors the lowest one. The gas evolved during the thick film formation is hydrogen (2). Hydrogen evolution at an anode is unusual. In this case it is due to the chemical reduction of hydrogen ions by divalent silicon in the anode film. Hydrogen has also been observed from anodized aluminum (7) and magnesium (8) as the result of a similar chemical reduction process.

Fluoride ion has also been detected in the thick anode film by means of a spot test. This could be due to some HF being trapped inside but it also could mean that the film is composed of silicon subfluoride. Subfluorides of silicon have been reported in the literature. Attempts by Ruff (9) to repeat this work were unsuccessful, nor could he obtain evidence of a subfluoride by means other than those previously tried. Recently, however, Schmeisser (10) has reported forming subfluorides of silicon by the reduction of SiF_2Br_2 or SiFBr_3 with magnesium in an ether solution.

On the basis of the experimental results it appears likely that some silicon subfluoride $(\text{SiF}_2)_x$ is formed anodically. This is unstable in water solutions and is oxidized to tetravalent silicon with hydrogen gas evolved as follows:



Critical Current Density for Electropolishing

In order to enter the current-potential region where the electropolishing of silicon takes place, a critical current density, i_c , must be reached. The effects of temperature, HF concentration, viscosity, and the concentration of the final anode product, fluosilicic acid (H_2SiF_6), on i_c were determined. All of the data were obtained starting with a lapped surface.

Effect of temperature.—The E-I curve in Fig. 3 was obtained at 25°C. If the temperature of the silicon is varied, it is found that the critical current required to start electropolishing silicon also changes. The critical current density i_c is defined as the current density at which the thick anode film starts coming off and the transition to the electropolishing region takes place. Higher temperatures require higher current densities. This is illustrated in Fig. 5. At a given current density, the anode potential decreases with increasing temperature. It can be seen from Fig. 5, however, that the anode potential at

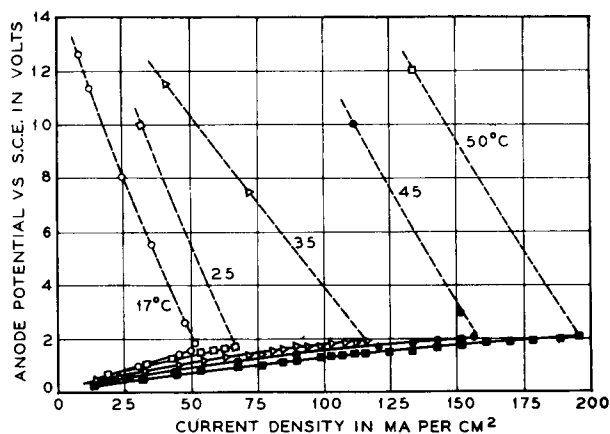


Fig. 5. Anode potential-current density curves for p-type silicon in 5% HF at various temperatures.

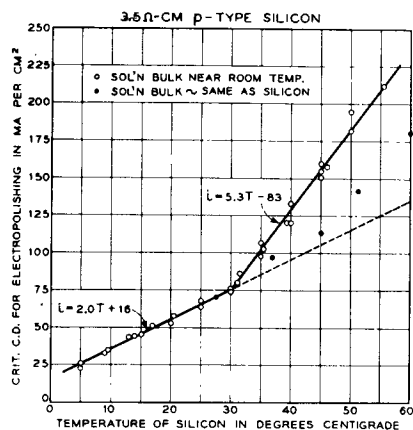


Fig. 6. Effect of temperature on the critical current density required to start electropolishing silicon in 5% HF.

which electropolishing starts, increases with temperature.

The critical current density required to start electropolishing silicon in 5% HF from 5° to 60°C is shown in Fig. 6. Most of the data were obtained with the bulk of the solution near room temperature. The points fall along two straight lines which intersect near room temperature. The critical current density is reproducible within ± 2 ma/cm² below 30°C. Above 30°C, the reproducibility decreased with an increasing temperature difference between the silicon and the solution bulk. A few additional points were obtained under conditions where the solution temperature was about the same as that of the silicon. These results will be discussed later.

Effect of HF concentration.—At a constant silicon temperature, the i_c is linearly related to the HF concentration. Data obtained at four temperatures, two below and two above 30°C, are shown in Fig. 7. The straight lines drawn are obtained from the empirical equations derived from the i_c - T data in Fig. 6. These equations were modified to include the effect of HF concentration, assuming that i_c is directly proportional to the HF concentration. The data obtained in the two experiments agree rather well.

Effect of viscosity.—The viscosity of the solution is known to be a factor in electropolishing metals. To test the effect of viscosity alone, it is necessary that an inert material be used to change the viscosity. Glycerin is often used and was chosen for this

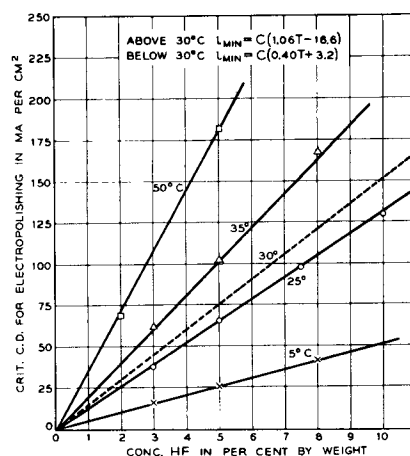


Fig. 7. Effect of HF concentration on the critical current density required to start electropolishing silicon at various temperatures.

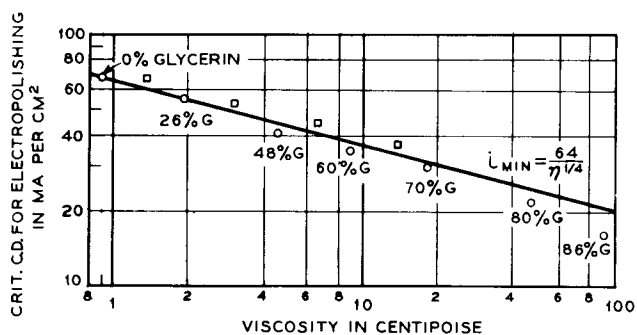


Fig. 8. Effect of viscosity on the critical current density required to start electropolishing silicon in 5% HF and glycerin at 25°C.

work. All solutions contained 5% by weight HF. Solution viscosities were obtained from published data on glycerin-water solutions (11). The data obtained in two series of experiments are presented on a log-log plot in Fig. 8. The straight line drawn for the empirical equation $i_c = 64\eta^{1/4}$ is a reasonable fit to the data. It shows that i_c is inversely proportional to the fourth root of the viscosity. Large deviations from this relation occur only at high viscosities, i.e., solutions 80 and 86% by weight glycerin.

Effect of H_2SiF_6 concentration.—Some workers (12) have found that the critical c.d. for electropolishing certain metals is decreased when the concentration of the metal in solution is increased. A series of six solutions were made up containing 5% HF and from 0 to 25% by wt fluosilicic acid (H_2SiF_6). The critical current density required to start electropolishing silicon in aqueous HF was not affected by the addition of fluosilicic acid.

Electropolishing n-Type Silicon

A few attempts were made to electropolish n-type silicon at 5°C where low polishing current densities can be used (~ 25 ma/cm²). The silicon was always pitted after the anodic treatment. This is due to the voltage barrier in the surface layer of the silicon which breaks down only at the points of pitting. It may be possible to obtain uniform breakdown of the voltage barrier by illuminating the silicon with a strong light. Even with a very strong light, however,

it will not be possible to electropolish *n*-type silicon rapidly since this requires a high current density.

Discussion

The experimental results suggest that silicon begins to electropolish in hydrofluoric acid solutions when the HF concentration at the anode surface decreases to a critical value. Hydrofluoric acid is consumed in the anode process. The supply of HF at the anode surface is determined by its rate of "mass transfer," i.e., by diffusion, convection, and migration from the bulk to the electrode surface. The nature of "mass transfer" of the reacting species to a horizontal silicon anode in HF solutions prior to electropolishing is complicated by the fact that an anode film is formed and gas is evolved. The contribution due to ion migration probably can be neglected. There are, however, several sources for "free convection" at the surface as a result of density differences in the solution near the surface. The thick anode film that forms consumes HF which tends to make the solution layer at the surface less dense than the bulk. The anode film reacts slowly with the electrolyte, however, to form fluosilicic acid and hydrogen gas. Fluosilicic acid should tend to counter the decrease in density due to the consumption of HF. The hydrogen gas that comes off produces a stirring effect like that due to density differences in fluids. Bubble size is probably an important factor in determining the effectiveness of stirring due to gassing. Thermal gradients in solutions also produce convection stirring. If the horizontal silicon electrode is colder than the solution above it, the solution layer at the surface is more dense than the bulk and there is no tendency for convection stirring due to thermal effects. When the silicon electrode becomes warmer than the bulk solution, however, the surface layer becomes less dense than the bulk and convection stirring results. The break in the $i_c - T$ curve in Fig. 6 shows this effect very clearly. Above 30°C the silicon is warmer than the bulk solution and the thermal gradient contributes to the "free convection." An attempt was made to thermostat the solution to the same temperature as the silicon. The few experimental points obtained under these conditions lie between an extension of the lower line and the upper line in Fig. 6. The results are in the right direction, but apparently thermal gradients have not been entirely eliminated.

If the reacting species reaches the electrode only by diffusion under steady-state conditions, the critical (or limiting) current density may be given by:

$$i_c = \frac{nFDC_b}{\delta} \quad (\text{I})$$

where n = the number of electrons involved in the electrode reaction, F = Faraday's constant, amp sec/g equivalent, D = diffusion coefficient, C_b = bulk concentration of reacting species, and δ = thickness of hypothetical diffusion layer. The diffusion layer thickness δ is not a constant under conditions that are nonsteady state and where "free convection" contributes to the "mass transfer" of the

reacting species. Tobias, Eisenberg, and Wilke (13) have shown that the diffusion layer thickness depends on the electrolyte composition, viscosity, diffusion constant, density coefficient, electrode reaction, electrode height, shape, and orientation. With vertical electrodes under conditions of "free convection",

$$\delta = 1.91 \left[\frac{x \eta D \rho_b}{g(\rho_b - \rho_i)\rho} \right]^{1/4} \quad (\text{II})$$

where x = vertical height on electrode surface, η = viscosity, ρ_b = bulk solution density, ρ_i = solution density at the surface, ρ = average solution density, and g = acceleration due to gravity. It is convenient to relate the density difference to the concentration difference by a specific densification coefficient, α , defined by:

$$\alpha = \frac{\rho_b - \rho_i}{\rho_b(C_b - C_i)} \quad (\text{III})$$

where C_i is the reacting species concentration at the surface. At i_c , $C_i = 0$, then from Eqs. (I)-(III)

$$i_c = 0.52 nFD^{3/4} C_b^{5/4} \left[\frac{g \alpha \rho}{x \eta} \right]^{1/4} \quad (\text{IV})$$

The general form of this equation has been verified experimentally by Wagner (14) and Wilke, *et al.* (15).

A similar mathematical analysis for horizontal electrodes has not been developed because of the complexity of the problem. However, empirical studies by Schmidt (16) on heat transfer and Fenech (17) on copper deposition under free convection conditions indicate that the critical or limiting current density on horizontal electrodes is proportional to the 4/3 power of the bulk concentration and is inversely related to the 1/3 power of the viscosity.

The critical current density at which electropolishing starts on a horizontal silicon electrode in HF solutions was found experimentally to vary linearly with HF concentration and temperature and inversely with the fourth root of viscosity. The diffusion constant and viscosity in Eq. (IV) are both temperature sensitive. Over a short range of temperatures, i_c should be approximately a linear function of temperature since $D \propto T$ and $\log \eta \propto 1/T$. These effects of HF concentration, viscosity, and temperature are in the right order of magnitude to assume that the i_c for electropolishing silicon in HF solutions is controlled by the rate of "mass transfer" of HF from the bulk to the surface. The sudden change in the slope of the $i_c - T$ curve in Fig. 6, signifying the start of convection stirring due to thermal effects, is also indicative that i_c is controlled by the "mass transfer" of HF to the silicon surface.

The mechanism for electropolishing silicon in HF solutions involves an understanding of the significance of the critical current density required to start electropolishing. Experimental results, while not extensive, do suggest that i_c is determined by the rate of "mass transfer" of HF from the bulk to the surface. As long as the HF concentration at the surface remains above a critical value, silicon dis-

solution is divalent and a solid anode film is formed, presumably $(\text{SiF}_2)_x$. At i_c , there is insufficient HF at the anode surface to continue this process and the next anode reaction begins. This involves dissolution of silicon in the tetravalent form. The anode product formed under these conditions produces the electropolishing film. The most likely assumption is that it is some form of SiO_2 . Silicon dioxide is readily dissolved in HF which is consistent with the observation that the electropolishing film on silicon is always very thin—less than interference-color thickness.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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Electrochemical Measurement of Oxide Formation

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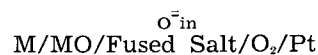
ABSTRACT

Measurements have been made of the potential developed between a metal wire covered with its oxide and a platinum wire over which air or oxygen was passed. The electrolyte was the eutectic mixture of Li_2SO_4 and K_2SO_4 , containing dissolved CaO and operated at various temperatures between 550° and 750°C . Heavy metal oxides are only very slightly soluble in this melt, so that the measured potential corresponds to the formation of metal oxide from the elements. Iron probably formed FeO , nickel formed NiO below 658° and probably a solid solution of LiNiO_2 in NiO at higher temperatures, while copper formed Cu_2O . Gold showed only the thermoelectric potential expected. The values found are in agreement with the free energy of formation of the oxides as determined by other methods.

An electrode reversible to oxygen gas and oxygen ion is useful both for thermodynamic measurements involving oxide formation and for determining the oxide ion activity in reactions of metallurgical interest. Such an electrode has not been possible in water solution, but it was shown many years ago that molten metal in contact with oxygen gas appeared to serve as such an electrode in fused salts at high temperatures (1). More recently a study of solid metal electrodes with oxygen gas in fused salts has been published by Lux (2), whose work has been critically reviewed and extended by Flood, Forland, and Motzfeldt (3). These last workers showed that a platinum wire surrounded by oxygen and immersed in a fused salt gave reproducible potentials,

depending on the oxide ion concentration in the melt. The dependence of the potential on the concentration was discussed by Flood and Forland (4).

The authors combined this electrode with one made from a heavy metal covered with its oxide. The cell may be represented as



The metals studied form oxides which are only very slightly soluble in the molten salt, the melt giving no chemical test for the metal after use. The authors assume saturation with the metal oxide and, therefore, assume that the reaction measured is the formation of the metal oxide from its elements. In such a reaction, the oxide ion concentration should have no effect on the measured potential, which was found to be the case, save in one experiment to be

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