

# ANODIC OXIDATION OF SILICON

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(Received 26 May 1969; revised 15 November 1969)

The set-up used to grow silicon dioxide anodically on silicon surfaces has been described and the results obtained are discussed. Such layers have been used in obtaining information about diffused layers, getting planar structures and reducing the thickness of slices by known amounts. The method has certain advantages over other techniques like thermal oxidation, sputtering etc. which are dealt in the paper.

There are several references to the anodization of silicon in nonaqueous solvents like *N*-methylacetamide, tetrahydrofurfuryl alcohol and ethylene glycol. The anodic oxidation of silicon in a solution of 0.04 normal potassium nitrate in ethylene glycol containing small amounts of water has been reported by Duffek<sup>1</sup> et. al. Dense silicon dioxide films of varying thicknesses have been produced by them using a constant current anodization procedure. This work showed that stoichiometric silicon dioxide films can be obtained on a reproducible basis in the above solution in the presence of 0.5 to 3 per cent water.

Authors have used a constant voltage anodization cycle to grow silicon dioxide films of upto 2100 Å thickness. Silicon dioxide layers have been used in masking impurity diffusions, determining impurity profiles and reducing epitaxial layer thicknesses by known amounts.

## APPARATUS

The anodization cell used was a pyrex tube 30 cm in length, 10 cm in diameter with both ends closed. A slot 3 cm wide was cut along the axis on one side. This opening served as a port to pour the electrolyte into the cell and for introduction of the cathode and the silicon slice (anode). The tube was then suspended in the tank of an ultrasonic cleaner, the tank being filled with water upto the requisite level. This arrangement helped in maintaining the electrolyte properly mixed during anodization and at a constant temperature in the range 20 to 30°C.

The cathode was a strip of tantalum dipped into the electrolyte. The silicon slice suitably prepared was dipped into the solution such that only a known area of it was getting oxidized. The anodizing current was supplied by a constant voltage type of regulated d.c. power supply capable of delivering 0 to 50 mA upto 1200 volts.

The schematic experimental set-up is shown in Fig. 1 and the anodization cell used is shown in Fig. 2. The solutions used as electrolytes were prepared just prior to an experiment and had the following compositions :

Solution	Ethylene glycol (cc)	Potassium nitrate (gm)	Distilled deionized water (cc)
A	500	2.022	5
B	500	2.022	10
C	500	2.022	20

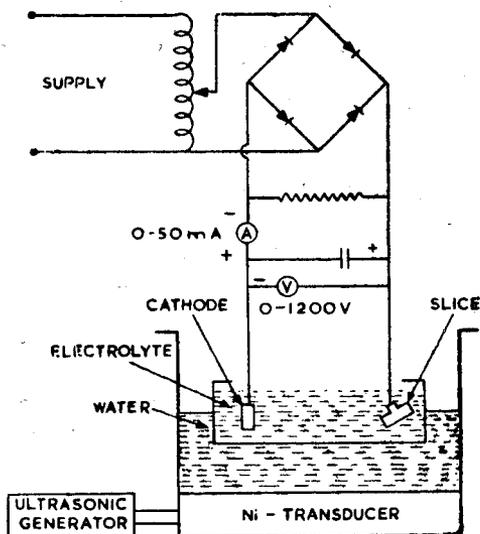


Fig. 1—Schematic experimental set-up.

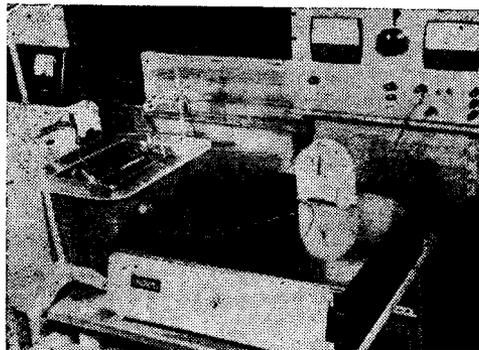


Fig. 2—Anodization cell.

Due to hygroscopic nature of ethylene glycol, the required amount of potassium nitrate was added to the bottled ethylene glycol and mixed just before usage. The almost closed shape of the anodization cell used in the experiments also helped in preventing any excessive absorption of moisture during the course of the experiment.

### SLICE PREPARATION

In the electrode reactions which take place during the anodic oxidation of silicon, the surface of the slice is converted to silicon dioxide. Thus the surface preparation of slice plays an important role in determining the resulting oxide surface.

When the oxide is to be used to prevent the diffusion of certain impurities over selected areas of the slice, the slice preparation prior to oxidation depends upon the diffusion depth and the allowable tolerances on it.

When the oxide is to be used to remove known thicknesses of, say, an epitaxial layer, then as-grown epitaxial layers could be employed in the anodization experiments. Similarly for use in determining the impurity profile within a diffused layer or an epitaxial layer one can start with as-diffused or as-grown slices respectively if they do not contain any other phase except silicon at their surface.

In all cases, however, the slices have to be degreased in hot trichloroethylene to remove traces of organic contaminants on the slice surface, and rinsed in acetone and finally in deionized water. A rinse in hydrofluoric acid (49%) for 20 sec would remove any thin oxide (10–30 Å) layer formed on the slice due to atmospheric oxidation. A further rinse in deionized water followed by immediate introduction into the electrolyte is resorted to.

TABLE I  
COLOUR AND FORMING VOLTAGE OF SILICON DIOXIDE FILMS

Film thickness (Å)	Colour	Net forming voltage
100	grey	—
300	tan	—
500	brown	90
800	blue	144
1000	violet	180
1500	blue	270
1800	green	325
2100	yellow	380

The procedure described above is suitable if the slice can be suitably shaped such that a clip-on type of electrode contact can be provided, while facilitating introduction to the required depth. But if a soldered type of electrode contact is being used, the cleaning procedure should also employ suitable solvents to remove any contaminants (metallic or otherwise) left over by such an operation in the area of interest.

#### GROWTH MECHANISM

For a given electrolyte temperature, area of slice and distance between the electrodes, the electrical impedance offered by the electrolyte system is a constant. But the impedance between the two electrodes will be due to the oxide layer also, apart from the above component. Thus if one maintains the applied voltage fixed at a particular value, the initial current will depend upon the initial impedance between the electrodes, and as the anodic reaction starts and oxide layer formation proceeds, the current starts falling from the initial value. When the oxide layer formation is complete, the current will become constant or else, when the layer formation is approaching saturation, the rate of decrease of current falls to small values.

When the slice is fresh, the impedance between electrodes is a minimum and hence the maximum initial voltage which can be applied is limited by the maximum current available from the power supply. Also, there is a threshold voltage below which anodic reactions do not take place, as indicated by the constancy of the current with time. Thus one is left with the choice of starting with a voltage which can have a value in between the threshold and maximum initial voltage.

Duffek et. al<sup>1</sup>. in their experiments on anodic oxidation of silicon, employing a constant current power supply, have determined the forming voltage (difference between the final voltage attained and initial starting voltage) necessary for various oxide thicknesses. A fairly accurate estimate of oxide thickness can be obtained by observation of its colour under normal illumination. Table I gives certain oxide thicknesses which have distinctive colours<sup>2</sup> and forming voltage.

The constant voltage which has to be applied between the electrodes for any given oxide thickness would follow the relationship.

$$\left. \begin{array}{l} \text{Constant voltage applied for} \\ \text{any oxide thickness ( } V_a \text{ )} \end{array} \right\} = \left\{ \begin{array}{l} \text{Forming voltage for that} \\ \text{oxide thickness ( } V_f \text{ )} \end{array} \right\} + \left\{ \begin{array}{l} \text{Threshold Voltage} \\ \text{( } V_t \text{ ) (I)} \end{array} \right\}$$

### EXPERIMENTAL RESULTS

Three solutions containing varying percentages of water were used in the experiments conducted to determine the effect of water on the anodization cycles. In all cases lapped and chemically polished *n*-type, 30 ohms cm silicon slices have been used.

TABLE 2  
THRESHOLD VOLTAGE FOR SOLUTION A  
(current density, 25 mA/cm<sup>2</sup>)

Bath temp	Constant voltage applied (volts)	Colour of the oxide	Calculated threshold voltage from equation (I) (volts)
24°C	300	blue (800 Å)	156
30°C	320	blue (800 Å)	170
—	420	blue (1500 Å)	150
—	550	yellow (2100 Å)	170

TABLE 3  
THRESHOLD VOLTAGE FOR SOLUTION C  
(oxide thickness 2100 Å)

Anodization current density (initial) (mA/cm <sup>2</sup> )	Voltage applied (volts)	Temperature of bath (°C)	Calculated threshold voltage (volts)
15	480	30	100
20	500	31	120
25	500	—	120

TABLE 4  
MAXIMUM INITIAL VOLTAGES

Solution	Volts
A	320
B	240
C	290

(a) *Threshold voltages*—First, the threshold voltages for the solution A was determined by fixing the distance between the electrodes at 20 cm, and area of slice used for oxidation as 2 cm<sup>2</sup>. The experimental determination was done as follows. After introducing the electrodes into the anodization cell and filling up the electrolyte upto the proper level (to get 2 cm<sup>2</sup> area of the slice dipping), the power supply was turned on and the voltage gradually applied. The current flowing in the circuit was monitored and if there was no decrease in current with time within first 2 to 3 minutes, a higher voltage was impressed. This way we could determine the minimum voltage required to get a decreasing current versus time behaviour. For solution A, a threshold voltage of 160 volts was obtained at a bath temperature of 21°C. In Table 2 the threshold voltage for the same solution is calculated from experimental values of applied voltage and oxide thickness obtained.

We can see that the calculated threshold voltage value is quite close to the experimentally determined value of 160 volts. The small deviation observed may be due to slight temperature effects.

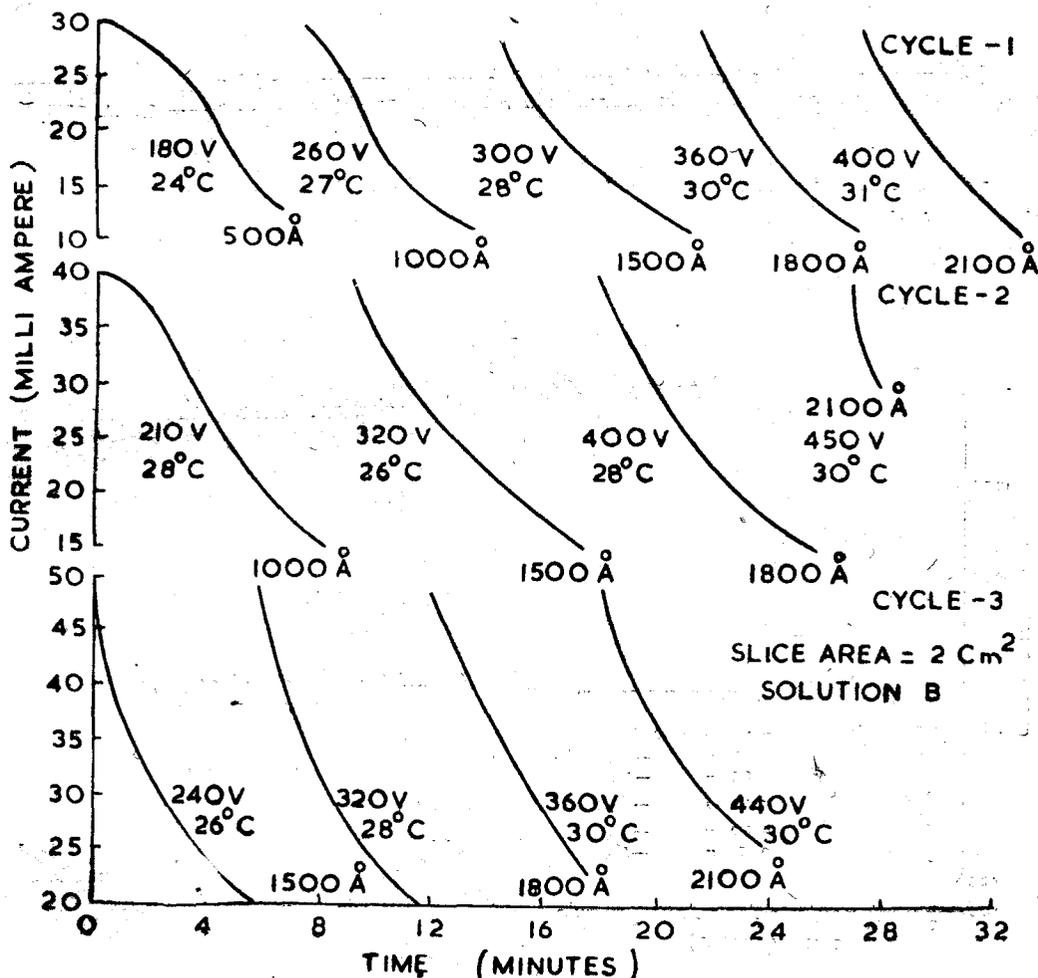


Fig. 3—Growth cycles for solution B.

The variation of threshold voltage with various initial current densities was studied and it was found that the current density had no marked effect on the threshold voltage. Calculated values of threshold voltage for solution C are given in Table 3. The effect of temperature is apparent from Table 3. It should be pointed out here that the actual temperature at the vicinity of the anode may be different from the temperature of the bath and may undergo variations at a much faster rate than the bath temperature. These effects are expected to be minimized by using ultrasonic agitation.

The threshold voltage values observed under similar conditions for solution B were around 75 volts.

(b) *Growth cycles*—Due to the current limitation of the power supply, the maximum initial voltage we could apply in case of the three solutions were as in Table 4. The maximum initial oxide thickness was 800 Å in all the three cases.

The maximum output current from the d c power supply was 50 mA, the distance between electrodes 20 cm, area of anodization 2 cm<sup>2</sup>, and bath temperatures  $29 \pm 1^\circ\text{C}$ .

Hence to grow layers of silicon dioxide greater than 800 Å in thickness by the application of a single voltage was not possible in any of the three cases. Thus we resorted to a growth cycle to achieve thicker layers as follows :

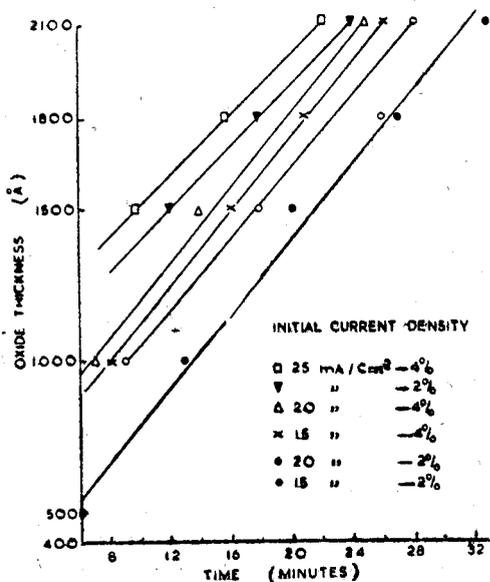


Fig. 4—Growth time versus oxide thickness,

*Step (1)*—Apply an initial voltage greater than the threshold voltage for the solution. Allow the current to fall.

*Step (2)*—Increase the applied voltage to a higher value when current density starts falling at a rate of 0.5 mA/cm<sup>2</sup>/min. Allow the current to fall.

*Step (3)*—Repeat step (2) as many times as required till the oxide thickness reaches the desired value.

The maximum thickness of oxide we have been able to grow was 2100 Å. The typical growth cycles for solution B, for a slice area of 2 cm<sup>2</sup> are shown in the curves of Fig. 3. The growth cycle curves for solutions A and C were similar in form.

(c) *Effect of initial current density*—It can be observed that the voltage applied in steps (1) and (2) can be as high as possible so as not to exceed the maximum current limitation of the power supply. The results for such a growth cycle are shown in Fig. 3, in cycle 3. Here the initial current density for each of the individual subcycles has been held constant at 25 mA/cm<sup>2</sup>.

The effect of maintaining lower initial current densities have been studied and the results are given in Fig. 3. Cycle 1 shows the subcycles undergone by the slice to achieve an oxide layer thickness of 2100 Å when the initial current density was limited to 15 mA/cm<sup>2</sup>. Cycle 2 shows the subcycles undergone by the slice when the initial current density was limited to 20 mA/cm<sup>2</sup>.

The first difference which is obvious from Fig. 3 is that the total time required for attaining an oxide thickness, of 2100 Å increases as we go from cycle 3 to cycle 1, namely, as the initial current density is reduced. This is an observation which is also in support of the contention that the oxide thickness grown should be commensurate with the number of Coulombs passed. For a given oxide thickness the amount of charge to be passed through the electrolyte is fixed for a given electrolyte, electrode separation, bath temperature and area of the slice. When the latter are held constant the time required should fall as the average current level increases. This is observed very clearly from the growth subcycles for different oxide thicknesses.

Another, less apparent effect of reduced initial current density needs a little more careful observation of the first few subcycles in the first two cases. The rate of fall of current varies within a subcycle and from one subcycle to another. The fall rate of current within a subcycle is small in the beginning and becomes large as time elapses and again becomes



Fig. 5—Electron reflection diffraction photo of anodically grown silicon dioxide.

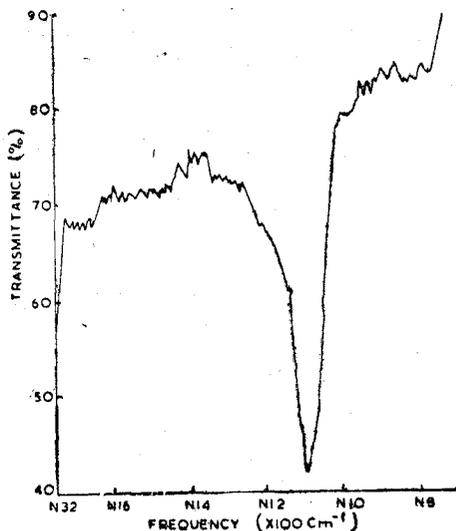


Fig. 6—Transmittance of silicon dioxide versus frequency.

small within a subcycle. We can interpret this as due to slow reaction at the start of a subcycle, the tempo of anodic oxidation increasing subsequently till saturation sets in. After the initial few subcycles are over, the anodization rate appears to proceed identically, without any slow pick-up, further on in the cycle.

(d) *Growth time*—The time required for growth of oxide layers computed from the growth cycles for solutions B and C are presented in Fig. 4. Suitable corrections have been applied to take into account the slow pick-up times. The criteria for termination of a subcycle has been that the fall rate of current density has equalled  $0.5 \text{ mA/cm}^2/\text{min}$ . This is an arbitrary choice, since theoretically a subcycle should be terminated only when the current becomes constant. But it is however felt that the rate of growth of oxide during this portion of the subcycle being small, no large error would creep in by considering a subcycle as ended when the fall rate has become small. The fall rate of current density observed during the subcycles are as high as  $5$  to  $6 \text{ mA/cm}^2/\text{min}$ , when the reaction is proceeding at its best, and hence a termination criteria of  $0.5 \text{ mA/cm}^2/\text{min}$  for the fall rate is a reasonable one.

The thickness of the oxides has been estimated by their colours, as in Table 1 and whenever transition colours have been observed (as in subcycle 1, cycle 3 in Fig. 3) such a point has been omitted in Fig. 4. The accuracy of the plots, therefore, are quite high on both the thickness as well as time axes.

Highest growth rates have been obtained for cycles with initial current densities of the order of  $25 \text{ mA/cm}^2$ . Solution C containing 4% water yields oxide layers slightly faster than solution B containing 2% water, at this current density. The same trend is observed as we change the initial current density to  $20 \text{ mA/cm}^2$  and  $15 \text{ mA/cm}^2$ . The difference in growth rates between solutions C and B increases as we decrease the initial current density.

#### PROPERTIES OF THE OXIDE LAYERS

The dielectric strength, refractive index and porosity of anodically formed Silicon dioxide have been studied in detail by Duffek et. al<sup>1</sup>. The layers grown have been subjected to electron diffraction studies which have shown that the films are amorphous. A typical photograph is given in Fig. 5. Fig. 6 shows the infrared absorption spectrum of a silicon dioxide layer of  $1500 \text{ \AA}$  thickness. The absorption peak around nine microns is a clear proof of the stoichiometry of the composition.

Etch rates of the films have been determined using a freshly prepared *p*-etch solution<sup>3</sup> made up of 15 parts of hydrofluoric acid (49%), 10 parts of nitric acid (70%) and 300 parts of distilled water by volume. The etch rates of anodically formed layers are found to be around  $21 \text{ \AA}/\text{sec}$  whereas under similar conditions thermally grown oxides etch at  $2 \text{ \AA}/\text{sec}$ .

#### ADVANTAGES OF ANODIC OXIDATION

The process of anodic oxidation provides us a method of converting silicon surfaces into oxide of known thickness, at a temperature of the order of  $25$  to  $30^\circ\text{C}$ . The temperatures needed are greater than  $900^\circ\text{C}$  for thermal oxidation<sup>4</sup>,  $500^\circ\text{C}$  for reactive sputtering<sup>5</sup> and  $1000^\circ\text{C}$  for chemical deposition<sup>6</sup> of silicon dioxide films. Due to these high temperatures impurity redistribution<sup>7</sup> at the silicon/silicon dioxide interface takes place due to the phenomenon of diffusion of impurities. Thus each of the latter processes will not ensure the same impurity profile within the slice before and after oxidation.

TABLE 5

COMPARISON OF VARIOUS METHODS USED FOR DEPOSITING OXIDE FILM

	Anodic oxidation	Thermal oxidation	Reactive sputtering or glow discharge	Chemical deposition
Apparatus required	Regulated d c power supply Ultrasonic agitator	Temperature controlled high temp furnaces	High vacuum set-up High voltage sources	RF generator with temperature controller
Materials required	Pyrex tube Ethylene glycol Potassium nitrate Distilled water	High purity quartz boats and tubes High purity oxygen or other gases	High purity silicon or alk-oxy silane High purity argon and oxygen	High purity quartz wares Silicon tetrachloride or silane High purity hydrogen gas

Another point of difference is that while anodic oxidation and thermal oxidation convert the parent silicon into silicon dioxide, sputtering or chemical deposition provide a silicon dioxide layer above the initial surface of the parent silicon. This restricts use of anodic oxidation (and thermal oxidation) to only silicon substrates, whereas the other two methods can be used also for non-silicon substrates depending upon the actual deposition temperatures involved. However, certain applications like removal of known thicknesses of silicon and determination of impurity profiles within silicon are not possible by the very nature of sputtering or chemical deposition.

Thermal oxidation cannot be used in the determination of impurity profiles in silicon mainly due to the high temperatures involved. As these temperatures are well above 900°C for reasonable growth rates of thermal oxide, there are effects due to impurity diffusion, change in minority carrier lifetimes and propagation of dislocations. All these are deleterious effects and hence thermal oxidation is not recommended even for reduction of layer thicknesses by known amounts.

Last but not the least, one has to consider the simplicity of the set-up, as well as availability of materials required.

It can be seen from Table 5 that anodic oxidation method offers advantages over other methods on both counts. The use of ethylene glycol as a solvent in anodic oxidation has the further advantages of low cost, high purity, electrolyte solubility and good stability toward heat and electrolysis.

## ACKNOWLEDGEMENTS

The authors thank Dr. N. B. Bhatt the then Director, SPL for his permission to present the paper at Ninth Seminar on Electrochemistry held at the Central Electrochemical

Research Institute, Karaikudi in December 1968. They record their grateful thanks to their colleague Shri R. Kesavan for conducting electron diffraction and IR absorption studies on the samples as well as presenting the paper at the seminar.

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