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Title THERMAL GROWTH AND CHEMICAL ETCHING OF SILICON DIOXIDE FILMS

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Some important factors that affect the dimensional control of oxide films on silicon were studied. Both N- and P-type silicon with resistivities in the range of 0.014 to 200 ohm-cm and a (111) surface orientation were employed in this experiment. The etching rates of silicon dioxide in hydrofluoric acid (HF) were studied as a function of the concentration of HF, temperature, and stirring speed. The experimental results show that the etching rates varied directly with these variables, but no difference in etching rate was found due to concentration or type of impurity in the silicon substrate over the range studied.

The oxide layers on silicon used in this experiment were prepared by five different oxidation methods. They are: wet oxygen, dry oxygen, steam, wet nitrogen during diffusion of boron, and dry oxygen during diffusion of phosphorus. The etching rates of the oxide layer grown by the above methods have the same average

value except for the oxide layer grown in dry oxygen during a phosphorus diffusion which has a much faster etching rate.

The thickness of the oxide layers employed in this experiment was determined by a multiple-beam interference method. Comparisons of this method to other optical interference methods were made. It was found that the multiple-beam method was the most accurate of the four interference techniques.

THERMAL GROWTH AND CHEMICAL ETCHING OF SILICON DIOXIDE FILMS

by

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THERMAL GROWTH AND CHEMICAL ETCHING OF SILICON DIOXIDE FILMS

INTRODUCTION

The oxide film on a silicon surface has the property of masking against certain elements from diffusing into the silicon. Therefore, it is widely employed in the fabrication of semiconductor devices. With the development of integrated circuits, the precise geometric control of the mask is becoming more important. The dimensional control of the oxide film involves how the oxide film is grown, and the method of sectioning.

Thermal oxidation methods of growing oxide films on silicon are widely employed as a means of preparing masks. A number of investigations have been reported concerning the thermal oxidation of silicon, including reaction kinetics and masking effects. However, very little information is available concerning the etching rate of silicon dioxide in hydrofluoric acid (HF).

In order to understand the important factors that affect the dimensional control of chemical etching, it is necessary to investigate the important variables involved and their effects on the kinetics of the etching rate of the silicon dioxide layer. The results of this study are concerned with how the concentration of the etchant, the temperature, and the stirring speed affect the etching rate. Also comparisons were made on the

etching rates of silicon dioxide layers which were prepared in different thermal oxidation atmospheres. These are: wet oxygen, dry oxygen, steam, wet nitrogen during a boron diffusion, and dry oxygen during a phosphorus diffusion. These studies are designed to clarify some of the surface problems that are associated with semiconductor device fabrication.

THERMAL OXIDATION MECHANISM

The diffusing substance during the process of thermal oxidation has been investigated by some workers. In steam oxidation, mobile oxygen species that diffuse through the oxide network is responsible for the growth of the oxide. (13) Also, Karrube, Yamamoto, and Kamiyama (10) have concluded from their experiment that when silicon is oxidized at 1250°C in oxygen flow, the pertinent process proceeds with the transport of oxygen through the oxide layer. When oxygen comes to the interface between the oxide and silicon, it reacts with unoxidized silicon, forming only one stable solid oxide, i.e., SiO_2. Also, Brewer and Greene (3) confirmed from infrared absorption measurements that SiO_2 is the only stable solid oxide formed in this process.

Several papers have reported the parabolic growth of the film when oxidation is carried out in an oxygen ambient. The parabolic law can be expressed as $w^2 = kt$ where w is oxide weight or thickness; t, oxidation time; and k, rate constant. (6)

MATERIAL PREPARATION

Both N-and P-type silicon with resistivities in the range of 0.014 to 200 ohm-cm were cut into circular slices about 10 mm in diameter, 0.60 mm in thickness, and in (111) surface orientation. These samples were mechanically lapped with 600 grit silicon carbide on a Beuhler polishing machine, and then polished to a mirror finish with 1 micron alumina powder as a final abrasive. Then they were degreased in hot acetone and rinsed first in 48% hydrofluoric acid and then in deionized water. Some of the samples were further chemically polished in a solution consisting of 10 parts of concentrated nitric acid to 1 part of 48% hydrofluoric acid to 6 parts of glacial acetic acid. Thermally grown layers were prepared on the mechanically polished samples as well as the chemically polished samples.

THERMAL OXIDATIONS

The oxidations were carried out in a 5 cm diameter open-ended quartz tube in a tube diffusion furnace. The following atmospheres were used: (i) wet oxygen -- the oxygen was bubbled through deionized water at a rate of 1.0 liter/min. at room temperature; (ii) dry oxygen -- the oxygen passed through a gas drying unit filled with calcium sulfate ($CaSO_4$), and then to the furnace at a rate of 1.0 liter/min. at room temperature; and (iii) steam -- the steam was provided by boiling deionized water. All of the oxidations were performed at atmospheric pressure and at the temperature of 1150^{o}C. The desired thickness of the oxide layer was obtained by varying the oxidation time.

Figure 1 shows the curves obtained for the three methods of thermal oxidation. In every case, a parabolic rate law of growth of oxide was obeyed over most of the thickness range which was studied. However, the steam rate was greater than those of wet and dry oxygen.

It was found that both mechanically polished and chemically polished samples have the same rate of growth of oxide. Also no differences in the rate of oxide growth were found due to concentration or type of impurity in the silicon wafers with resistivities ranging from 0.014 ohm-cm to 200 ohm-cm.

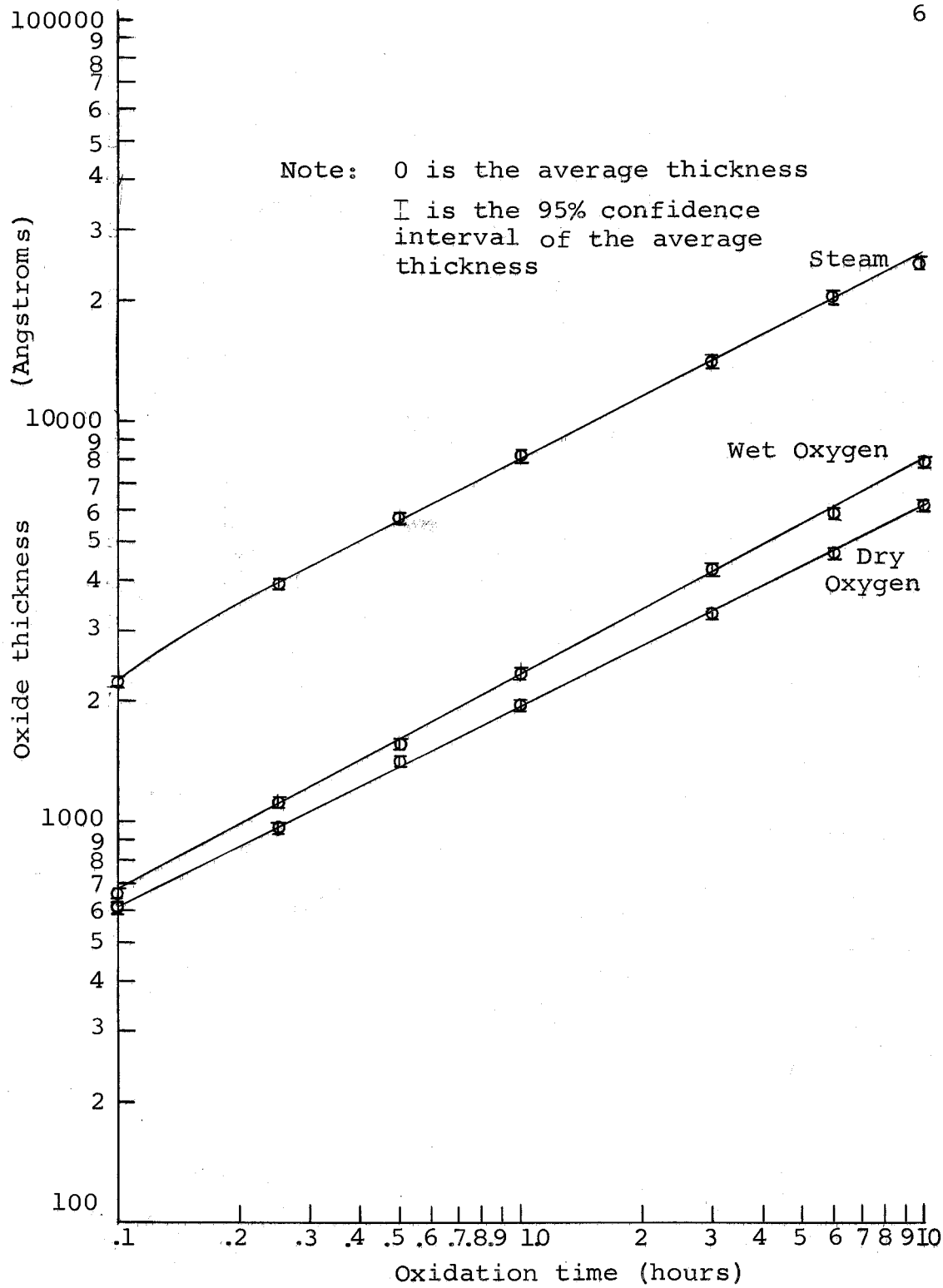

Figure 1. Oxide thickness versus oxidation time at 1150°C with various sources

SEQUENTIAL OXIDATIONS (6)

Silicon slices were first oxidized in wet oxygen for three hours, then in dry oxygen for another three hours, and then in steam for four hours all at 1150^{o}C. Figure 2 shows the curves obtained from these data. (Appendix Table II). The solid line is the actual oxidation process of these sequential oxidations and the dotted lines are the theoretical curves for growth of oxide in wet oxygen, dry oxygen, and steam. The theoretical curves are plotted according to the data of the thermal oxidations. (Appendix Table I) Since the zero-time reference point of each theoretical curve is not the same as Figure 1, they are curves instead of straight lines. By investigating the theoretical curve (efgh) of dry-oxygen oxidation and the curve of actual dry-oxygen oxidation (bc), the study shows that the portion (fg) of the theoretical curve is coincident with (bc) of the actual oxidation curve. The same situation exists in steam oxidation. Thus, the investigation shows that the first oxidation has no effect on the subsequent oxidations, nor do the combination of the first and second oxidations have any effect on the third.

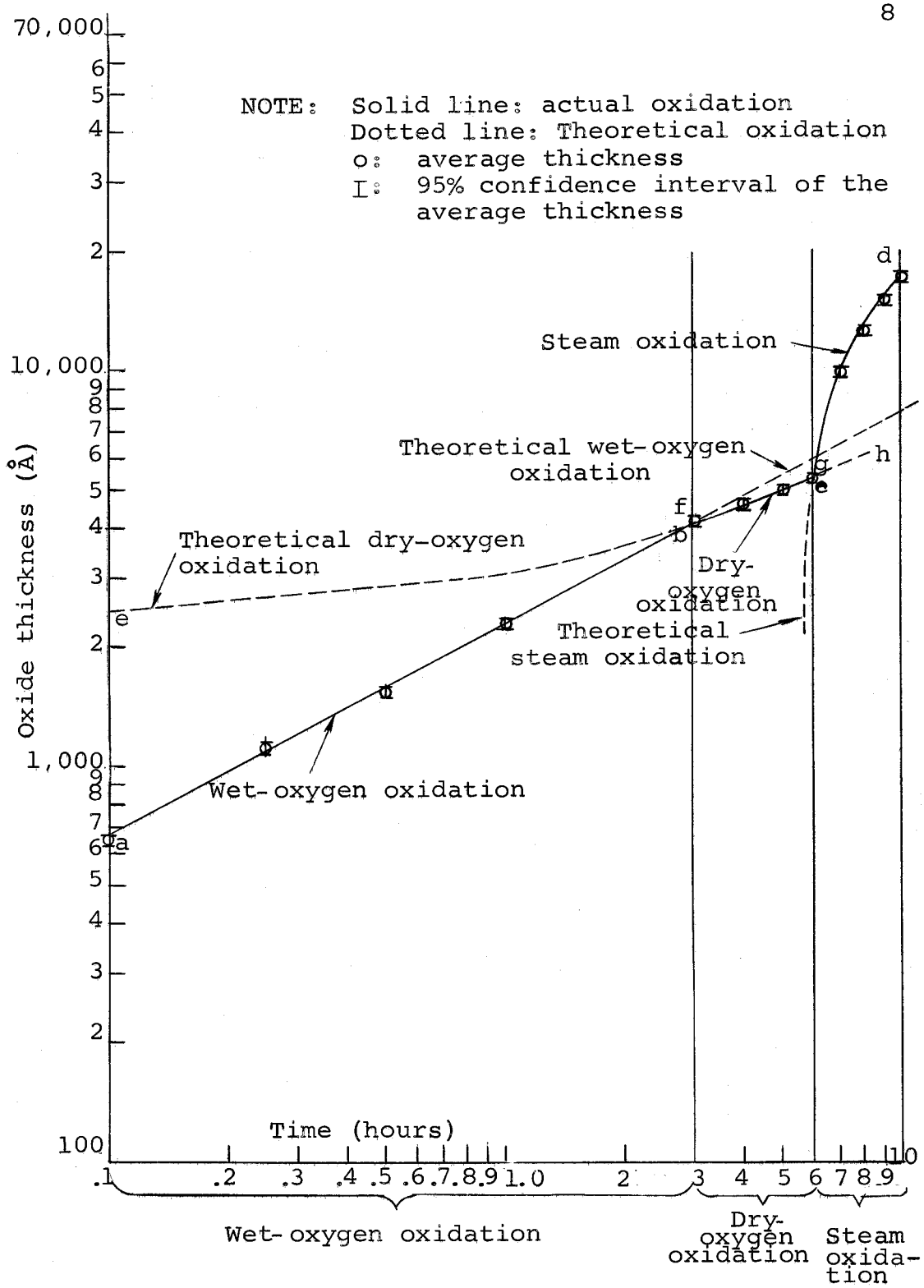

Figure 2. Sequential oxidations with the same samples in wet oxygen, dry oxygen and steam at 1150°C

MEASUREMENT OF THE THICKNESS OF THE OXIDE LAYER

The etching rate of silicon dioxide in HF is evaluated by means of first etching the sample for certain length of time then comparing the remaining oxide film thickness to the oxide thickness of an unetched sample. Therefore, some means for determining the thickness of the oxide layer must be employed.

There are several ways to determine the thickness of an oxide layer: (i) optical interference methods, (ii) weight change method (weighing the samples in a microbalance before and after the oxide growing process), and (iii) the color reference method (comparing the color of the unknown film with the colors of a set of standard films of different thickness).

The optical interference methods (1) were employed in this experiment for determining the thickness. There are four different optical interference methods which are: two-beam interference method with metallized sample; two-beam interference method with non-metallized sample; wedge method, and multiple-beam interference method. Their accuracies were compared by measurements made on a set of six samples. Figure 3 shows a comparison of the optical interference methods for each of the six samples.

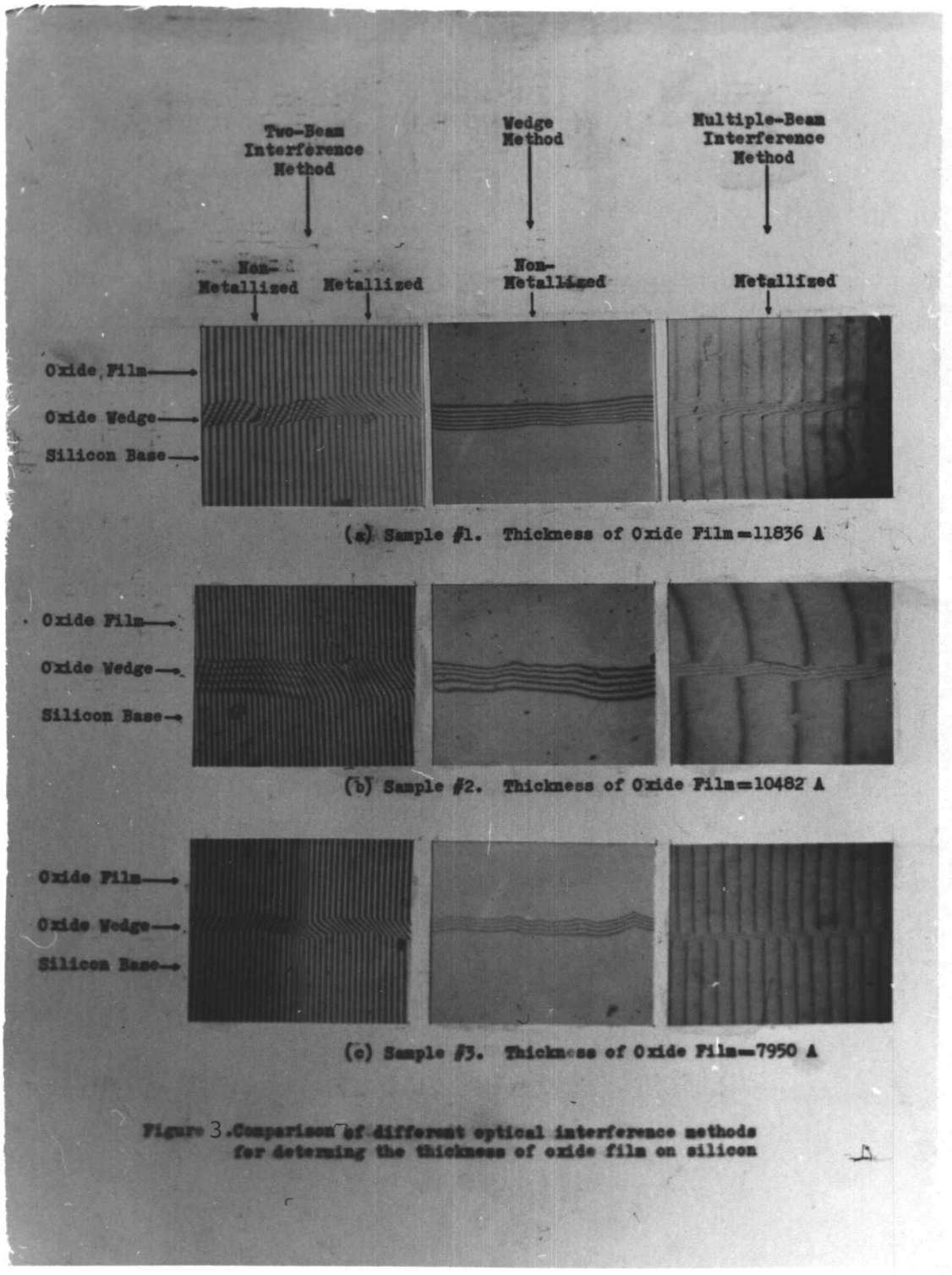

Figure 3. Comparison of different optical interference methods for determing the thickness of oxide film on silicon

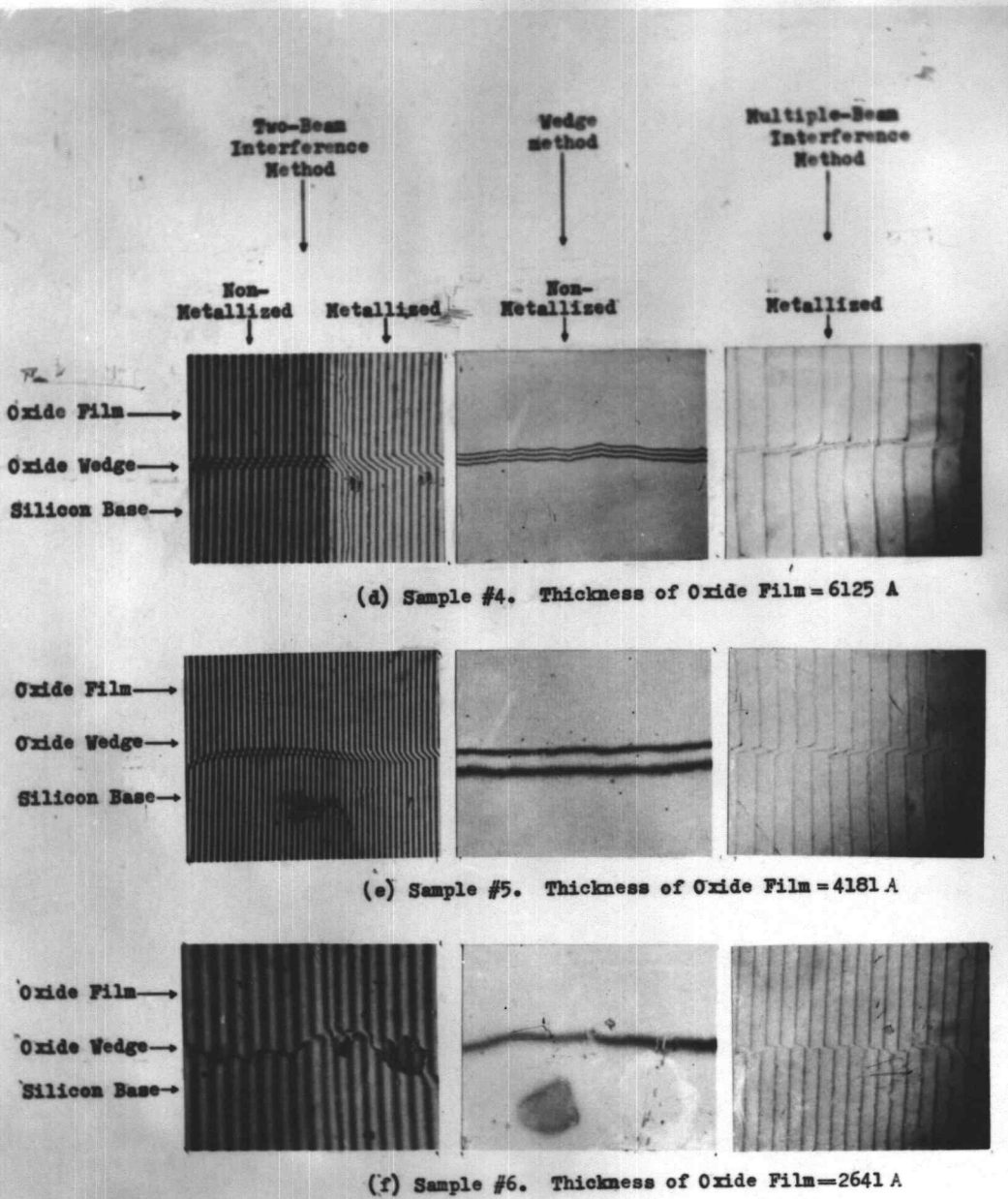

Figure 3. Comparison of different optical interference methods for determing the thickness of oxide film on silicon

(i) Two-beam Interference Method with Metallized Samples

A solution of Apiezon W wax in toluene was applied with a brush to a portion of the silicon sample surface possessing the oxide film (Figure 4a). The toluene rapidly evaporated, leaving a hard wax surface film. The sample was immersed for 60 seconds in HF (48%) to dissolve the unprotected portion of the oxide film (Figure 4b). The sample was then thoroughly rinsed, and the wax was removed (Figure 4c) with trichloroethylene. Undercutting of the wax layer by the HF produced a relatively uniform wedge-shaped oxide film step.

A portion of a slice possessing an oxide film was metallized (Figure 4d) by deposition of silver on the surface with a vacuum evaporator. The sample was examined with a Unitron metallurgical microscope equipped with Watson interference objective and sodium light source which has a wave length of 5889 Å and 5895 Å, where 5890 was used in all the calculation of this experiment. In the metallized portion of the sample, a single fringe system occurred (Figure 3), and the displacement of the fringes on going from the silicon base to the oxide film corresponded to a step up. The film thickness d is given by (1)

$$d = p\frac{\lambda}{2} \qquad 1$$

where p is the fringe displacement and λ is the wavelength of sodium light.

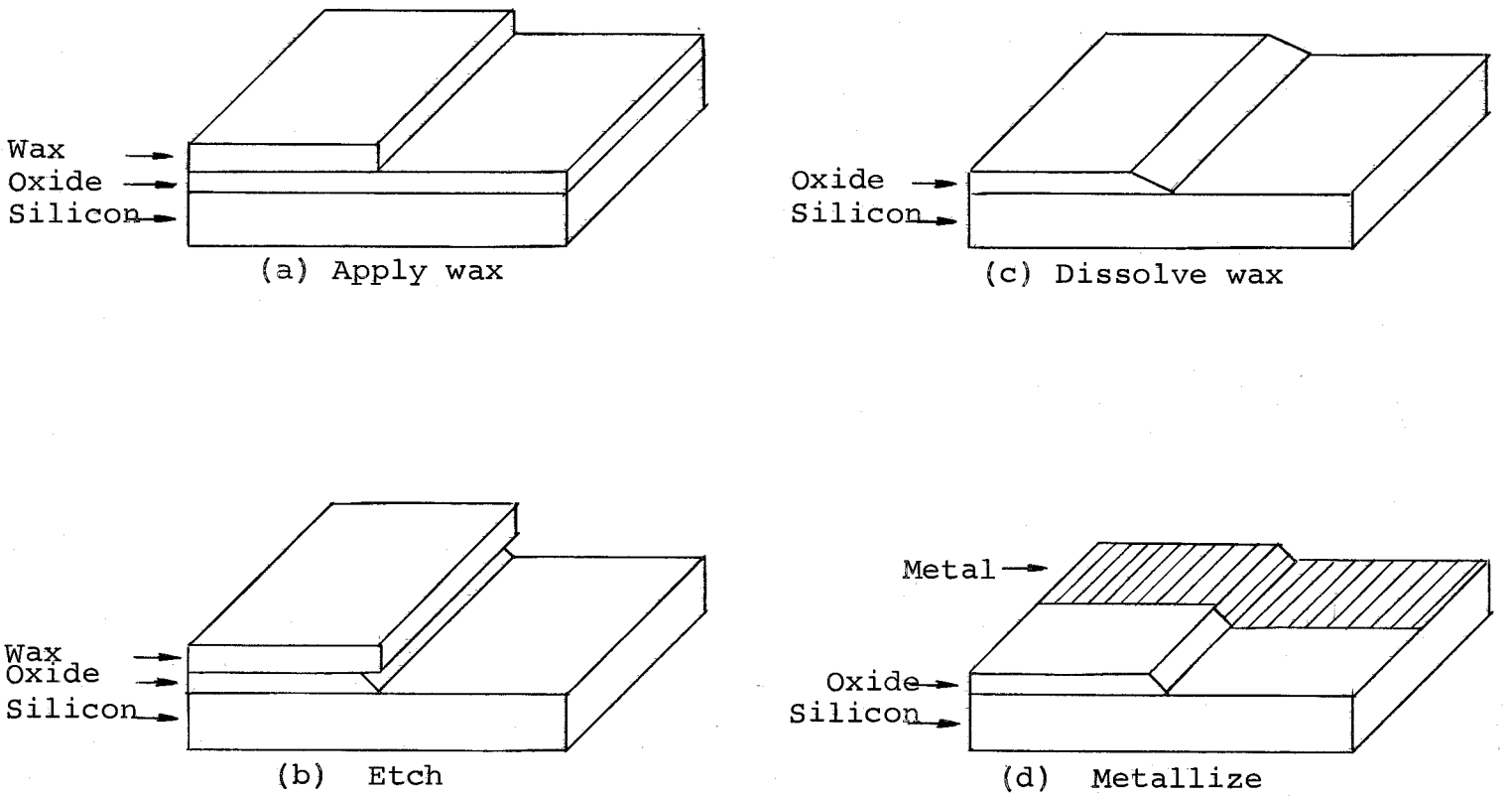

Figure 4. Preparation of the oxide film step and subsequent metallizing.

(ii) Two-beam Interference Method with Non-metallized Samples

The same procedure was employed except the sample was examined in the non-metallized portion (Figure 3c). The film thickness is given by (1)

$$d = q \frac{\lambda}{2(n - 1)} \qquad 2$$

where q is the fringe displacement, n is the refractive index of the oxide film. The published values of n for oxide films on silicon are in the range 1.48 - 1.5.

(iii) Wedge Method

The wedge-shaped step in the oxide film was formed by the standard procedure (Figure 4). The non-metallized portion of the sample was examined by a metallurgical microscope equipped with a sodium light source. The third fringe system occurred (Figure 3). The film thickness is given by (1)

$$d = r \frac{\lambda}{2n} \qquad 3$$

where r is the number of fringes within the wedge area. The number of fringes r is counted from the silicon base toward the oxide film. The fractional fringe is estimated from the degree of grayness.

(iv) Multiple-beam Interference Method

The standard method for obtaining multiple-beam fringes is shown in Figure 5. One surface of a glass reference slide was silvered to be approximately 80%

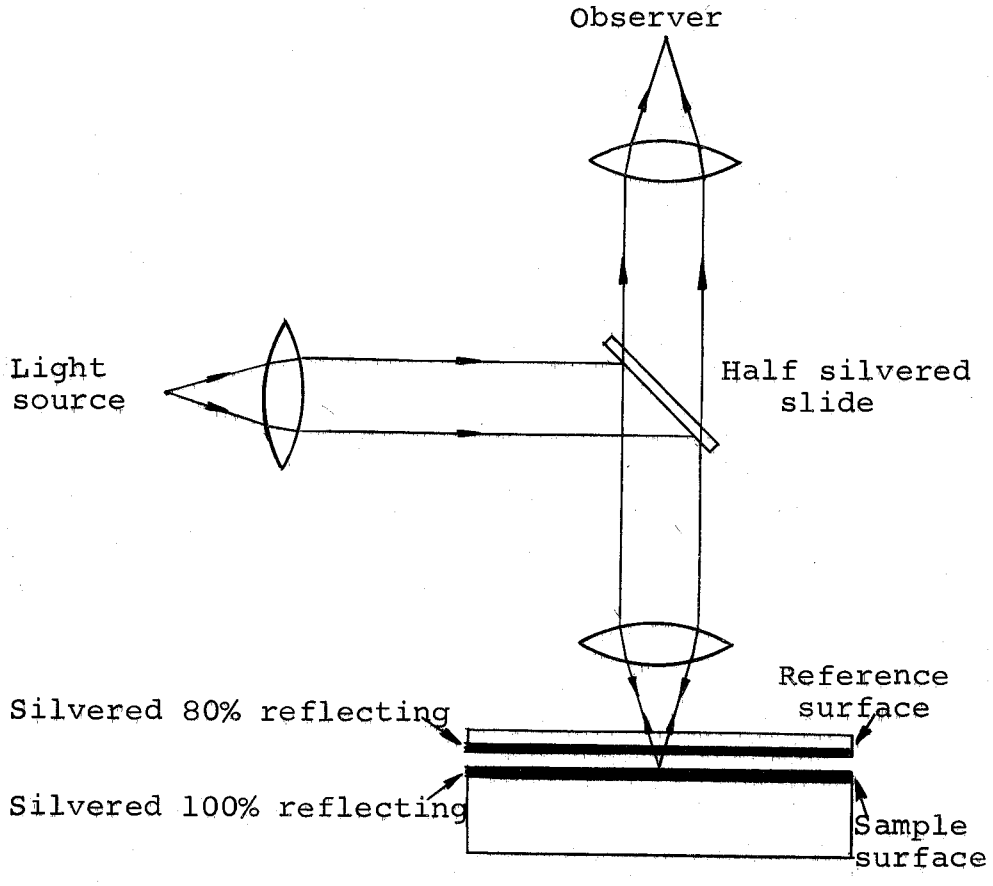

Figure 5. Optical system using a silvered glass slide for forming multiple-beam interference fringes.

reflecting, and the surface of the sample was silvered to be approximately 100% reflecting. The two silvered surfaces were placed close together with the glass slide on top, and the combination was examined with a metallurgical microscope equipped with a sodium light source. Light entering the combination undergoes a series of multiple reflections, giving rise to narrow sharp fringes. The silvered surface of the glass slide acted as a reference plane, and the fringes revealed the irregularities associated with the surface of the sample. The wedge-shaped step in the oxide film was formed by the standard procedure. The film thickness is given by Equation 1.

For the thickness of the oxide films in the range of about 2000 to 12,000 Å, the 95% confidence interval for these four methods was evaluated from a set of six samples by taking five readings from each sample for each method. The 95% confidence intervals of the standard deviation of a normal distribution (2, p. 225) were $148<\sigma<222$ for the two-beam interference method with metallized samples, $210<\sigma<357$ for the two-beam interference method with non-metallized samples, $171<\sigma<296$ for the wedge method, and $71<\sigma<126$ for the multiple-beam method. Hence, the conclusion was drawn that the multiple-beam method is most accurate, and therefore, this method was employed in the present experiment.

THE ETCHING RATES OF SILICON DIOXIDE IN HYDROFLUORIC ACID

Etching Procedure

The etching was carried out in a specially constructed apparatus which provided a close control of the etchant temperature as well as a means for stirring the solution at a constant rate. The etching solution was contained in a 100 milliliter plastic beaker which was held by clamps connected to a motor. Most of the beaker was immersed in a tank of water which was kept at constant temperature. Figure 6 shows a schematic of the apparatus.

Statistical Evaluation

Etching rates in Angstroms-per-minute were calculated from multiple-beam interference measurements. Three readings were taken from each sample. The method of least squares (2, p. 243-246) was employed to estimate the etching rates, and a 95% confidence interval (2, p. 246-252) was established for the etching rates. A sample calculation is shown in Appendix A, Sample Calculations.

The Effect of Impurity Type and Concentration on Etching Rate

Both N-and P-type silicon with resistivities in the range of 0.014 to 200 ohm-cm were oxidized in wet

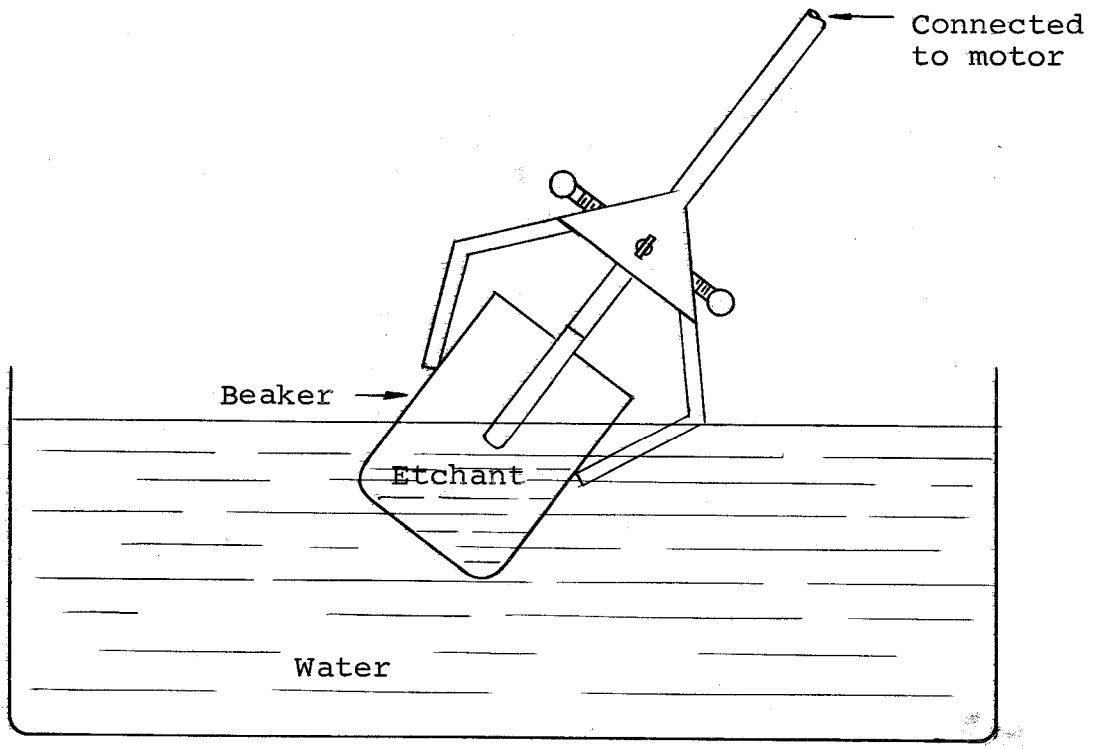

Figure 6. Etching apparatus

oxygen, and then etched in 8% HF at a constant temperature and a stirring rate of 100 rpm. The etching rates were evaluated, and no difference could be detected due to impurity type or concentration over the range studied.

Etching Rates of Silicon Dioxide Grown on Mechanically Polished and Chemically Polished Silicon Surfaces

The mechanically polished and chemically polished silicon wafers were oxidized in wet oxygen, then etched together in 12% HF at a temperature of 25°C and at a stirring rate of 100 rpm. The experimental results indicated no detectable difference in etching rates for the two types of surfaces.

Etching Rate of Silicon Dioxide in Different Concentrations of Hydrofluoric Acid

The rate of silicon dioxide dissolution in hydrofluoric acid was examined for concentrations of hydrofluoric acid ranging from 0% to 48%. Seven sets of silicon samples that had been oxidized in wet oxygen were employed. Each set contained four wafers which had oxide layers of the same thickness. Each set of four wafers was used to test a particular concentration of HF. Wafer #1 of each set was kept as reference; wafers #2, #3 and #4 were individually etched for different lengths of time in 30 milliliters of a particular concentration of HF at a constant temperature of 25°C and at a 100 rpm stirring. The reduced thickness

of oxide layer of each wafer caused by the etching in their respective length of time was calculated, and then the etching rate for each particular concentration was evaluated from each set of samples by the method of least squares. The etching rate was found to increase with the concentration of HF. The curve representing these data (Appendix, Table III) is shown in Figure 7.

The Effect of Temperature on Etching Rate

From a technological standpoint, the temperature dependence of the etching rate of silicon dioxide in HF is most important whenever a high degree of dimensional control must be considered. The effect of the temperature on the etching rate was studied in the range of $0^{o}C$ to $50^{o}C$ in 12% HF.

The experimental procedures were the same as in the study of the etching rates of silicon dioxide in different concentrations of HF, except that in this study the concentration of the etchant was kept constant at 12% HF while the temperature was varied from $0^{o}C$ to $50^{o}C$. The etching rate of the silicon dioxide in HF was found to increase with temperature. A curve of these data (Appendix, Table IV) is shown in Figure 8.

The Effect of the Stirring Speed on Etching Rate

The relationship between the etching rate of a

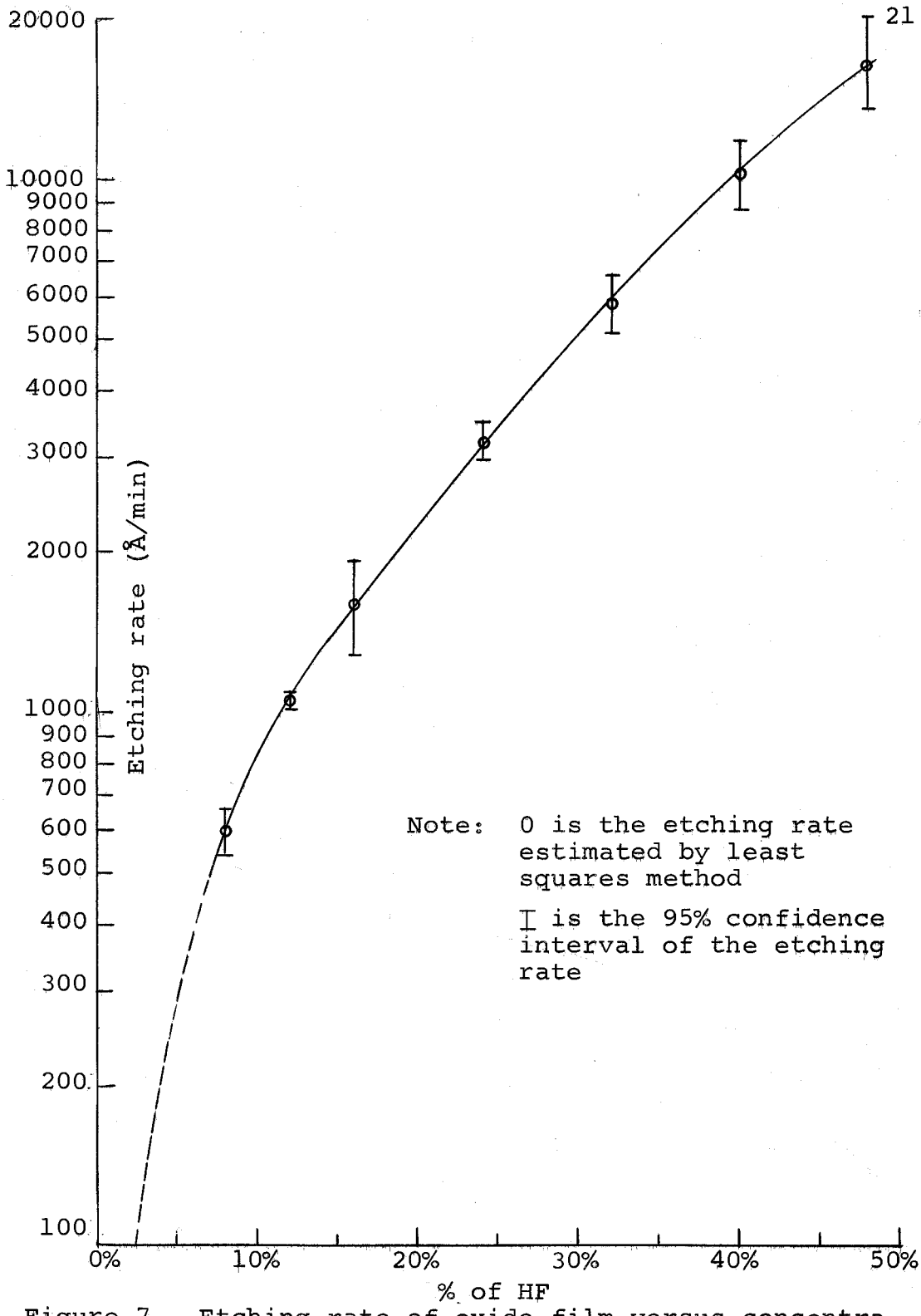

Figure 7. Etching rate of oxide film versus concentration of HF at a temperature of 25°C and at a stirring rate of 100 rpm.

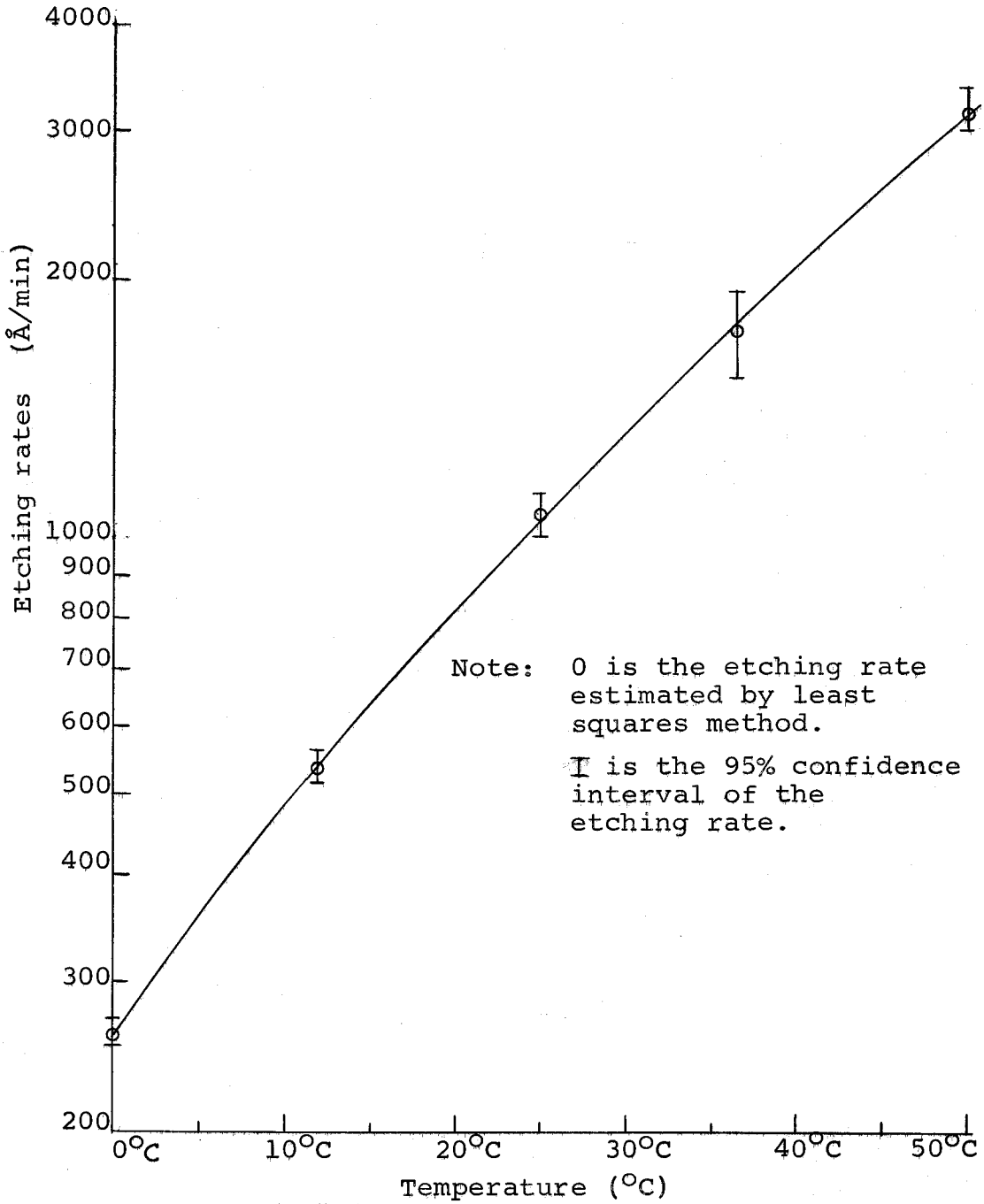

Figure 8. Etching rate versus temperature in 12% HF and at a stirring speed of 100 rpm.

silicon dioxide layer and the rotation speed of the beaker which contained the etchant was examined. The same experimental procedure of studying the etching rates of silicon dioxide in different concentrations of HF was also employed here with the exception that the concentration of etchant was kept constant at 4.8% HF while the rotational speed was varied from 0 rpm to 150 rpm. The curve of the etching rate versus rotation speed is shown in Figure 9. (Appendix, Table V) It was found that the etching rate was slightly increased with rotation speed for the above HF concentration. Further study showed that the dependence of etching rate on rotation speed became smaller when the HF concentration was increased. When the concentration of HF reached 8%, the etching rate dependence on rotation could not be detected.

Comparison of the Etching Rates of Silicon Dioxide Grown in Wet Oxygen, Dry Oxygen and Steam

The etching rate in HF of silicon dioxide prepared in the three different atmospheres, i.e., dry oxygen, wet oxygen and steam, were studied and compared with each other.

The experimental procedure was as follows. Three sets of samples were oxidized with wet oxygen, dry oxygen and steam. Each set contained four wafers with oxide layers of the same thickness. Sample #1 of each

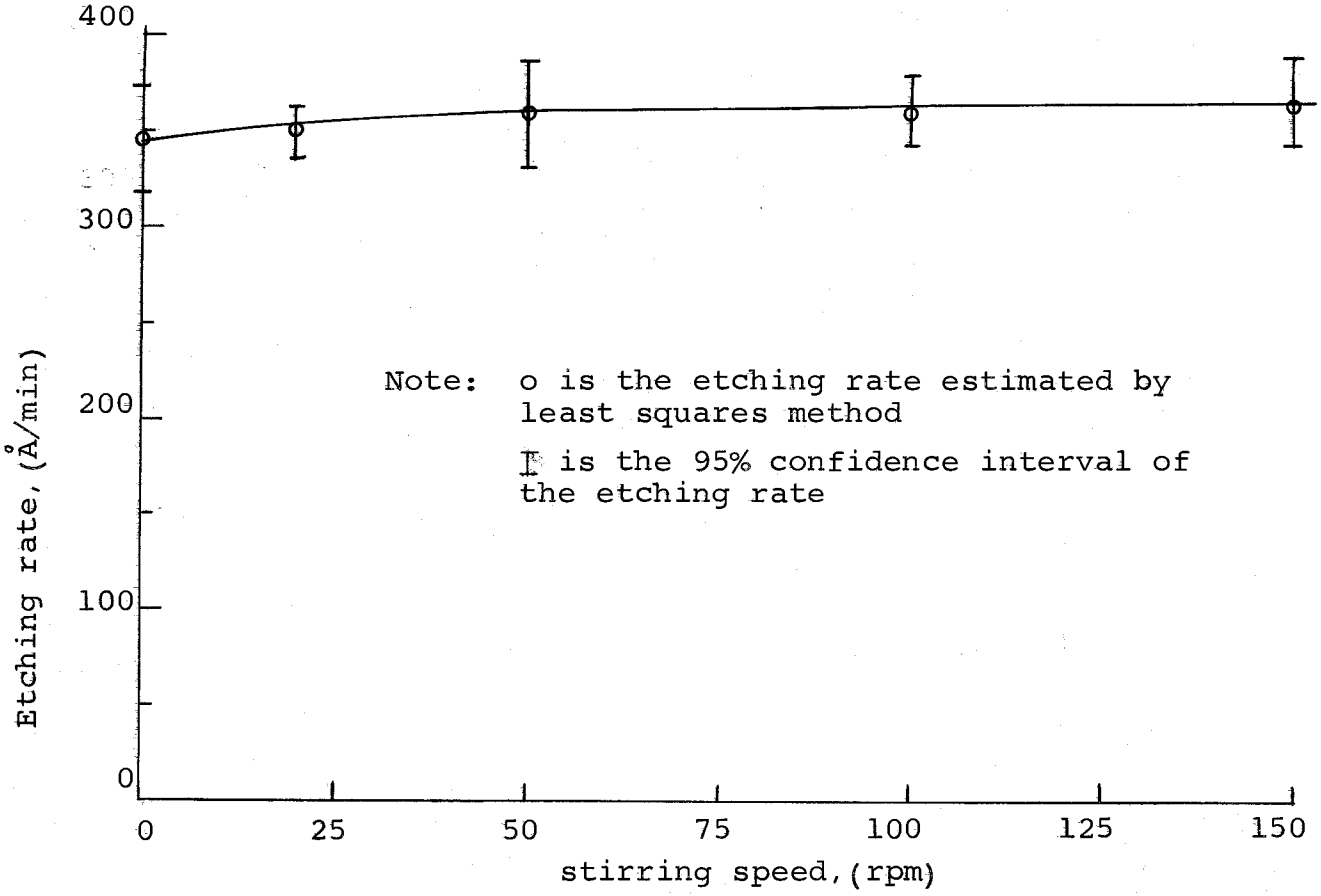

Figure 9. Etching rate versus stirring speed in 4.8% HF at a temperature of 25°C.

set was kept as a reference. The #2 samples of each set were etched together for a definite length of time in 30 milliliters of 12% HF solution at a constant temperature of 25°C and at a stirring rate of 100 rpm. Sample #3 of each set was etched as above but with a different length of time, and so was sample #4 of every set. The etching rates of these three sets were evaluated. The average of these three were very close. (Appendix, Table VI). Therefore, a non-parametric H test (4, p. 194) was used. It was found that 95% of all the three sets of etching rates have the same average.

The Etching Rate of Silicon Dioxide Grown in Wet Nitrogen During the Diffusion of Boron Into Silicon

Boron was diffused into N-type silicon slices having a resistivity of 2.3 ohm-cm in a closed-tube method. (11, p. 274-276) The slices and dopant source (a mixture of 0.1 gram B_2O_3 and 1.0 gram SiO_2) were placed in a quartz tube with a loose-fitting cover. The tube was then placed in an open-tube diffusion furnace with wet nitrogen flowing at a rate of 1.0 liter/min. The nitrogen was first bubbled through distilled water which was held at room temperature, before entering the furnace.

During the diffusion process, an oxide film was grown. The average thickness of the oxide film after nine hours was 5542 Å. Each of these samples was

etched for different lengths of time in 30 milliliters of 8% HF at 25°C and at a stirring rate of 100 rpm. The curve representing these data (Appendix, Table VII) is shown in Figure 10. It was found that the etching rate was the same as oxides grown in dry oxygen, wet oxygen or steam.

The Etching Rate of Silicon Dioxide Grown in Dry Oxygen During the Diffusion of Phosphorus into Silicon

Phosphorus diffusion is performed in a two-step process. (11, p. 271-274) P_2O_5 was used as a source. The schematic diagram of the diffusion system is shown in Figure 11. P-type silicon slices with a resistivity of 1.2 ohm-cm were held at 1150°C, but the P_2O_5 source was at 200°C. The temperature increased gradually between the source and the silicon slices so that material evaporated at the source would not condense on the furnace walls. Dry oxygen was used as a carrier gas, which passed over the source at a rate of 1 liter/min; then passed over the silicon slices and out the exhaust vent.

During the diffusion process, an oxide film was grown. The average thickness of the oxide film after three hours of diffusion was 5876 Å. Each sample was etched for a different length of time in a 30 milliliter of 0.02% HF at a constant temperature of 25°C and at a stirring rate of 100 rpm. A low concentration

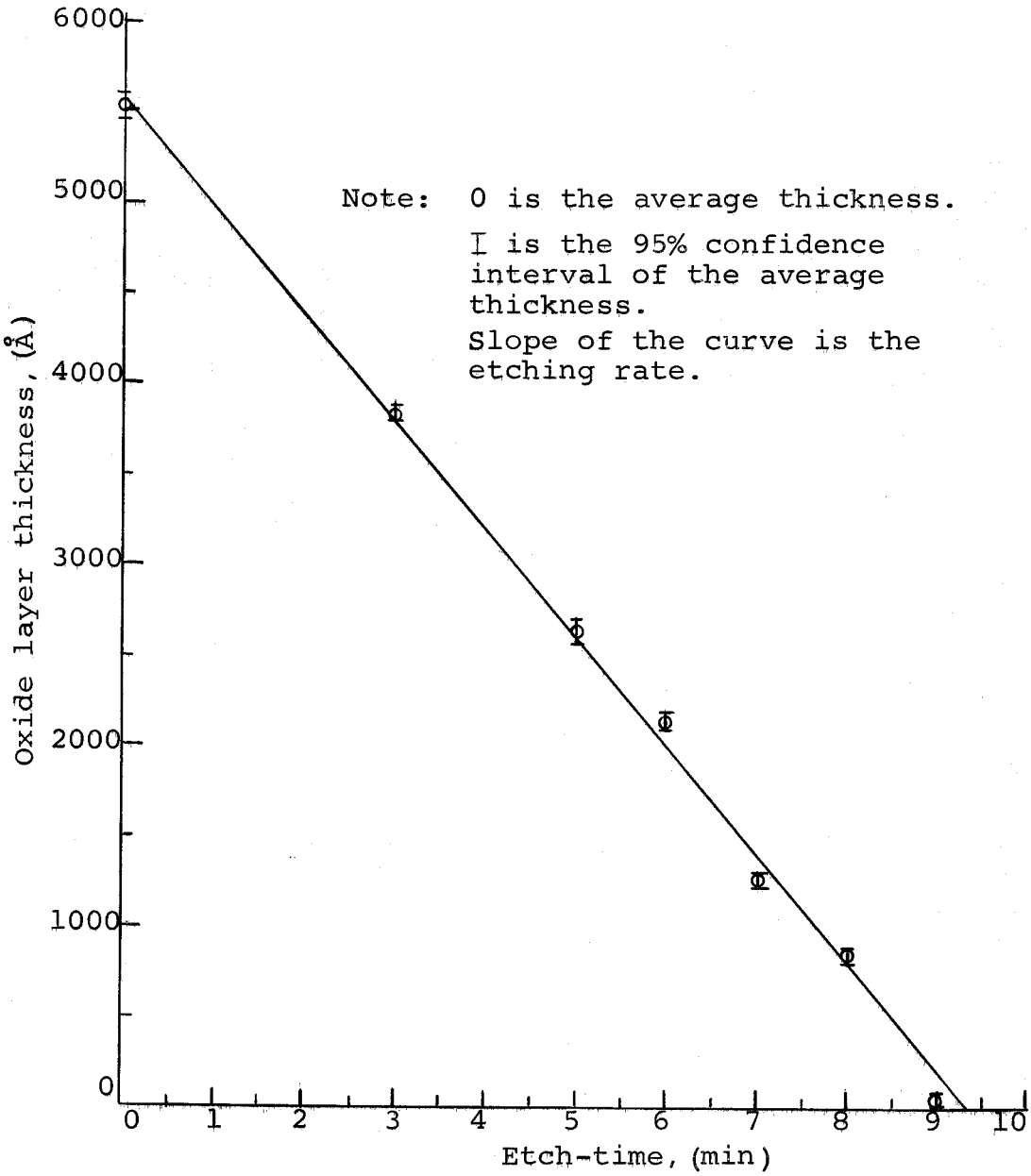

Figure 10. The thickness of oxide layer grown in wet nitrogen during boron diffusion versus etch-time in 8% HF at a temperature of 25°C and at a stirring speed of 100 rpm.

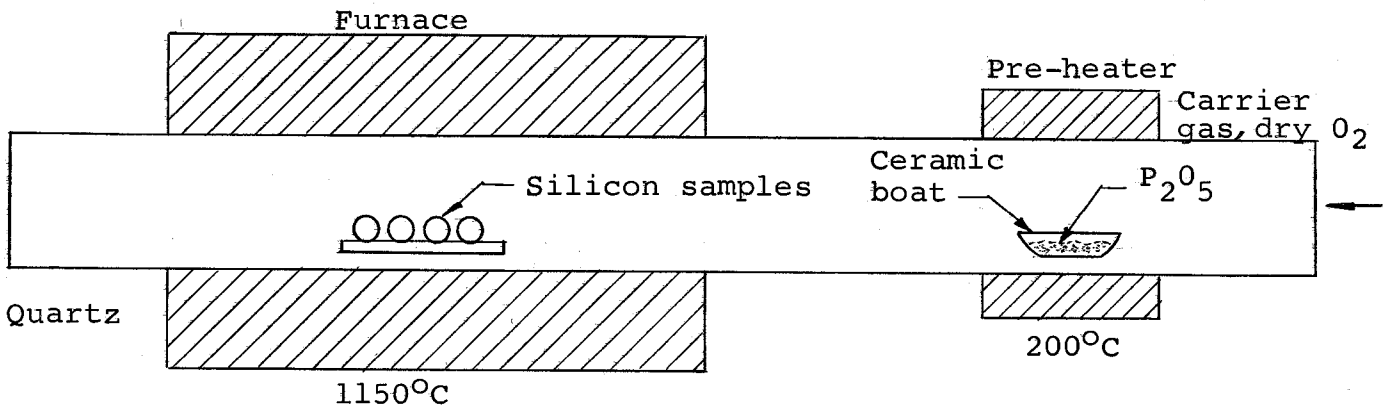

Figure 11. Schematic diagram of phosphorus diffusion system.

solution of HF was used because the etching rate of this oxide was much faster than the oxide grown by any previous oxidation method. The curve representing these data (Appendix, Table VIII) is shown in Figure 12. The slope of the curve is the etching rate. In the first seven minutes, the curve is a straight line which means the etching rate is constant in this region, and then the etching rate slows down.

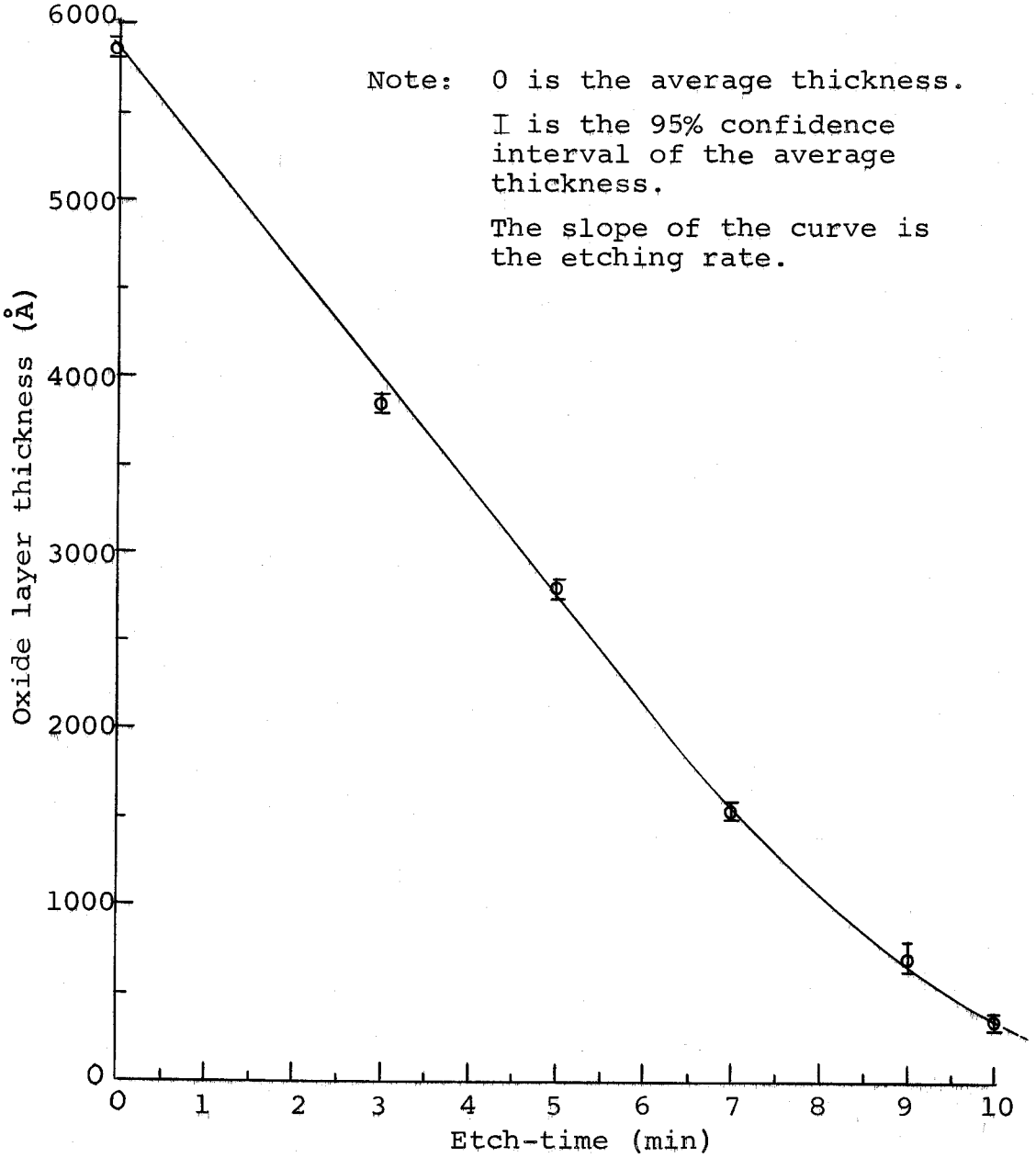

Figure 12. The thickness of oxide layer grown in dry oxygen during phosphorus diffusion versus etch-time, in 0.02% HF at a temperature of 25°C and at a stirring speed of 100 rpm.

SUMMARY AND DISCUSSION

The thermal oxidations were carried out with atmospheres of wet oxygen, dry oxygen and steam at 1150^{o}C. The process has been found to obey a parabolic law over the thickness range studied. The curves of the wet- and dry-oxygen oxidations were straight lines on log-log coordinates, which means the oxidation rates are controlled by the diffusion of one of the reactants through the oxide. (6) In steam oxidation, the oxide initially grows at a slower rate, and the reason for this was tentatively explained on the basis of a reaction between the steam and the oxide to form a volatile component. (5)

Oxidation of silicon was carried out consecutively in wet oxygen, dry oxygen, and steam. It was observed that the first oxidation had no effect on the subsequent oxidations nor did the combination of the first and the second oxidation have any effect on the third.

Both N-and P-type silicon with resistivities in the range of 0.014 ohm-cm to 200 ohm-cm were employed in this experiment. No difference in the rate of oxide growth and the rate of etching of the oxide layer was found due to impurity type or concentration in this resistivity range.

The rate of silicon dioxide dissolution in HF has

been examined in different concentrations of HF ranging from 0% to 48%. The etching rate was found to vary directly with the concentration of HF while the other variables remained constant. Similarly, the effect of the temperature on the etching rate was studied in the range of $0^{o}C$ to $50^{o}C$. The plotted curve (Figure 7) shows that the etching rate increased with temperature. By the same manner, the relationship between the etching rate of the oxide layer and the stirring speed was examined. It was found that the etching rate increased slightly with rotational speed for a 4.8% HF concentration. Further study in higher concentrations of HF showed that the dependence of etching rate on rotation vanished. The rate at which silicon dioxide is removed will be dependent on the rate of arrival of HF species at the silicon dioxide surface. (12) If the HF species are consumed immediately at the surface of the sample by this reaction

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

the surface concentration of HF will become zero. Therefore, increasing the rotation speed will increase the rate at which the HF arrives at the slice surface. With HF concentrations above 8%, apparently there is enough HF species in the vicinity of the slice so they will quickly reach the surface of the slice, even without rotation. This explains why the etching rate does not

depend upon rotation speed when the concentration of HF is increased.

The etching rates in HF of silicon dioxide prepared in atmospheres of dry oxygen, wet oxygen, and steam were studied and compared. The calculations indicate that 95% of all the measurements of the three etching rates have the same average. Also, the etching rates of oxide layers grown during diffusion of boron and phosphorus into silicon were studied. The etching rate of the oxide grown during boron diffusion was found to be the same as the oxides grown in wet oxygen, dry oxygen and steam. However, the oxide grown during phosphorus diffusion had a much faster etching rate.

This experiment indicates that the arrangement of apparatus, the temperature, the concentration of etchant, and the stirring speed affect the etching rate. Therefore, these factors must be taken into account when precise dimensional control in the etching of silicon dioxide is desired.

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APPENDIX

Oxidation Time	Wet Oxygen			Dry Oxygen			Steam		
	Oxide Thickness (Å)	Ave. Oxide Thickness (Å)	95% Confidence Interval Limit (Å)	Oxide Thickness (Å)	Ave. Oxide Thickness (Å)	95% Confidence Interval Limit (Å)	Oxide Thickness (Å)	Ave. Oxide Thickness (Å)	95% Confidence Interval Limit (Å)
6 min	654 673 660	662	±13	624 615 630	623	±10	2268 2290 2235	2264	±28
15 min	1143 1149 1138	1143	± 7.5	965 980 960	968	±14	3946 3910 3970	3942	±30
30 min	1561 1583 1565	1570	±16	1428 1415 1433	1425	±13	5889 5900 5860	5883	±21
1 hr	2362 2389 2340	2364	±36	1973 1985 1970	1976	±11	8200 8231 8257	8229	±29
3 hrs	4153 4100 4120	4123	±37	3378 3340 3390	3369	±36	14180 14130 14000	14160	±151
6 hrs	5977 5930 5990	5967	±42	4727 4700 4770	4732	±48	20616 20590 20660	20622	±35
10 hrs	7922 7990 7963	7958	±47	6185 6120 6200	6168	±58	24738 24980 23990	24569	±511

TABLE I. Oxide thickness versus oxidation time at 1150°C with various sources.

TABLE II. Sequential oxidations with the same samples in wet oxygen, dry oxygen and steam at 1150°C.

Oxidation Method	Oxidation Time	Oxide Thickness (Å)	Average Oxide Thickness (Å)	95% Confidence Interval Limit (Å)
Wet Oxygen	6 min	654 670 660	662	± 13
	15 min	1143 1149 1138	1143	± 7.5
	30 min	1561 1583 1565	1570	± 16
	1 hr	2362 2389 2340	2364	± 34
	3 hrs	4153 4100 4120	4123	± 37
Dry Oxygen	4 hrs	4668 4600 4670	4646	± 55
	5 hrs	5051 5110 5032	5061	± 56
	6 hrs	5434 5390 5540	5455	± 42
Steam	7 hrs	9939 9870 9940	9916	± 55
	8 hrs	12664 12100 12250	12338	±394
	9 hrs	14850 14996 14630	14825	±248
	10 hrs	17376 17000 17600	17325	±435

TABLE III. Etching rate of oxide film versus concentration of HF at a temperature of 25°C and at a stirring speed of 100 rpm.

Set No.	Sample No.	% of HF	Etch Time (min)	Remain. Thickness (Å)	Etching Rate (Å/min)	95% Confidence Interval Limit (Å)
1	1	8	0	8894 8835		
	2	8	5	5919 5890		
	3	8	10	2886 2945		
	4	8	13.5	765 736	600	± 61
2	1	12	0	11368 11515		
	2	12	3	8334 8452		
	3	12	6	5124 4977		
	4	12	9	2003 1914	1060	± 26
3	1	16	0	11368 11515		
	2	16	2	7657 7922		
	3	16	4	4211 4476		
	4	16	6	1855 1826	1612	±333
4	1	24	0	11368 11515		
	2	24	1	8246 8423		
	3	24	2	4889 4711		
	4	24	3	1814 1767	3249	±269

TABLE III. (Continued)

Set No.	Sample No.	% of HF	Etch Time (min)	Remain. Thickness (Å)	Etching Rate (Å/min)	95% Confidence Interval Limit (Å)
5	1	32	0	11368 11515		
	2	32	0.5	8482 8540		
	3	32	1.0	5301 5183		
	4	32	1.5	2680 2739	5893	± 695
6	1	40	0	11338 10897		
	2	40	10 sec	9218 9453		
	3	40	20 sec	7333 7657		
	4	40	40 sec	4241 4241	10314	±1608
7	1	48	0	11515 11368		
	2	48	10 sec	8452 8511		
	3	48	20 sec	5360 5272		
	4	48	30 sec	3181 3210	16742	±3228

TABLE IV. Etching rate of silicon dioxide versus temperature in 12% HF and at a stirring speed of 100 rpm.

Set No.	Sample No.	Temperature (°C)	Etch Time (min)	Remain. Thick-ness (Å)	Etching Rate (Å/min)	95% Confi-dence Interval Limit (Å)
1	1	0°	0	11368 11515		
	2	0°	4	10013 10013		
	3	0°	8	9130 9130		
	4	0°	12	8069 8423	262	± 9.4
2	1	12°	0	11368 11515		
	2	12°	4	9218 9336		
	3	12°	8	7100 7150		
	4	12°	12	5013 4948	538	± 24
3	1	25°	0	11368 11515		
	2	25°	3	8334 8452		
	3	25°	6	5124 4977		
	4	25°	9	2003 1914	1060	± 64
4	1	36.5°	0	11368 11515		
	2	36.5°	3	6037 6067		
	3	36.5°	4.5	3622 3622		
	4	36.5°	6	942 854	1750	±215

TABLE IV. (Continued)

Set No.	Sample No.	Temperature (°C)	Etch Time (min)	Remain. Thick-ness(Å)	Etching Rate (Å/min)	95% Confi-dence Interval Limit (Å)
5	1	50°	0	11368 11515		
	2	50°	1	8482 8305		
	3	50°	2	5183 4918		
	4	50°	3	1973 1914	3184	±190

TABLE V. Etching rate of silicon dioxide versus stirring speed in 4.8% HF and at a temperature of 25°C.

Set No.	Sample No.	Stirring Speed (rpm)	Etch Time (min)	Remain. Thickness (Å)	Etching Rate (Å/min)	95% Confidence Interval Limit (Å)
1	1	0	0	11780 11780		
	2	0	10	8452 8393		
	3	0	15	6567 6479		
	4	0	20	4800 4918	347.7	±28
2	1	20	0	11780 11780		
	2	20	10	8305 8246		
	3	20	15	6479 6479		
	4	20	20	4712 4889	350	±14
3	1	50	0	11780 11780		
	2	50	10	8040 8069		
	3	50	15	6332 6322		
	4	50	20	4712 4416	360.7	±29
4	1	100	0	11780 11780		
	2	100	10	8158 8099		
	3	100	15	6332 6272		
	4	100	20	4565 4565	361.6	±17

TABLE V. (Continued)

Set No.	Sample No.	Stirring Speed (rpm)	Etch Time (min)	Remain. Thick-ness (Å)	Etching Rate (Å/min)	95% Confi-dence Interval Limit (Å)
5	1	150	0	11780 11780		
	2	150	10	8069 8128		
	3	150	15	6214 6273		
	4	150	20	4506 4565	363.6	±25

TABLE VI. Etching rates of silicon dioxide prepared in wet oxygen, dry oxygen and steam oxidations; in the etchant of 12% HF, at the temperature of 25°c and at the stirring speed of 100 rpm.

Set No.	Sample No.	Oxidation Method	Etch Time (min)	Remain. Thickness (Å)	Etching Rate (Å/min)	Average Etching Rate (Å/min)	Standard Deviation (Å)
1	1	Wet	0	11780			
	2	Oxygen	3	8541	1080		
	3		6	5360	1070		
	4		9	2179	1067	1072	± 6.8
2	1	Dry	0	11486			
	2	Oxygen	3	8393	1031		
	3		6	5007	1080		
	4		9	1944	1060	1057	±24.6
3	1	Steam	0	11780			
	2		3	8541	1080		
	3		6	5567	1036		
	4		9	2548	1026	1047	±28.7

TABLE VII. Etching of oxide layer grown in wet nitrogen during boron diffusion in 8% HF at 25°C and 100 rpm.

Sample No.	Etch Time (min)	Remain. Thickness (Å)	Average Remain. Thickness (Å)	95% Confidence Interval Limit of the Average Thickness (Å)
1	0	5500 5595 5530	5542	± 66
2	3	3810 3843 3860	3838	± 35
3	5	2620 2680 2690	2646	± 59
4	6	2120 2165 2170	2152	± 38
5	7	1260 1281 1293	1278	± 23
6	8	846 854 866	855	± 14
7	9	28 30 32	30	± 3

Note: average etching rate = 591 Å/min

TABLE VIII. Etching of oxide layer grown by dry oxygen during phosphorus diffusion in 0.02% HF at 25°C and 100 rpm.

Sample No.	Etch Time (min)	Remain. Thickness (Å)	Average Remain. Thickness (Å)	95% Confidence Interval Limit (Å)
1	0	5840 5889 5899	5876	± 43
2	3	3878 3843 3830	3850	±34
3	5	2800 2798 2816	2804	±24
4	7	1585 1570 1550	1572	±25
5	9	780 650 680	703	±91
6	10	365 359 340	355	±17

Note: Average etching rate for the first seven minutes = 635 Å/min

Sample Calculations

1. The method of least squares (2, p. 243-246) was used to estimate the etching rate of silicon dioxide in 8% HF. (Set No. 1, Table III)

$$b = \frac{\sum X_i Y_i - n \bar{X} \bar{Y}}{\sum X_i^2 - n \bar{X}^2} \quad \text{(2, p. 252)}$$

where b = estimated etching rate
X_i = etching time
Y_i = remaining thickness of oxide
$\bar{X}$ = average of X's
$\bar{Y}$ = average of Y's
n = total number of observations in this set of samples

$$b = \frac{137{,}619 - 8\left(\frac{57}{8}\right)\left(\frac{3687 0}{8}\right)}{614 - 8\left(\frac{57}{8}\right)\left(\frac{57}{8}\right)}$$

$$= 599.9 \cong 600 \text{ Å/min}$$

2. Calculation of the 95% confidence interval for the etching rate.

Confidence interval for b is (2, p. 252)

$$b \pm [t_{(\alpha/2);\gamma}]\, s_b$$

where t is the student's distribution
γ is the degree of freedom
for 95% confidence

$t_{(0.025);7} = 2.365$ (2, p. 55 8)
s_b is the standard deviation of b

Therefore the 95% confidence interval for the estimated etching rate is

$$600 \pm 61$$