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ISOLATION OF COMPONENTS ON A SILICON WAFER USING SiO_2

by Glenn W. Skouson

Prepared by
WESTINGHOUSE DEFENSE AND SPACE CENTER
Baltimore, Md.
for Goddard Space Flight Center

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ABSTRACT

A feasible method of isolating components on a silicon wafer has been developed which circumvents undesirable parasitic capacitance resulting from standard p-n junctions electrical isolation techniques. The end product is a wafer composed of a polycrystalline substrate and a layer of single crystalline islands isolated from the substrate and each other by a thin layer of SiO_2. Experiments in the vital groove cutting operation using both standard wet chemical and new high temperature HCl etching methods indicate that pending refinements in the latter process, the wet chemical method is preferable. The determining factor is the groove depth limitations of the high temperature process which restricts the thickness of the useful single crystalline n-layer. A series of experiments in depositing silicon dioxide and polycrystalline silicon into etched silicon grooves indicates that silicon dioxide deposited by the reaction of $CO_2 + SiCl_4$ in the presence of hydrogen is useful as a dielectric and that successful polycrystalline growth can be accomplished.

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ISOLATION OF COMPONENTS ON A SILICON WAFER USING SiO_2*

by
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Aerospace Division

INTRODUCTION

A method of isolating components on a silicon wafer is discussed briefly which circumvents undesirable parasitic capacitance resulting from standard p-n junction electrical isolation techniques. (The capacitance limits the use of functional electronic blocks for high frequency applications.) The end product is a wafer composed of a polycrystalline substrate and a layer of single crystalline islands isolated from the substrate and each other by a thin layer of SiO_2. Specific step-by-step instructions for the various operations involved are given in Appendix A. Data on a series of experiments in the vital groove cutting operation are presented in Appendix B. In this series of experiments, adjacent operations were successfully coupled to avoid handling the slices, thus reducing the contamination problem inherent in most wafer or slice handling techniques.

GENERAL PROCESS

Outlined below are the various steps in isolating components on a silicon wafer by groove etching and silicon dioxide deposition.

1. Slice Preparation

The silicon material used is processed by standard lapping and polishing techniques. The slices are lapped (both sides) on a Dallons Planetary Lapper with 12μ grit size Al_2O_3 to remove damage from the prior slicing operation. They are then mounted on stainless steel holders and lapped with 3μ grit Al_2O_3 to give a smoother surface. Following this a 1μ grit compound is used for the final polishing operation. After the slices are taken from the work holders, residual preparation materials are removed from the slices by using solvents and high temperature H_2SO_4 cleaning baths followed by de-ionized water rinses. Slices are swabbed with trichloroethylene (TCE) immediately prior to loading into the epitaxial reactor.

*Prepared under Contract NAS 5-3758.

2. Conduction Epitaxial Layer

The cleaned slices of silicon are placed in the epitaxial reactor on a quartz protective envelope covering a graphite susceptor. After proper purging with nitrogen and then hydrogen, the slices are heated to 1200°C and exposed to a mixture of anhydrous HCl in H_2 for a time sufficient to remove all residual surface damage caused by material polishing operations through the following reaction:

$$4\ HCl_{(g)} + Si_{(s)} \rightleftharpoons SiCl_{4(g)} + 2\ H_{2(g)}$$

Then the slices receive a deposition (about 10 microns thick) of n-type silicon by passing a mixture of $SiCl_4$ and H_2 at 1150°C through the reactor, resulting in the reaction:

$$SiCl_{4(g)} + 2\ H_{2(g)} \rightleftharpoons 4\ HCl_{(g)} + Si_{(s)}$$

3. Deposition of First Oxide and Polycrystalline Layers

After the required thickness of silicon is deposited, CO_2 is introduced into the reactor to deposit a layer of silicon dioxide through the reaction:

$$2\ H_{2(g)} + SiCl_{4(g)} + 2\ CO_{2(g)} \longrightarrow 2\ CO_{(g)} + SiO_{2(s)} + 4\ HCl_{(g)}$$

Following this, a layer of polycrystalline silicon is deposited on the surface at an accelerated rate. Figure 1 illustrates a cross section of the silicon wafer after the deposition of the first epitaxial, oxide and polycrystalline layers.

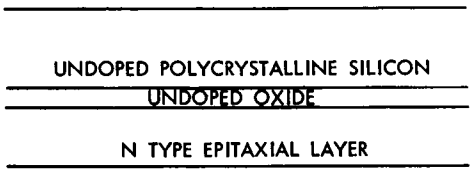


Figure 1—First epitaxial operation. (a) After vapor etching the p-type substrate on n-type epitaxial layer is deposited. (b) Over this an undoped layer of silicon dioxide is deposited. This in turn is covered with (c) a layer of polycrystalline material to be used for mechanical stability during subsequent handling.

4. Removal of Original Substrate Material

The slices are now ready for removal of the original substrate material. Two methods have been used: (1) electrochemical etching and (2) the standard lapping–polishing techniques originally used to prepare the slices. To date the best results are obtained from the lapping-polishing method. Care must be taken to lap the surface of the polycrystalline layer to remove all spurious growth. This insures a more nearly perfect parallelism between the original epitaxial layer and the lapping plate to which the slices must be

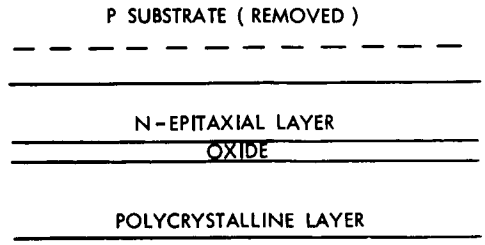


Figure 2—Lapping-polishing operation to remove p-type substrate (slice has been inverted).

mounted for subsequent lapping-polishing operations. The slices are then lapped and polished by standard material preparation mechanical methods. Final polishing is completed when the original substrate material has been removed (Figure 2).

5. Masking

For the second epitaxial operation, the slices are again loaded into the reactor and a layer of silicon dioxide is deposited on the epitaxial layer exposed by the removal of the original substrate material (Figure 3) in the same manner as in step 4. The wafers are removed and windows are cut through the oxide by standard photoengraving techniques (Figure 4) thus exposing the n-layer of silicon through which grooves will be etched.

6. Grooving

Grooves are etched completely through the n-type layer by a 4% concentration of anhydrous HCl at 1200°C or by a wet chemical etch as has been used in many standard processes (Figure 5a).

7. Deposition of Third Oxide and Second Polycrystalline Layer

While yet in the reactor a third layer of silicon dioxide is deposited (Figure 5b) which laterally isolates individual areas from each other. Immediately, a layer of polycrystalline

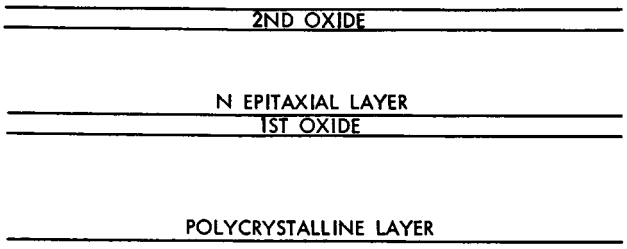


Figure 3—Second epitaxial operation.

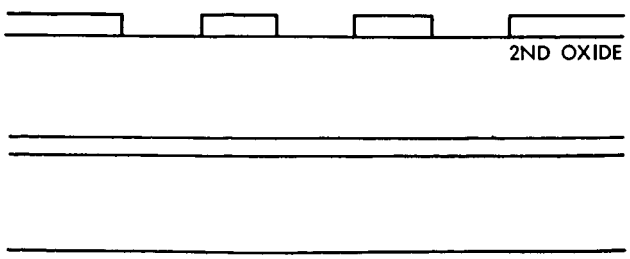


Figure 4—Windows cut through second oxide by standard photoresist methods.

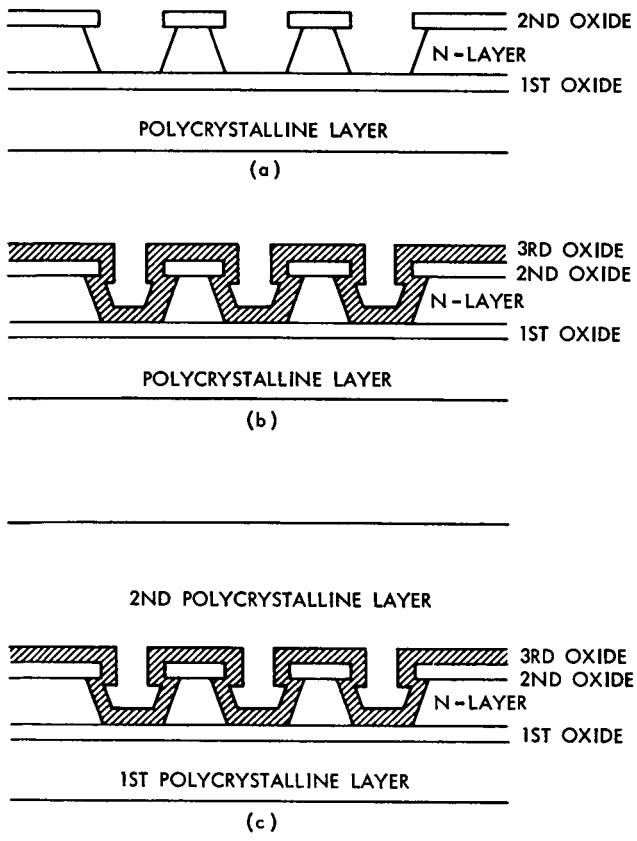
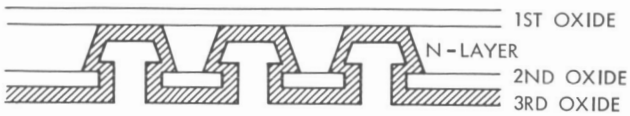


Figure 5—Third epitaxial operation. (a) Grooves are etched through silicon to first oxide layer. (b) Third or isolation oxide is deposited. (c) Second polycrystalline silicon layer is deposited.

silicon is deposited (Figure 5c) which becomes the substrate for the slice during subsequent device manufacturing operations.

8. Removal of Original Polycrystalline Layer

The wafer is taken out of the reactor and the original polycrystalline layer is then removed by etching thus exposing the silicon dioxide protective coating over the islands of n-type single-crystal silicon of the original epitaxial layer. (Figures 6 and 7). Figures 8 and 9 show the silicon n-type single crystalline layer sandwiched between layers of silicon dioxide. Figure 10 shows the lateral isolation oxide barrier deposited at the periphery of the "island."



2ND POLYCRYSTALLINE LAYER

Figure 6—Final isolation diagram (slice re-inverted)—showing silicon islands isolated by oxide barrier after first polycrystalline silicon layer is removed by etching.

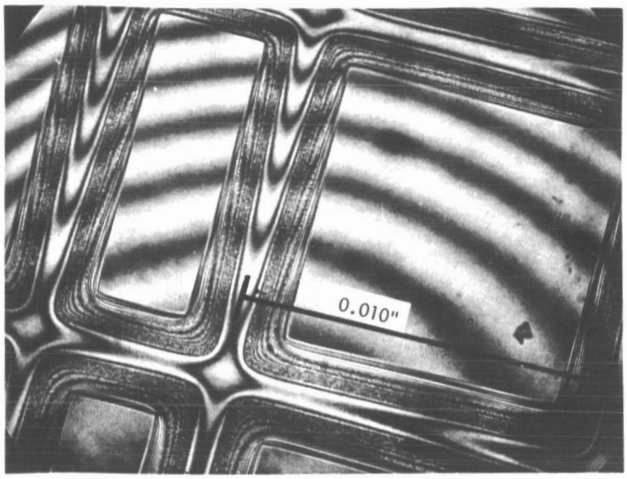


Figure 7—Photomicrograph of isolated island surrounded by oxide barrier and polycrystalline silicon.

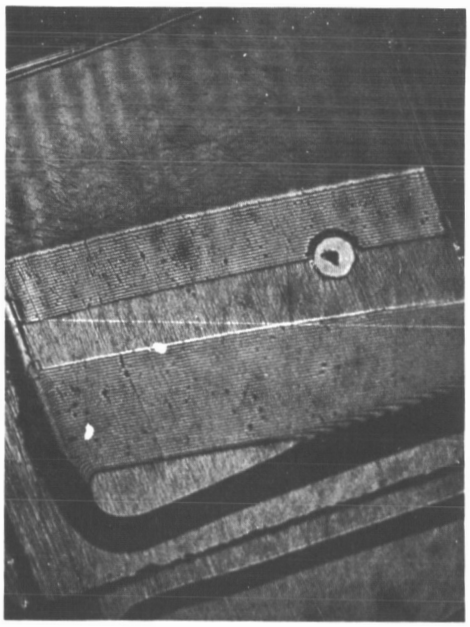


Figure 8—n-type single crystalline silicon layer sandwiched between layers of silicon dioxide.

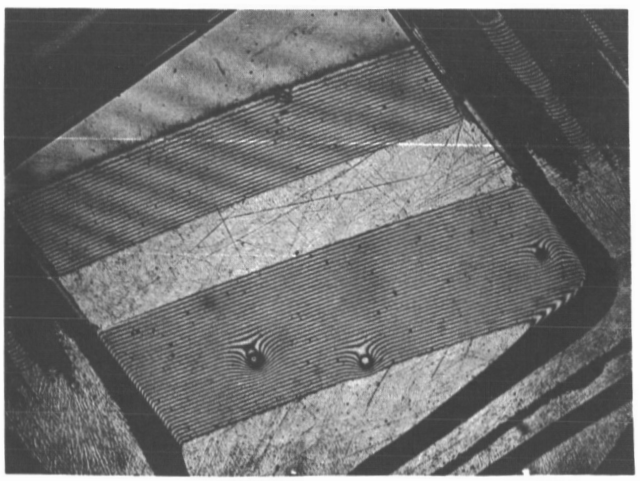


Figure 9—Silicon sandwiched between oxide layers.

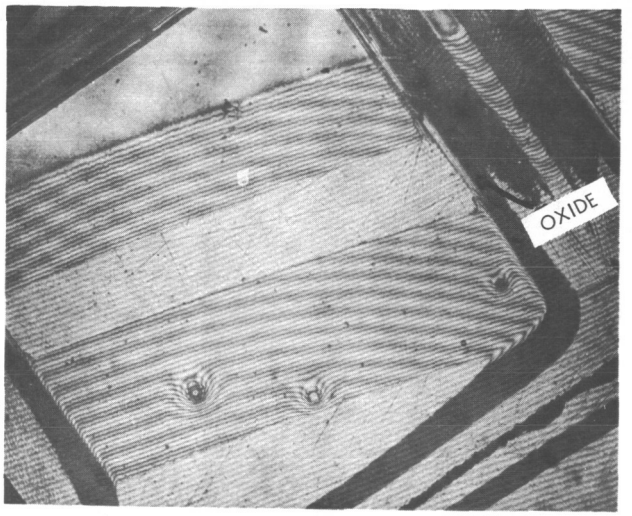


Figure 10—Oxide barrier at periphery of island.

PROCEDURAL DETAILS AND DISCUSSION

This section will discuss in more detail the procedures followed in some of the steps enumerated above.

High Temperature HCl Etching Process

After preparation of the slices in the manner described in steps 1 through 6, the slices were processed by standard photoetching methods to open windows through the oxide. The two mask series used (138 and 141) were prepared with the geometry shown in Figures 11a, b, and c.

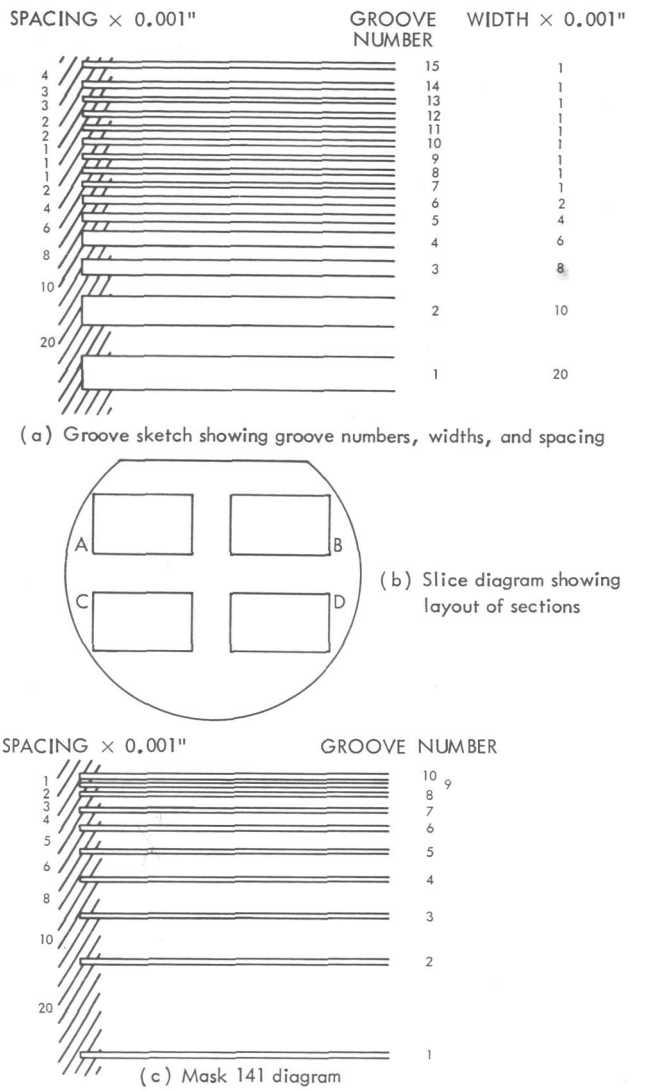


Figure 11—(a) Groove sketch showing groove numbers, widths, and spacing (mask 138). (b) Mask 141 diagram. (c) Slice diagram showing layout of sections.

The slices were given a clean-up, placed on a quartz envelope over a graphite susceptor and then placed into the epitaxial reactor tube. After purging properly, the slices were heated in a H_2 ambient to the desired temperature. HCl was metered into the gas train and controlled to approximately a 4% concentration for the desired etch time.

Temperature was controlled manually and measured by a Leeds and Northrup (Catalog No. 8622-C) optical pyrometer. Measurements of groove depths were then made on each groove or series of grooves on a slice and data was recorded.

Variations of concentrations of etchant and flow rates were studied, and typical thermal gradient and temperature profiles were made using the L & N optical pyrometer. (All pyrometer readings are uncorrected.)

Groove depth measurements as well as junction depth measurements were made by the standard angle lapping—staining techniques. A mercury vapor light with adequate filters supplied the proper light. The measured interference fringes were used as the unit of depth in all tests (one fringe = 0.273 microns).

Findings on High Temperature Process

From the series of experiments with the high temperature HCl process referred to in the introduction and presented in Appendix B, the following findings have been derived.

1. General

Groove etching of silicon wafers by a high temperature (1200°C) mixture of about 4% HCl in H_2 is feasible. It is a useful method of providing contaminant-free material for investigation of isolation techniques. The depths of grooves etched in silicon through protective masks of silicon dioxide can be controlled by the groove width and the spacing between grooves. The high temperature gaseous etchant mixture (HCl in H_2) has wide latitude of composition and flow rate. The flow rates and compositions for the clean-up etch used in standard epitaxial processes are convenient and adequate, if not optimum, for groove etching.

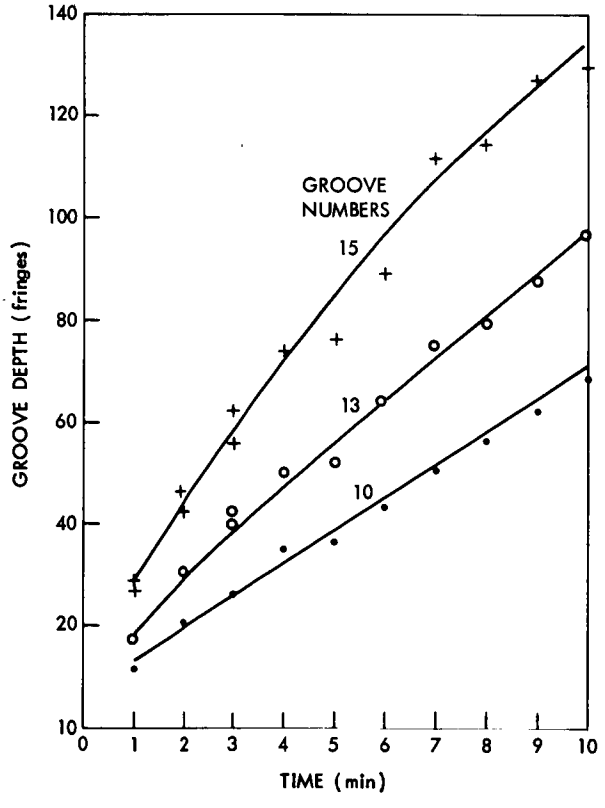


Figure 12—Groove depth vs. time (composite).

2. Etch Rate

The etch rate in any given groove is approximately linear with time (Figure 12). However, there is some deviation from linearity as the etch time increases. This may be explained by the postulated mechanism of etching (see "Mechanism of Etching," Appendix B) and the probable temperature gradient from the top to the bottom of the slice.

3. Geometry Dependence

There is some correlation of the width of the groove to the depth of the groove (i.e., the narrower the window in the mask, the deeper the groove); however, there is a great correlation of the masked spaces between grooves and the groove depth and for uniform width windows, the depth of etched grooves will vary as the spacing.

The curved bottoms of wide grooves is attributed to a heat transfer and insulation mechanism as explained previously. There is no detectable dependency on the gas flow direction. However, crystal orientation may play a part in the appearance of the ends of the grooves, e. g., the flat at the bottom of a groove end is parallel to the growth flat on the edge of a mis-oriented slice. This points out the advisability of designating the top and the bottom of the slices by orientation marks on the ingot prior to the slicing operation.

Some similarities of characteristics in all wide groove experiments (mask 138) are (1) the wider the spacing between grooves the deeper the edges of the grooves; (2) the nearer edges of adjacent wide grooves are of comparable depth, while opposite edges of these adjacent grooves show large differences. These edge depth differences are dependent upon the extent of the adjacent spacing (Figure 13).

4. Emissivity Effects

It is felt that if the emissivity of silicon plays any part in controlling the etching processes, it is so small as to be overshadowed by other characteristics such as the chemical kinetics of the etching reaction. Although they are not necessarily conclusive, these experiments indicated that any effect of emissivity on etching is minimal.

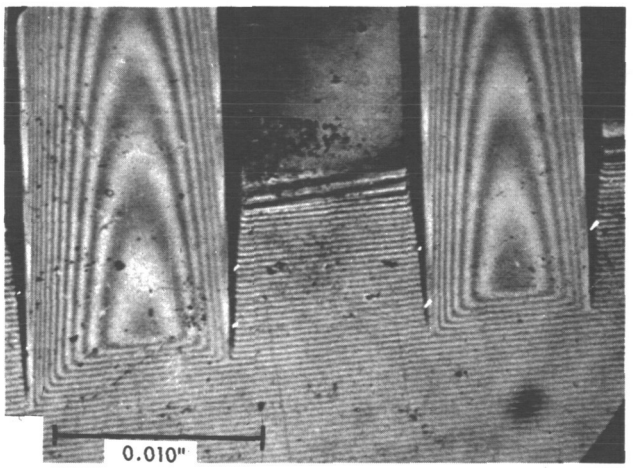


Figure 13—Curved bottoms of wide grooves.

5. Recommendations

Care must be taken in mask preparation to avoid undesirable interactions of adjacent grooves. Variations in groove depth is more noticeable at the intersection of wider grooves. Narrow grooves are recommended for isolation processes involving etching techniques.

6. Limitations of High Temperature HCl Process

An inherent disadvantage of the high temperature HCl etch process is that groove depth and consequently the thickness of the useful single crystalline silicon layer (through which for isolation purposes the grooves must be completely etched) is quite limited. This is because etch depth, being time-dependent, is limited by the gradual deterioration of the oxide mask in contact with anhydrous HCl at 1200°C.

Wet Chemical Etch

An alternative method not subject to the n-layer thickness limitations of the high temperature process is the wet chemical etch used in many standard processes. Since the resulting slices with

a thicker n-layer (Figure 14) have wider semiconductor application, the wet chemical process will probably be more useful until refinements in the high temperature etch are developed. There is one drawback, however, to the wet chemical process—it leaves a groove which widens at the top, resulting in some loss of useful area at the surface of the slice (Figure 15).

In the wet chemical process, after the second epitaxially (thermally) deposited layer of silicon dioxide has had windows opened, the exposed silicon is etched with a mixture of HNO_3:HF:HAc (in the ratio of 84:8:8). This cuts away silicon in the open window through to the original thermally deposited oxide. Subsequently, the overhang of the silicon on the islands is removed by HF. Thereafter, the operations proceed exactly as stated above, i.e., the slice is subjected to a deposit of silicon dioxide by the $CO_2 + SiCl_4 + H_2$ method, which is then covered by polycrystalline silicon.

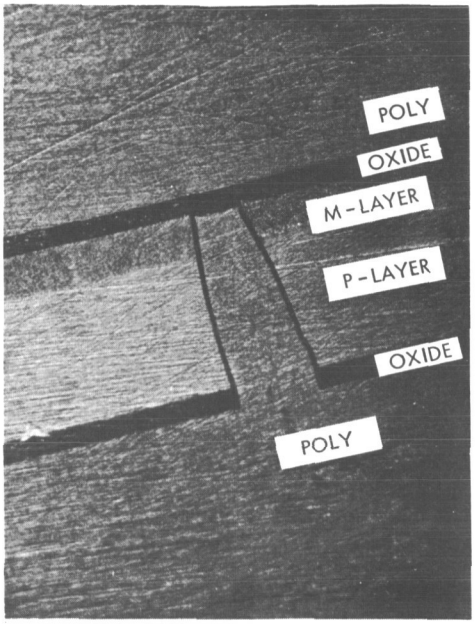


Figure 14—Photo showing island lateral isolation oxide barrier as well as sandwiched single crystalline silicon between top and bottom polycrystalline and oxide layers (wet chemical process).

Deposition of Oxide and Polycrystalline Layers over Grooves

A series of experiments was made to ascertain growth parameters of silicon oxide and polycrystalline material on slices of silicon. It was found that silicon dioxide deposited by the reaction of $CO_2 + SiCl_4$ in the presence of hydrogen was useful as a dielectric.

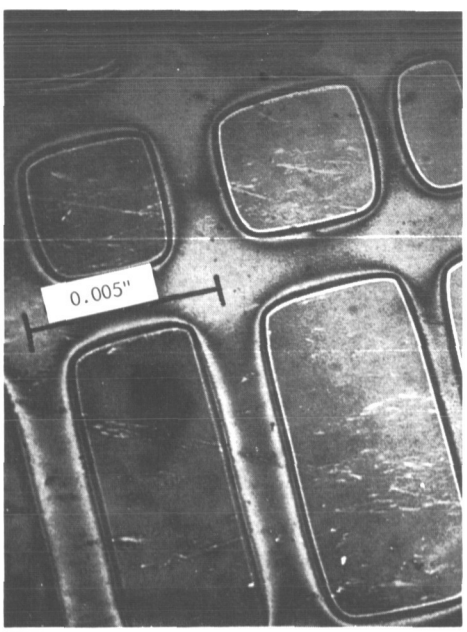


Figure 15—Top surface of wet chemical process slice.

Initial experiments indicated that subsequent silicon deposition was inhibited by lack of nucleation sites on the freshly deposited oxide (Figure 16). Etching these oxides with diluted HF acid made the deposited polycrystalline silicon layer more uniform in appearance (Figure 17). In later experiments, it was possible to achieve similar results by treating the freshly deposited oxide with nitrogen at an elevated temperature immediately prior to the silicon deposition step. The actual mechanism of this treatment is not completely understood; however, two possible causes for increased nucleation sites are: (1) an etching mechanism to dissolve silicon dioxide and thus expose more sites or (2) a deposition of some compound such as silicon nitride during the nitrogen treatment. (The residual $SiCl_4$ and CO_2 in the presence of both H_2 and N_2 could conceivably form silicon nitride which would act as a nucleation site.) Successful polycrystalline silicon growth has been accomplished;

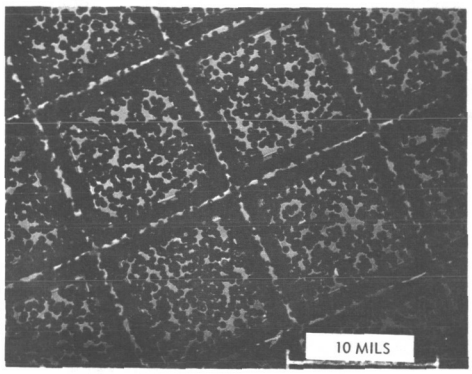


Figure 16—Photo of hemispherically shaped mounds of polycrystalline silicon groove on an etched silicon dioxide (squares are 0.010" x 0.010").

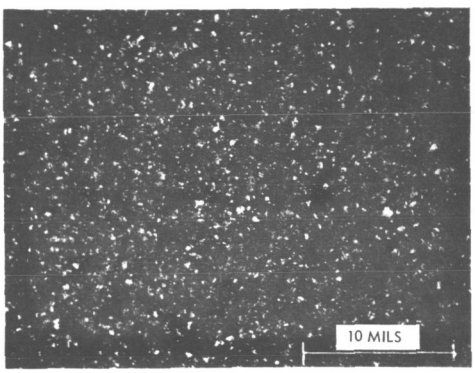


Figure 17—Photo of polycrystalline silicon layer deposited after the silicon dioxide layer has received a high temperature (1200°C) nitrogen heat treatment.

the rate of growth can be controlled as desired. Figures 18 and 19 show the general configuration of grooves which have received both an oxide barrier as well as a polycrystalline silicon deposition. Also evident is the spacing-dependence of groove etch depth.

Rate of Oxide Growth

The rate of deposition is controllable over a wide latitude. Growth rate on the surface of the silicon has been established at 0.11μ/min ± 15%. This same rate of deposition is obtained in all grooves over 4 mils wide. However, for grooves 1 mil wide, the rate of deposition is about 70% of that on the surface. Grooves between 1 and 4 mils in width show a deposition rate dependence upon width which varies from about 70% to 100% of the surface deposition rate (Figure 20).

Rate of Polycrystalline Silicon Growth

Upon completion of silicon dioxide deposition, the surface of the oxide must be treated to form nucleation sites.

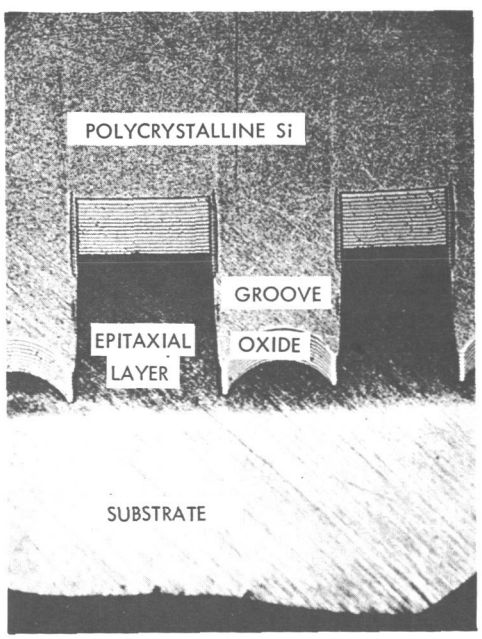


Figure 18—Photo showing substrate, epitaxial layer, etched grooves, silicon dioxide fill and polycrystalline silicon backing material (lapping angle about 2° from surface).

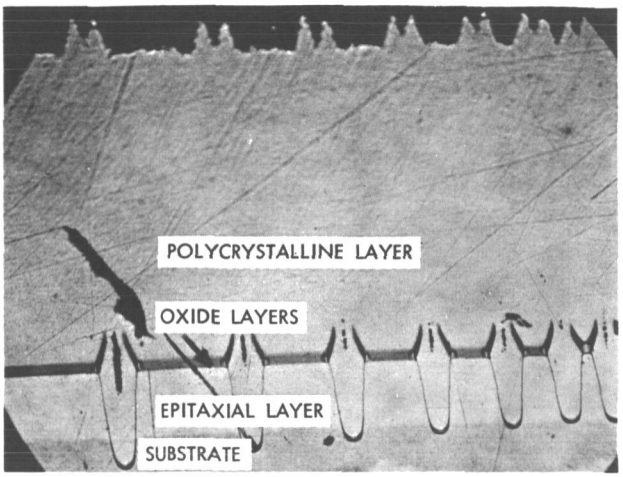


Figure 19—Photo showing various layers on a 5° angle lapped sample. (Note geometry transfer of substrate through the polycrystalline silicon.)

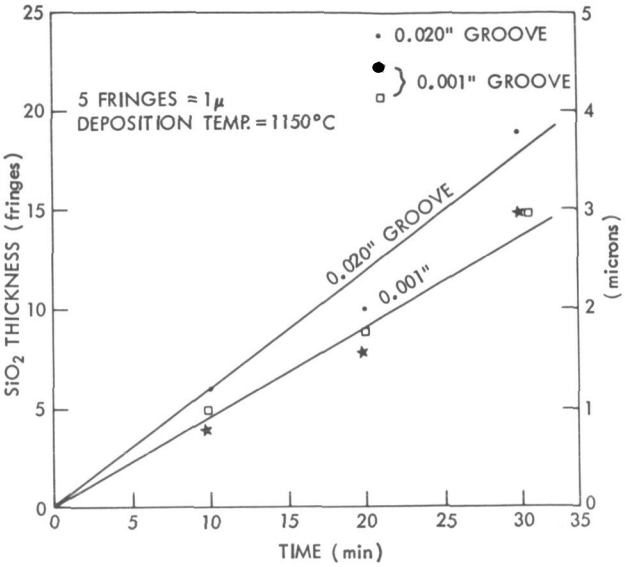


Figure 20—Deposited silicon thickness vs. time.

This has been done by chemical etch and lately by using a nitrogen heat treatment at 1200°C for approximately 3 minutes. This operation effects the formation of nucleation sites which control the initial growth rate of subsequently deposited polycrystalline layers. Indeed, if nucleation sites are few and scattered there can be no general growth. Growth will be noted upon individual hemispherical shaped mounds which capture available silicon from the ambient (Figure 16). By increasing the number of nucleation sites either by chemical or high temperature etching, the deposition becomes more nearly uniform (Figure 17).

Polycrystalline silicon growth passes through three well defined time-dependent phases.* The first or nucleation phase exhibits no detectable mass accumulation or growth. This time, being dependent upon the degree of supersaturation to which the ambient and system is subjected, is not controllable, which leads to poor reproducibility.

The second phase is attributed to lateral growth of the nucleous and shows mass accumulation by accretion at the periphery and surface of hemispherically shaped mounds. Individual mounds thicken and will connect with another only as its lateral growth extends to a neighboring mound. Eventually the surface of the oxide will be covered; however, here as during the first phase, the growth is uncontrollable, being dependent upon both the number of nucleation sites and hemispherical mounds and the area of the silicon that has been deposited. The mass accumulation rate increases approximately with time; however the surface will not be smooth and/or useable.

The third phase exhibits a constant deposition rate and except for irregularities on the surface of the substrate, the growth will be smooth and uniform in appearance.

*Johnson, J. E., "Kinetics of CdS Evaporated Film Formation," Pittsburgh: Westinghouse Research Laboratories, April 16, 1964.

It appears that etching or heat treatment increases the number of nucleation sites; thus the time of the first two phases is greatly reduced and the third phase of constant growth rate is reached much sooner.

During standard deposition of epitaxial single crystal layers, the rate of deposition is maintained near 1μ per minute. In view of the reasons for depositing the polycrystalline material (to be used as a backing or handle for subsequent operations) a faster deposition rate was deemed desirable. The rate used is approximately 2.3μ/minute (Figure 21).

(Manuscript received December 3, 1965)

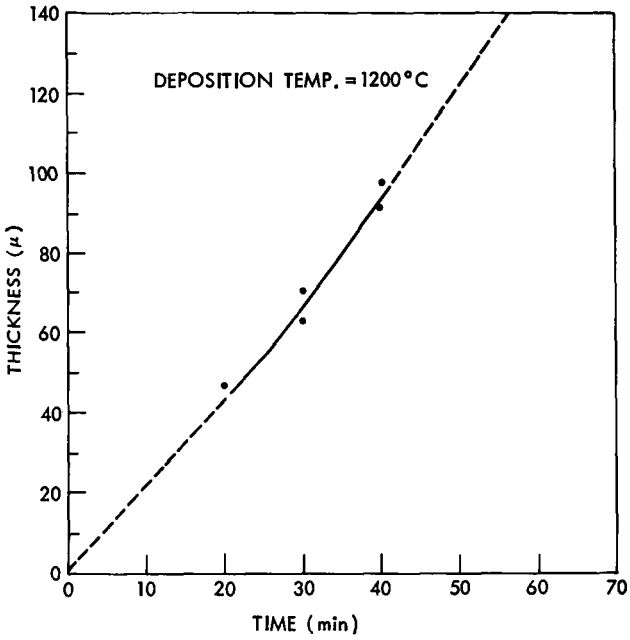


Figure 21—Polycrystalline layer thickness vs. time.

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Appendix A

Specifications for Epitaxial Processes

1. Equipment
   - 1.1 Gas control panel
   - 1.2 Epitaxial reactor
   - 1.3 RF generator
   - 1.4 Optical pyrometer
   - 1.5 4-point probe
   - 1.6 Angle lapping equipment
   - 1.7 Interference fringe apparatus
   - 1.8 Surface hydrogen purifier
   - 1.9 Tweezers
2. Material
   - 2.1 Silicon tetrachloride
   - 2.2 Diborane in H_2 (100 PPM)
   - 2.3 Silane in H_2 (100 PPM)
   - 2.4 Arsine in H_2 (100 PPM)
   - 2.5 Hydrogen
   - 2.6 Nitrogen
   - 2.7 Carbon dioxide (Coleman grade)
   - 2.8 Graphite susceptor
   - 2.9 Quartz envelope
   - 2.10 Quartz sled
   - 2.11 Silicon slice (previously polished and cleaned)
   - 2.12 Pyrex petri dishes
   - 2.13 Lint free paper
   - 2.14 Trichloroethylene

2.15 HF

2.16 HNO_3

2.17 HAc

2.18 Cotton balls

2.19 Anhydrous HCl

3. Procedure

3.1 Cleaning Process

3.1.1 Place slices of silicon in petri dish.

3.1.2 Cover slices with trichloroethylene (TCE). Note: Slices must not be allowed to become exposed to air by trichloroethylene evaporation; must be kept covered until removal.

3.1.3 Remove a slice; place on at least three thicknesses of lint free paper.

3.1.4 With plastic squirt bottle apply a small amount of TCE.

3.1.5 Swab slice with cotton swab or ball to physically remove any trace of foreign particle.

3.1.6 Place slice in clean petri dish (bottom of dish to be covered by disc of lint free paper.)

3.1.7 Repeat steps 3.1.3 through 3.1.6 until all slices have been cleaned.

3.2 Loading Boat and Reactor

3.2.1 Assemble graphite susceptor into quartz envelope.

3.2.2 Place assembly on sled.

3.2.3 Place slices of silicon on boat centered properly along midline.

3.2.4 Introduce sled and boat assembly with slices in reactor tube and center boat within extremes of RF load coil.

3.2.5 Replace end cap and start purge of reactor tube with N_2.

3.3 Epitaxial Processes

3.3.1 Vapor Etching by HCl

3.3.1.1 Purge reactor tube of all atmosphere by nitrogen flow (at least 3 minutes).

3.3.1.2 Purge reactor tube of all nitrogen by hydrogen (at least 3 minutes).

3.3.1.3 Turn on RF generator and allow temperature to reach 1200°C. Temperature is checked by optical pyrometer.

3.3.1.4 Set H_2 flow to desired rate.

3.3.1.5 Start HCl flow to desired rate and set timer to desired etch time; allow etch to proceed for this time.

3.3.1.6 Stop HCl flow after completion of time, allowing only H_2 to flow through reactor. If HCl etch only desired, move to step 3.3.2.5.

3.3.2 Epitaxial Deposition of Silicon

3.3.2.1 Set temperature to 1150°C

3.3.2.2 Set gas flow rates (according to desired doping levels) for H_2 flow through $SiCl_4$ bottle (H_2 bypasses $SiCl_4$ bottle) and for doping gases are desired (arsine or phosphorus for n-type and diborane for p-type). The gas flows of doping gases are directed to exhaust.

3.3.2.3 Start flow of H_2 through $SiCl_4$ bottle and direct doping gas flow from exhaust to reactor. (Set timer for desired length of time.) Allow deposition to continue for length of time necessary to deposit desired thickness of layers.

3.3.2.4 Stop H_2 flow through $SiCl_4$ and direct doping gas from reactor to exhaust.

3.3.2.5 Allow reactants to purge from reactor by H_2 flow (at least 2 minutes).

3.3.2.6 Turn off RF generator and allow reactor to cool. Turn off dopant supplies.

3.3.2.7 Purge H_2 from reactor with nitrogen (at least 2 minutes).

3.3.2.8 Slices may be removed from the reactor by removing sled and boat assembly.

3.3.2.9 Place slices in clean petri dish on clean lint free paper.

3.3.2.10 Evaluate test slices for layer thickness and resistivity by 4-point probe and thickness evaluation equipment.

3.3.3 Oxide Deposition - If an oxide layer is desired for masking or protection, follow procedure of epitaxial deposition 3.3.2 through step 3.3.2.3, then proceed with the following:

3.3.3.1 Allow H_2 flow to continue through $SiCl_4$ bottle; divert doping gas from reactor to exhaust; start and set CO_2 flow to reactor and start timer for desired time and thickness.

3.3.3.2 Allow to proceed for desired time.

3.3.3.3 Stop H_2 flow through $SiCl_4$, stop CO_2 flow to reactor, maintain temperature (1150°C)

3.3.3.4 Stop all H_2 flow to reactor and introduce nitrogen flow.

3.3.3.5 Allow nitrogen to flow for time required.

3.3.3.6 If this is final step, proceed according to the following:

3.3.3.7 Turn off RF generator and allow reactor to cool.

3.3.3.8 Remove slices per 3.3.2.8 through 3.3.2.10.

3.3.4 Polycrystalline silicon deposition (on oxide). If a polycrystalline layer is desired over the oxide continue oxide deposition (3.3.3) up to step 3.3.3.4 and then proceed with the following:

3.3.4.1 Continue nitrogen flow through the reactor for at least 3 minutes.

3.3.4.2 Stop nitrogen flow; start H_2 flow and purge nitrogen from the reactor.

3.3.4.3 Start H_2 flow through $SiCl_4$ at the setting desired to deposit silicon at the proper rate. Set timer.

3.3.4.4 Allow deposition to proceed for time necessary

3.3.4.5 Stop H_2 flow through $SiCl_4$.

3.3.4.6 Allow H_2 to purge reactor (at least 2 minutes).

3.3.4.7 Turn off RF generator.

3.3.4.8 Proceed to cool down and remove slices according to steps 3.3.2.7 through 3.3.2.9.

3.4 Groove Cutting by Wet Chemical Method.

3.4.1 Slices with windows cut through the second epitaxially grown (thermal) oxide are mounted on a glass slide by apiezon wax (black wax). Care must be taken to keep wax from face of the wafer.

3.4.2 A mixture of HNO_3, HF and HAc is prepared in the ratios of 84:8:8 respectively.

3.4.3 The mounted slice is introduced to the acid mixture and etched (with constant agitation) until the original oxide layer is exposed. (This will be noted by the reflection being very clear).

3.4.4 The slice is now removed from the acid mixture and cleaned in D.I. water for at least five separate rinses.

3.4.5 The slices are submerged in HF (48%) until all the overhanging silicon dioxide has been removed. (This also can be detected visually.)

3.4.6 Slices are removed from glass slide and cleaned by organic solvents prior to continuing subsequent operations.

Appendix B

Experimental Data on Groove Etching

This appendix describes twelve series of experiments in silicon groove etching. The nature and purpose of each are summarized below:

I. Exploratory.

II. Exploratory, to improve oxide masking.

III. To ascertain effects of gas flow direction and to correlate slice-to-slice depth variations.

IV. Exploratory, to correlate gas flow direction.

V. To evaluate etching rates of various spacings between constant-width grooves.

VI. To evaluate geometry effect on groove etch.

VII. To evaluate spacing width and groove width variations on groove geometry.

VIII. To correlate temperature vs. etch rate.

IX. Exploratory, to evaluate gas flow and concentration of etchant.

X. To establish emissivity effects.

XI. To verify Experiment X results and to ascertain effects on wide groove bottoms.

XII. To verify Experiments X and XI.

Any changes from the general procedure are noted in experimental results. Data are recorded in tables and graphs.

Gas Supply/Reactor Systems

A horizontal type epitaxial reactor powered by a 10 kw, 450 kc Westinghouse radiofrequency generator was used in these tests. An ambient and doping gas supply panel (Figure B1) supplied HCl, H_2, $SiCl_4$, N_2, and CO_2 as well as PH_3, AsH_3 and B_2H_6 to the reactor in controllably metered quantities.

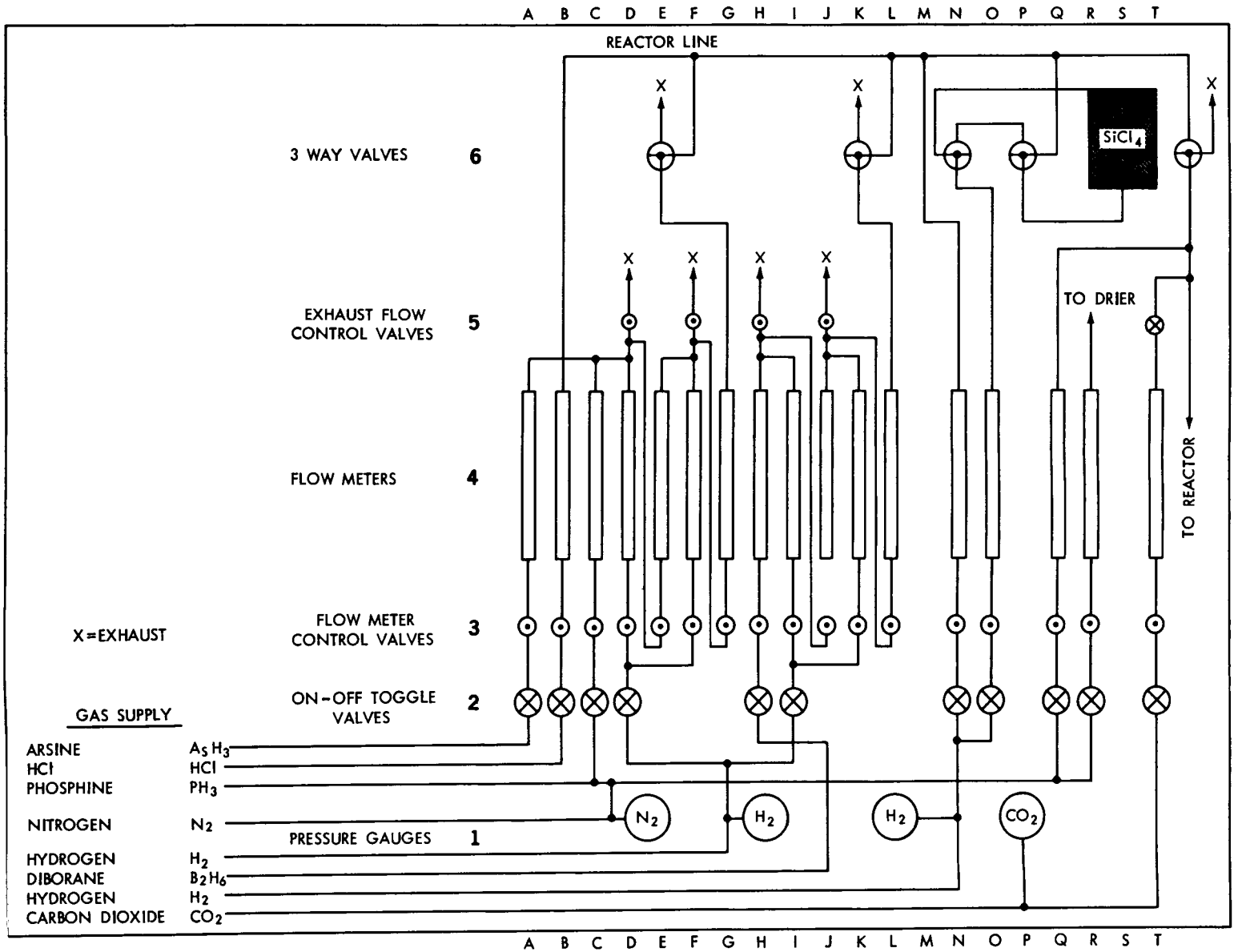


Figure B1—Schematic of gas panel controls.

Experiment I

Five slices of silicon (ff-20, 21, 32, 33 and 34) from crystal P-56-10.2 were given the following treatment:

Vapor etch at 1200°C for 15 minutes

Epitaxial deposition at 1125°C for 10 minutes PH_3 doped 1 ohm-cm

Oxide deposition at 1150°C for 10 minutes ($CO_2 + SiCl_4 + H_2$)

Nitrogen treatment at 1150°C for 3 minutes

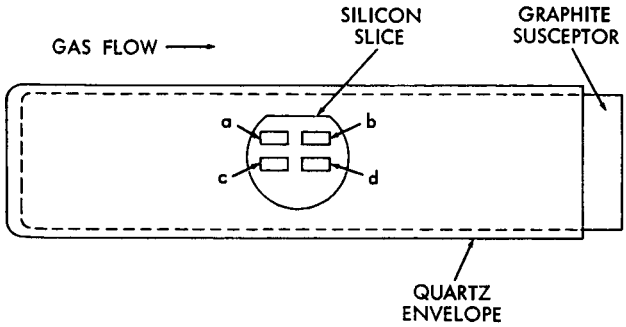


Figure B2—Position of slice on boat.

The slices were then processed through standard photoresist methods to cut windows in the oxide using mask 138 (Figures 11a and 11b) after which they were placed on a quartz boat and etched in 4% HCl in H_2 at 1200°C for the desired time. The gas flow was parallel to the direction of the grooves (Figure B2).

The slices were given a visual microscopic evaluation and sectioned, then groove depths were measured. The results are listed in Tables B1 and B2 and graphically shown in Figures B3 and B4.

Table B1

Visual Evaluation of Experiment I.

Experiment	Run	Slice	Time (min)	Visual Evaluation
I-1	593-1	ff-20	1	Ends of grooves show undercutting at ends and give an appearance similar to a match-stick (enlarged end). See Figure B5.
I-2	594-1	ff-21	1-1/2	Match-stick effect more pronounced. Ends touch on grooves 7, 8, 9, 10.
I-3	595-1	ff-32	2	Match-stick effect still greater—washout between grooves 7, 8, 9, 10. Upstream ends of grooves wider than down-stream ends.
I-4	596-1	ff-33	2-1/2	More pronounced effects - similar to ff-32 only greater lateral etching.
I-5	597-1	ff-34	3	Pinholes beginning through oxide. Spaces washed out between closer spaced grooves. Surface oxide between these grooves loose on surface.

Table B2

Average Groove Depth Measurements, Experiment I.
(in fringes; 1 fringe = 0.273 microns)

Experiment	Groove Number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
I-1	$7\frac{1}{4}$	$6\frac{1}{2}$	7	$7\frac{1}{2}$	$8\frac{1}{2}$	$10\frac{1}{4}$	$10\frac{3}{4}$	$10\frac{3}{4}$	11	$11\frac{3}{4}$	13	$14\frac{1}{4}$	14	21	$26\frac{1}{2}$
I-2	$12\frac{1}{2}$	12	$11\frac{1}{3}$	11	$15\frac{3}{4}$	$15\frac{1}{2}$	$15\frac{1}{2}$	$15\frac{1}{2}$	$15\frac{1}{2}$	16	18	20	$22\frac{3}{4}$	26	$33\frac{3}{4}$
I-3	$16\frac{1}{4}$	$14\frac{1}{4}$	14	$14\frac{3}{4}$	$17\frac{3}{4}$	19	$18\frac{3}{4}$	$18\frac{3}{4}$	$19\frac{1}{2}$	$20\frac{3}{4}$	$22\frac{3}{4}$	$27\frac{1}{4}$	$30\frac{1}{2}$	$35\frac{1}{4}$	$42\frac{3}{4}$
I-4	$21\frac{3}{4}$	$20\frac{1}{4}$	$20\frac{1}{4}$	$20\frac{1}{4}$	$22\frac{3}{4}$	24	24	$23\frac{1}{2}$	$24\frac{1}{2}$	$26\frac{1}{2}$	$26\frac{1}{2}$	$31\frac{3}{4}$	$36\frac{1}{2}$	$42\frac{1}{4}$	$51\frac{3}{4}$
I-5	$21\frac{1}{2}$	$24\frac{3}{4}$	$21\frac{1}{2}$	$24\frac{1}{2}$	$28\frac{1}{4}$	28	$25\frac{1}{2}$	$24\frac{1}{2}$	25	27	$31\frac{1}{4}$	35	$42\frac{1}{2}$	$49\frac{3}{4}$	$62\frac{1}{4}$

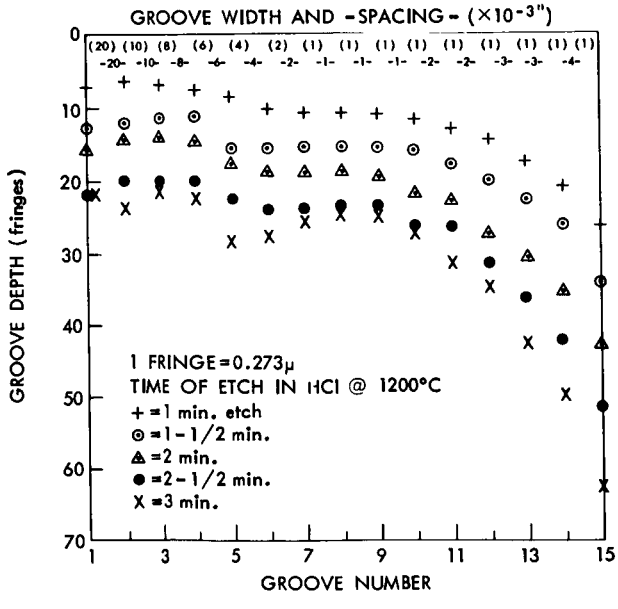


Figure B3—Graph of groove depth vs. groove number, Experiment I, mask 138.

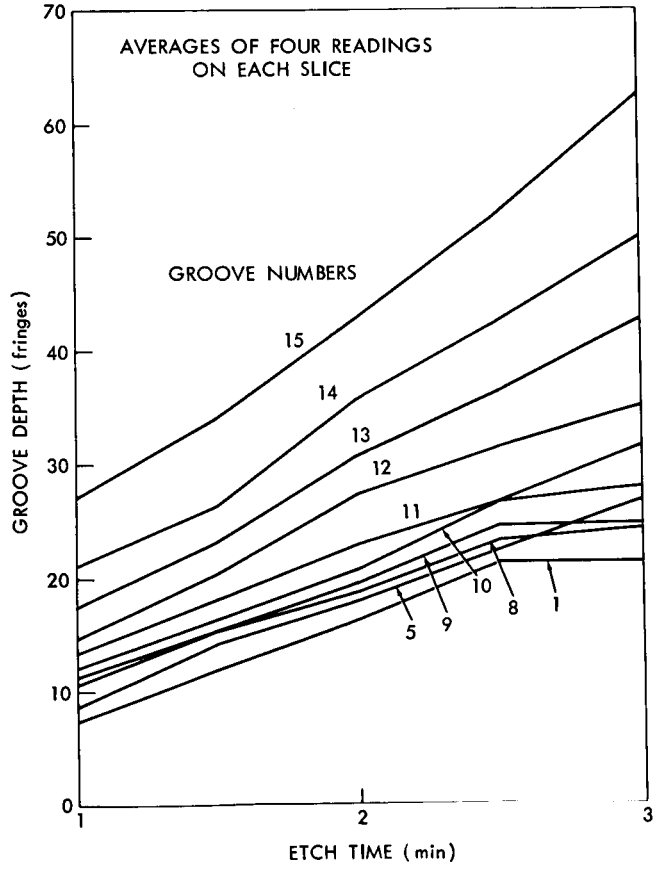


Figure B4—Groove depth vs. time, Experiment I, mask 138 (average of four readings for each slice).

Experiment II

Five slices, ff-35 through ff-39, were given the same preparation as Experiment I except time of oxide deposition was 20 minutes. Results are shown in Tables B3 and B4 and Figures B6 and B7.

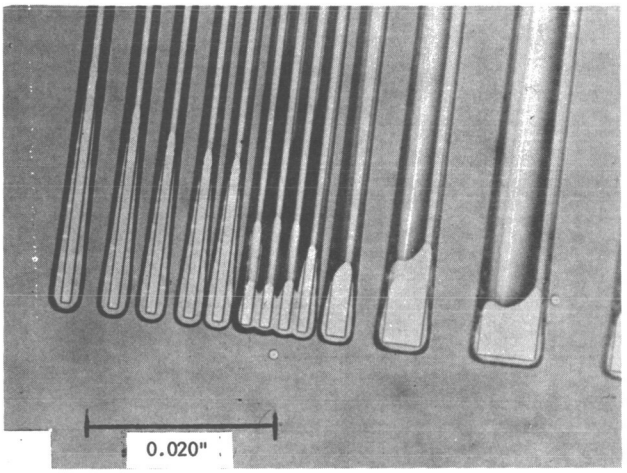


Figure B5—Match-stick ends of grooves.

Table B3

Visual Evaluation of Experiment II.

Experiment	Run	Slice	Time (min)	Visual Evaluation
II-1	598-1	ff-35	1	Match-stick ends - almost meet on 1 mil spacing. Oxide intact - no pinholes.
II-2	599-1	ff-36	2	Match-stick ends contact on 1 mil spacing, isolation possible in central portion of line. Oxide intact - no pinholes.
II-3	600-1	ff-37	3	1 mil spacing deleted by undercut; ends of 2 min. spacing lose isolation. Oxide intact elsewhere - 4 pinholes in area of grooves.
II-4	601-1	ff-38	4	1 and 2 mil spacing deleted by undercut; ends of 3 mil spacing lose isolation; oxide intact - no pinholes.
II-5	602-1	ff-39	5	1, 2, and ends of 3 mil spaces deleted by undercut; 4 mil spacing intact; undercut oxide flakes off; oxide intact; pinholes sparse but present; this appears to be upper time limit of oxide this thick.

Table B4

Average Groove Depth Measurements, Experiment II.
(fringes)

Experiment	Groove Number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
II-1	$9\frac{1}{4}$	$8\frac{1}{2}$	$7\frac{1}{2}$	$8\frac{1}{4}$	$9\frac{1}{4}$	$10\frac{1}{4}$	$10\frac{1}{4}$	10	$10\frac{1}{2}$	$11\frac{3}{4}$	$13\frac{1}{4}$	$15\frac{1}{2}$	$17\frac{3}{4}$	21	$28\frac{1}{2}$
II-2	$17\frac{1}{4}$	$14\frac{3}{4}$	14	15	$17\frac{3}{4}$	20	$19\frac{1}{4}$	$18\frac{3}{4}$	$19\frac{3}{4}$	21	24	$25\frac{3}{4}$	$30\frac{1}{2}$	36	$46\frac{1}{4}$
II-3	$19\frac{1}{3}$	$21\frac{1}{2}$	21	$21\frac{3}{4}$	$23\frac{3}{4}$	$26\frac{1}{4}$	$24\frac{1}{2}$	24	24	$26\frac{1}{4}$	$30\frac{1}{2}$	$34\frac{1}{2}$	$40\frac{1}{4}$	$47\frac{1}{4}$	58
II-4	$30\frac{1}{4}$	30	29	$31\frac{1}{4}$	$33\frac{3}{4}$	$34\frac{3}{4}$	33	32	$32\frac{1}{2}$	$35\frac{1}{4}$	$36\frac{3}{4}$	42	$49\frac{1}{4}$	58	$74\frac{3}{4}$
II-5	$37\frac{1}{2}$	38	$37\frac{1}{3}$	$36\frac{1}{3}$	39	$38\frac{1}{3}$	35	$34\frac{1}{2}$	$34\frac{3}{4}$	36	$43\frac{1}{2}$	$47\frac{1}{4}$	52	$62\frac{3}{4}$	$76\frac{3}{4}$

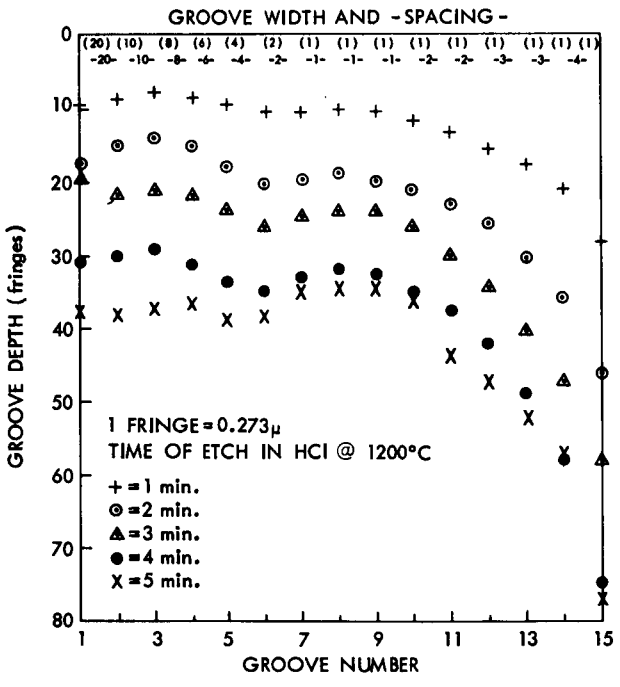


Figure B6 —Groove depth vs. groove number, Experiment II, mask 138.

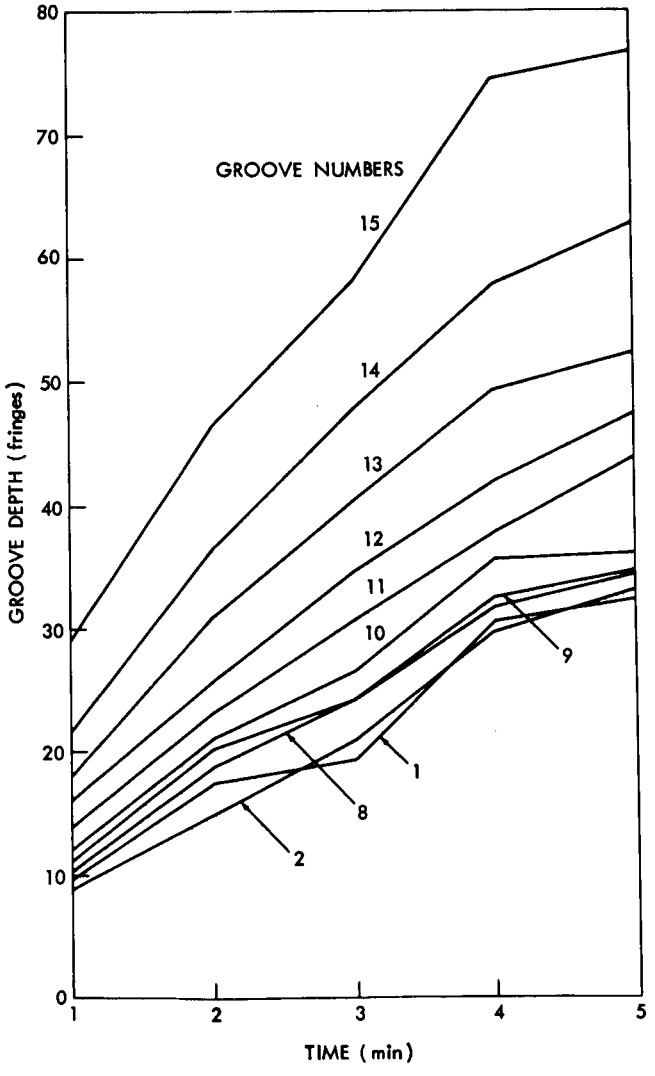


Figure B7—Groove depth vs. time, Experiments II and III, mask 138 (average of four).

Experiment III

Four slices, kk46 through 49, were given standard etch, epitaxial and oxide coating and then were given standard photoresist process to open windows by mask 138. Slices were placed on quartz envelope with a rotation of 90° clockwise for each subsequent slice (Figure B8).

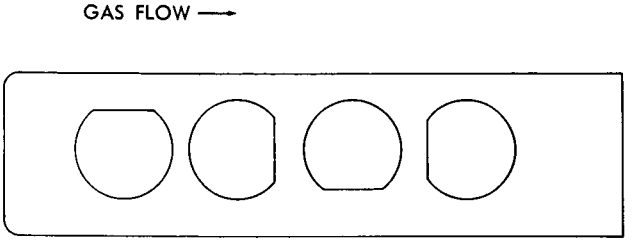


Figure B8—Position of slices for Experiment III (run 621-4).

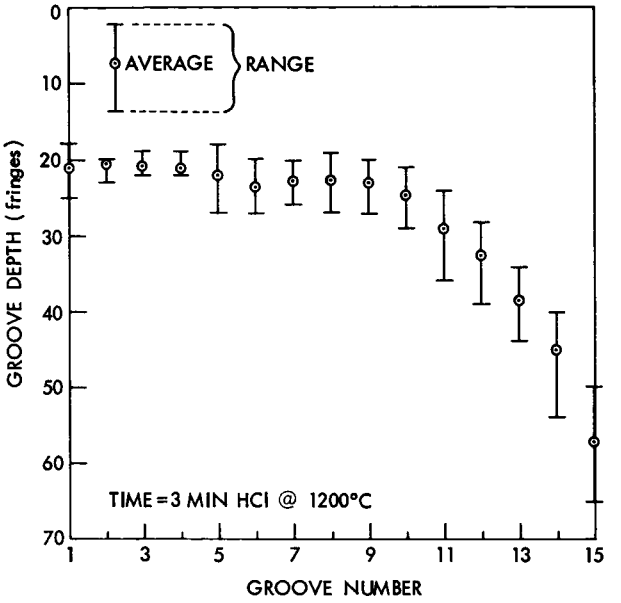
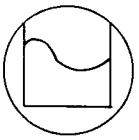
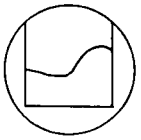
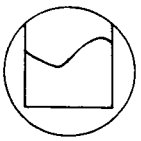
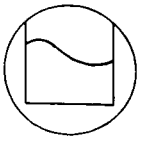


Figure B9—Average groove depth vs. groove number, Experiment III, mask 138.

Table B5

Visual Evaluation of Experiment III.

Experiment	Run	Slice	Time (min)	Visual Evaluation
III-1 	621-4	kk46	3	Prominent match-stick ends interconnecting at ends of 1 mil and 2 mil spacing; oxide intact, grooves clean (see microscope diagram of groove bottom).
III-2 	621-4	kk47	3	Same as kk46, except elongation of groove 1 on opposite side.
III-3 	621-4	kk48	3	Same as kk46 and 47 (note microscope diagram).
III-4 	621-4	kk49	3	Same as kk46, 47 and 48 (see diagram).

The two-fold purpose of this test was to ascertain the effects of ambient flow direction on groove geometry and correlate slice-to-slice depth variations in one run. All slices were given a simultaneous 3 minute HCl etch to cut grooves into silicon under same conditions as Test II-3. Measurements and evaluations are given in Tables B5 and B6 and Figure B9.

Further examination of the slices of Experiment III gave this information: The facets or flats at the bottom of the grooves are probably preferential etch planes as well as preferential limits of growth. Inasmuch as the slices used in these tests are intentionally off orientation (to promote epitaxial growth rate), facets appear at the edge of the slice after epitaxial growth. From visual observation the plane of these facets is parallel to the plane of the flats at the ends of the groove bottoms (as shown in the diagrams in Table B5).

This observation indicates that there is a definite way to differentiate between top and bottom of slices and that for more intricate device work which depends upon etching techniques, the top or bottom designation of slice surfaces should be prescribed. This could be done by an additional groove or flat ground on the ingot prior to the slicing operation and would insure that the same face would always be used from slice-to-slice.

Table B6

Average Groove Depth Measurements, Experiment III.
(fringes)

Experiment	Groove Number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
III-1 Ave. $\overline{X}$	$20\frac{1}{2}$	20	$20\frac{1}{4}$	$20\frac{3}{4}$	$21\frac{1}{4}$	$23\frac{1}{4}$	$22\frac{1}{4}$	22	$22\frac{1}{4}$	24	$27\frac{3}{4}$	$31\frac{1}{2}$	$37\frac{3}{4}$	$44\frac{3}{4}$	$58\frac{1}{4}$
III-2 Ave. $\overline{X}$	22	21	$20\frac{1}{4}$	21	$22\frac{1}{4}$	$23\frac{3}{4}$	$27\frac{1}{2}$	22	$27\frac{1}{2}$	24	$28\frac{3}{4}$	$32\frac{3}{4}$	$37\frac{1}{4}$	$43\frac{1}{4}$	$55\frac{1}{2}$
III-3 Ave. $\overline{X}$	22	$20\frac{3}{4}$	$20\frac{1}{2}$	$20\frac{3}{4}$	$22\frac{3}{4}$	24	$22\frac{1}{4}$	$22\frac{1}{4}$	$22\frac{1}{4}$	$24\frac{1}{4}$	$29\frac{1}{4}$	$33\frac{1}{4}$	$39\frac{1}{2}$	$46\frac{1}{2}$	$58\frac{3}{4}$
III-4 Ave. $\overline{X}$	$19\frac{1}{4}$	$20\frac{1}{2}$	$19\frac{3}{4}$	$20\frac{1}{2}$	22	24	$23\frac{1}{2}$	$23\frac{1}{4}$	24	26	$29\frac{1}{4}$	$32\frac{1}{2}$	$38\frac{1}{4}$	$44\frac{1}{2}$	$55\frac{3}{4}$
$\overline{XX}$	21	$20\frac{1}{2}$	21	21	22	$23\frac{3}{4}$	$22\frac{1}{2}$	$22\frac{1}{2}$	23	$24\frac{1}{2}$	29	$32\frac{1}{2}$	$38\frac{1}{2}$	45	51
Range	- 3	$-\frac{1}{2}$	- 2	- 2	- 4	$-3\frac{3}{4}$	$-2\frac{1}{2}$	$-3\frac{1}{2}$	- 3	$-3\frac{1}{2}$	- 5	$-4\frac{1}{2}$	$-4\frac{1}{2}$	- 5	- 7
	+ 4	$+2\frac{1}{2}$	+ 1	+ 1	+ 5	$+3\frac{1}{4}$	$+3\frac{1}{2}$	$+4\frac{1}{2}$	+ 4	$+4\frac{1}{2}$	+ 7	$+6\frac{1}{2}$	$+5\frac{1}{2}$	+ 9	+ 8
Percent Deviation	-14	-2.5	-9.5	-9.5	-18	-15.8	-11	-15.5	-13	-14.3	-17.3	-13.8	-11.7	-11.1	-12.3
	+19	+12	+4.7	+4.7	+22.5	+13.7	+15.5	+20	+17.4	+18.3	+24.2	+20	+14.3	+20	+14

Experiment IV

A group of 6 slices, numbered kk39, 40, 51, 42, 44 and 45, received deposition and oxide processes similar to prior tests. Slices were run individually and a progressive rotation of 90° clockwise was performed on each subsequent run (i.e., on first run flat was at 12:00 o'clock; second, 3:00 o'clock, etc.). The time varied progressively from 5 to 10 minutes. Results are shown in Tables B7 and B8 and on Figures B10 and B11.

Table B7

Visual Evaluation of Experiment IV.

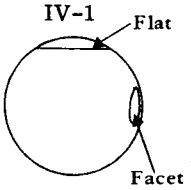
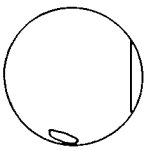
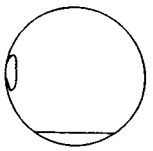
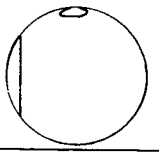
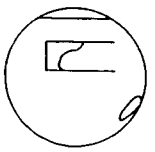
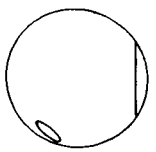
Experiment	Run	Slice	Time (min)	Visual Evaluation
IV-1 	634-1	kk39	5	Not a good etch; the planes at the ends of the grooves appear more uniform; 1 and 2 mil spaces deleted all along groove. 3 mil space very nearly at each end. Ends symmetrical, oxide intact, some pinholes.
IV-2 	635-1	kk40	6	Good etch; all surfaces smooth, match-stick ends symmetrical in flat plane; oxide beginning to show weaknesses; 1 and 2 mil spaces deleted.
IV-3 	636-1	kk41	7	Greater oxide breakdown; good etch; all surfaces smooth; ends nearly symmetrical; 1, 2, and 3 mil spaces deleted.
IV-4 	637-1	kk42	8	Oxide badly pitted, 1, 2, 3, and 4 mil spaces deleted ends slightly asymetrical.
IV-5 	638-1	kk44	9	Oxide pitted, 1, 2, 3 and 4 mil spaces deleted at ends. Asymetric flats on groove bottoms. See diagram.
IV-6 	639-1	kk45	10	Badly pitted oxide 1, 2, 3 and 4 mil spacing deleted (at ends) asymetrical flats on groove bottoms.

Table B8

Groove Depth Measurements, Experiment IV.
(fringes)

Experiment		Groove Numbers														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
IV-1		NO DATA TAKEN														
IV-2	a	X	X	X	X	X	X	X	X	X	43	50	54	62	71	88
	b	42	43	38	40	39	43	X	X	36	44	50	58	66	76	94
	c	X	X	X	X	X	X	X	42	42	48	51	57	65	74	89
	d	X	X	X	X	X	X	44	43	43	45	50	55	63	73	87
average	$\bar{X}$	42	43	38	40	39	43	44	$42\frac{1}{2}$	$40\frac{1}{3}$	45	$50\frac{1}{4}$	56	64	$73\frac{1}{2}$	$89\frac{1}{2}$
IV-3	a	X	X	X	X	X	X	53	53	53	60	66	73	81	93	114
	b	X	X	X	X	X	X	48	48	49	56	65	73	84	97	124
	c	X	X	X	X	X	X	38	37	37	41	45	62	70	80	100
	d	X	X	X	X	X	X	X	X	45	48	56	60	68	80	107
average	$\bar{X}$	X	X	X	X	X	X	$46\frac{1}{3}$	46	46	$51\frac{1}{4}$	58	67	$75\frac{1}{4}$	$87\frac{1}{2}$	$111\frac{1}{4}$
IV-4	a	X	X	X	X	X	X	56	56	57	63	69	78	90	106	133
	b	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	c	X	X	X	X	X	X	51	49	51	55	60	69	74	85	105
	d	X	X	X	X	X	X	49	47	48	52	59	65	74	85	106
average	$\bar{X}$	X	X	X	X	X	X	52	$50\frac{2}{3}$	52	$56\frac{2}{3}$	$62\frac{2}{3}$	$70\frac{2}{3}$	$79\frac{1}{3}$	92	$114\frac{2}{3}$
IV-5	a	X	X	X	X	X	X	X	X	X	74	80	81	100	111	140
	b	X	X	X	X	X	X	X	X	52	56	64	71	81	97	123
	c	X	X	X	X	X	X	X	64	64	68	76	82	93	104	130
	d	X	X	X	X	X	X	X	47	48	52	59	65	76	90	112
average	$\bar{X}$	X	X	X	X	X	X	X	$55\frac{1}{2}$	$54\frac{2}{3}$	$62\frac{1}{2}$	$69\frac{3}{4}$	$76\frac{1}{4}$	$87\frac{1}{2}$	$100\frac{1}{2}$	$126\frac{1}{4}$
IV-6	a	X	X	X	X	X	X	60	59	60	64	70	78	86	98	122
	b	X	X	X	X	X	X	X	64	65	70	76	85	98	114	138
	c	X	X	X	X	X	X	63	63	64	68	74	73	93	98	123
	d	X	X	X	X	X	X	69	69	70	74	80	89	100	113	135
average	$\bar{X}$	X	X	X	X	X	X	64	$63\frac{3}{4}$	$64\frac{3}{4}$	69	75	$83\frac{3}{4}$	$96\frac{1}{4}$	$105\frac{1}{4}$	$129\frac{1}{2}$

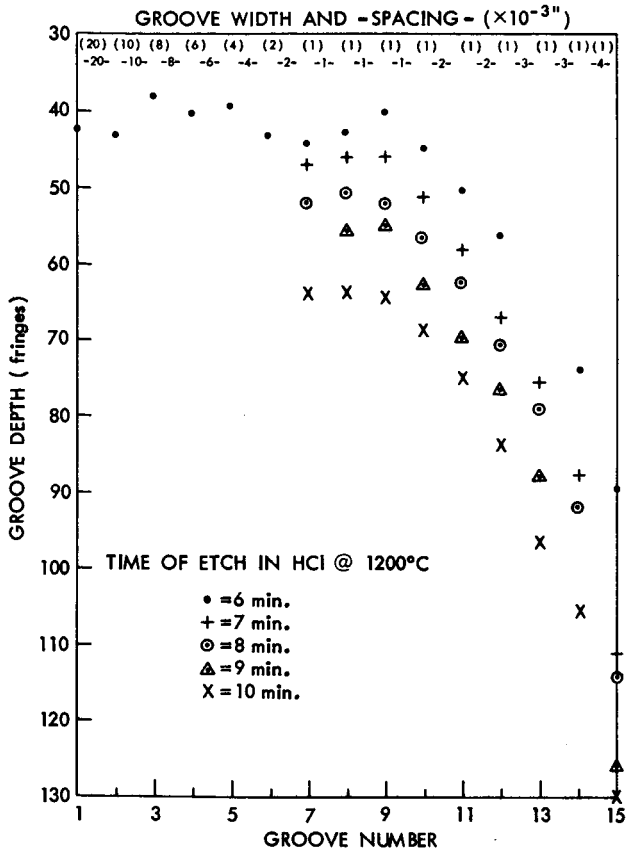


Figure B10—Average groove depth vs. groove number, Experiment IV, mask 138.

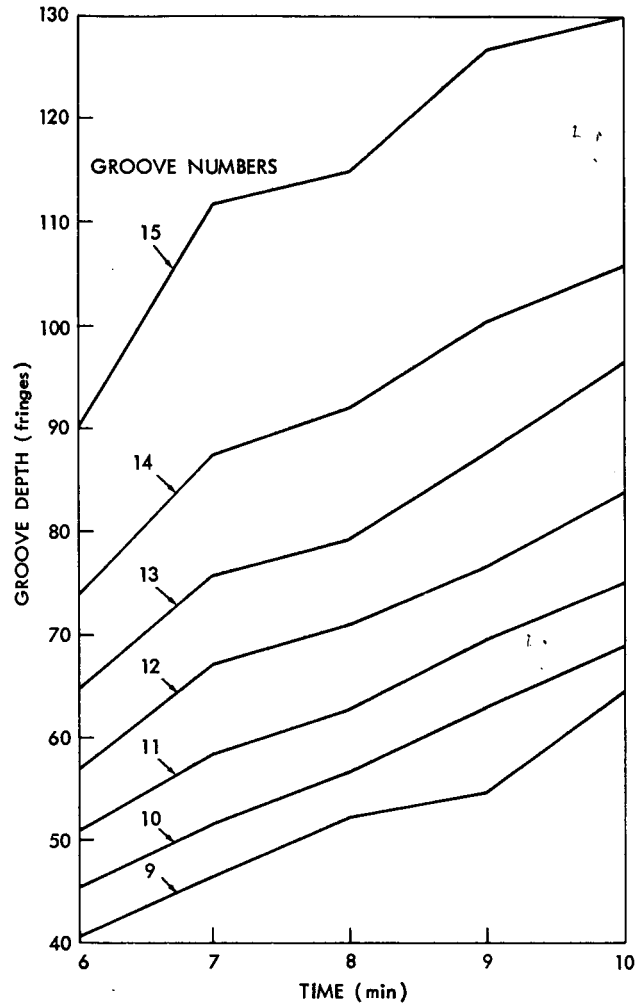


Figure B11—Groove depth vs. time, Experiment IV, mask 138.

Experiment V

To evaluate the effects of various spacings between constant-width grooves (0.001"), a mask was made by methods similar to mask 138 (Figure 11c). The layout on the slices is as shown on Figure B12.

Standard etch, epitaxial deposition and oxidation operations were made as in previous experiments; then standard photoresist procedures were followed. Slices were treated separately in the standard etching manner for times as shown in Table B9. Figures B13 and B14 show groove depth correlation.

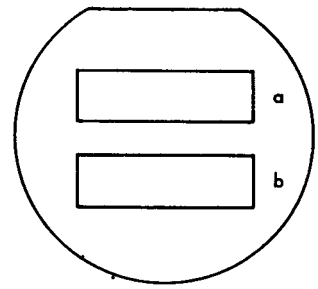


Figure 12—Slice with mask 141 layout.

Table B9

Groove Depth Measurements, Experiment V.
(fringes)

Experiment	Run	Slice	Etch Time (min)		Groove Number									
					1	2	3	4	5	6	7	8	9	10
V-1	647-1	kk65	1	a	X	22	19	18	16	16	15	14	14	11
				b	29	25	23	21	20	18	18	16	19	21
					$\overline{X}$ 29	$23\frac{1}{2}$	21	$19\frac{1}{2}$	18	17	$16\frac{1}{2}$	15	$16\frac{1}{2}$	19
V-2	648	kk66	2	a	X	41	35	33	29	27	26	26	26	31
				b	46	41	36	32	29	28	27	26	27	33
					$\overline{X}$ 46	41	$35\frac{1}{2}$	$32\frac{1}{2}$	29	$27\frac{1}{2}$	$26\frac{1}{2}$	26	$26\frac{1}{2}$	32
V-3	649	kk67	3	a	X	56	50	45	46	38	36	35	35	42
				b	58	60	52	45	41	39	37	36	37	42
					$\overline{X}$ 58	58	51	45	$40\frac{1}{2}$	$38\frac{1}{2}$	$36\frac{1}{2}$	$35\frac{1}{2}$	36	42
V-4	650	kk68	4	a	X	62	52	49	47	43	42	42	43	49
				b	75	64	57	51	48	44	43	42	42	50
					$\overline{X}$ 75	63	$59\frac{1}{2}$	50	$47\frac{1}{2}$	$43\frac{1}{2}$	$42\frac{1}{2}$	42	$42\frac{1}{2}$	$49\frac{1}{2}$
V-5	651	kk69	5	a	X	74	66	60	58	54	53	51	53	60
				b	89	78	71	65	57	55	53	51	52	59
					$\overline{X}$ 89	76	$68\frac{1}{2}$	$62\frac{1}{2}$	$57\frac{1}{2}$	$54\frac{1}{2}$	53	51	$52\frac{1}{2}$	$59\frac{1}{2}$
V-6	652	kk70	6	a	X	80	70	65	64	59	58	55	58	65
				b	109	85	79	70	64	60	59	57	60	67
					$\overline{X}$ 109	$82\frac{1}{2}$	$74\frac{1}{2}$	$67\frac{1}{2}$	64	$59\frac{1}{2}$	$57\frac{1}{2}$	56	59	66

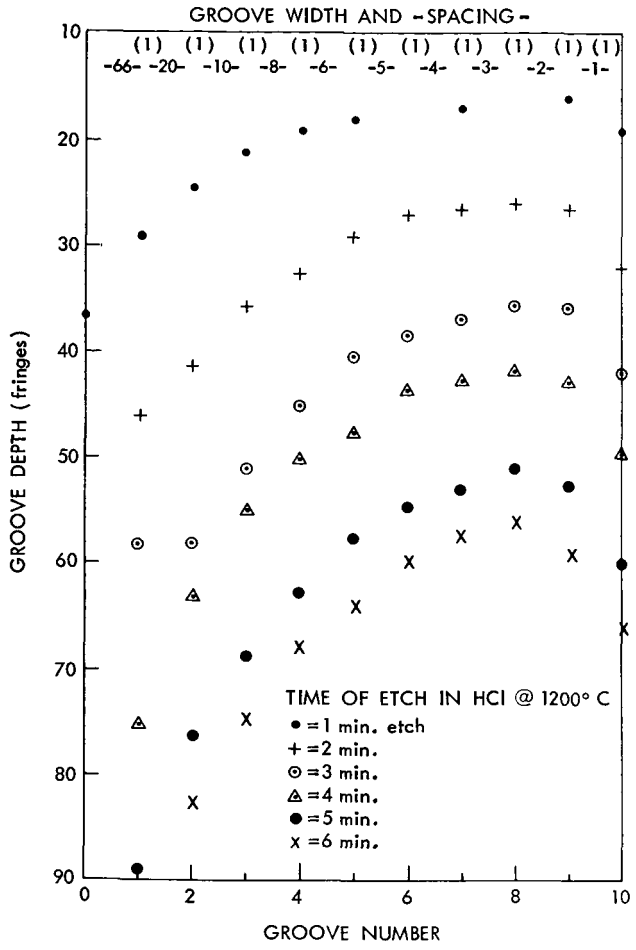


Figure B13—Groove depth vs. groove number, Experiment V, mask 141.

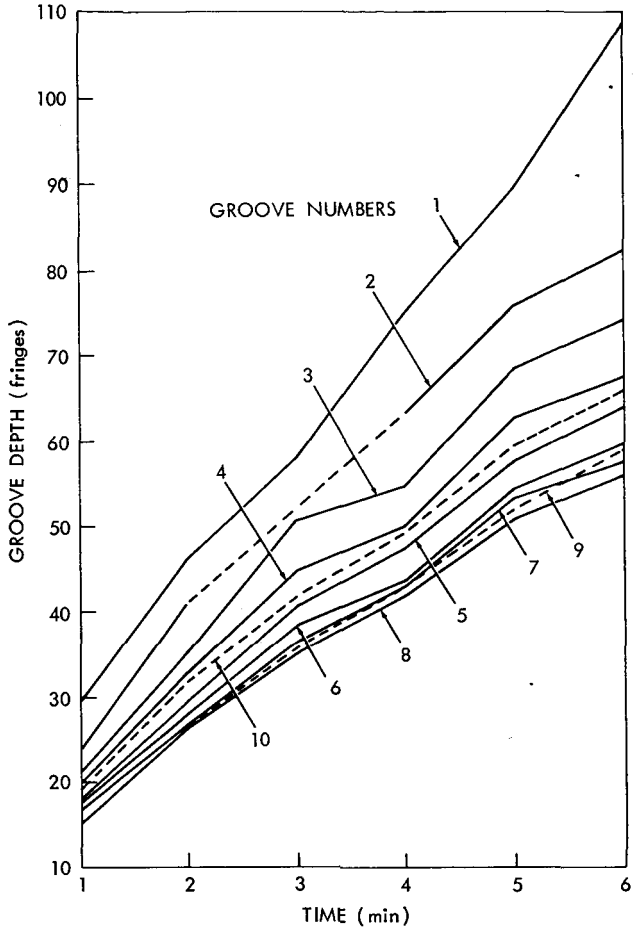


Figure B14—Groove depth vs. time, Experiment V, mask 141.

Experiment VI

To evaluate geometry effect on groove etch, tests were run on material prepared in a manner comparable to previous tests. Slices were then processed through standard photoresist steps except mask 141X was used. Mask 141X was made by two exposures with the mask plate at two positions 90° rotation from each other during the 50:1 deduction step in mask preparation (Figures B15 and B16). Three slices were then subjected to the standard HCl etch as shown in Table B6. Two slices were subjected to a chemical etch at room temperature. The formula for the etch is:

HNO_3, 84 cc; acetic acid (HAC), 8 cc; and HF, 8 cc.

During this etch, the slices were mounted on glass microscope slice plates with black wax (apiezon). The results of this test are also shown in Table B10. No groove depth measurements were taken on this series of tests.

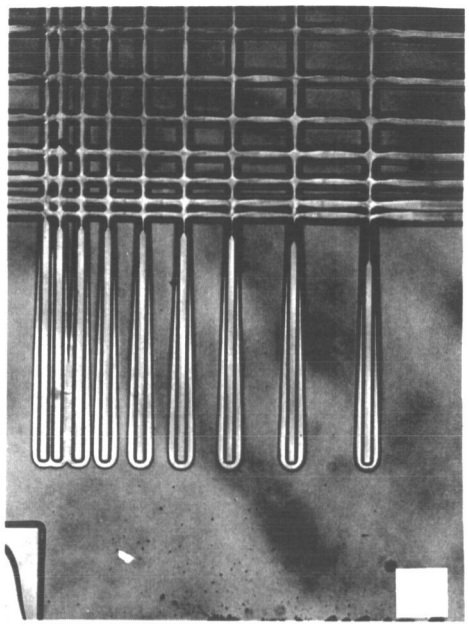


Figure B15—Crossed mask 141.

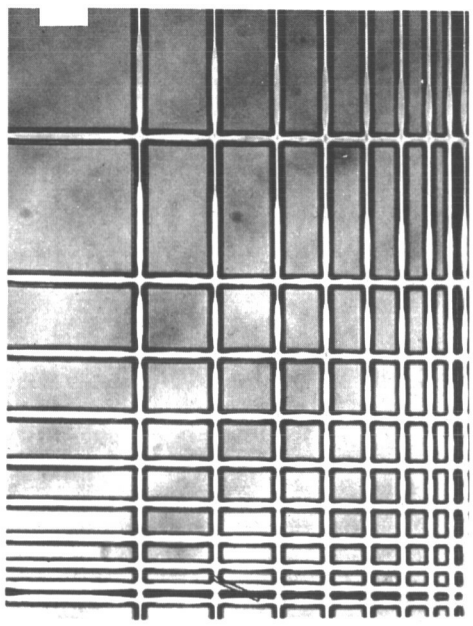


Figure B16—Crossed mask 141.

Table B10

Visual Evaluation of Experiment VI.

Experiment*	Run	Slice	Time (min)	Visual Evaluation (See Figures B15 and B16
VI-1	662	kk55	1	Oxide intact; grooves show variation in depth; spacing of crossed grooves affects geometry of groove bottoms at intersection of grooves; depths at intersections are variable.
VI-2	663	kk56	3	Etch undercutting deleted 1 mil spacing oxide; oxides intact; some pinholes; otherwise same as slice kk55.
VI-3	664	kk57	5	Oxide intact; various depth of oxide undercut apparent; 1 and 2 mil spacing deleted; smallest island left standing was 1 mil square where 2 mil square island should have been.
VI-4		kk58	15 sec	Surface at bottom of groove appeared heavily pitted; surface looked useable; light undercutting.
VI-5		kk59	30	All grooves and all islands appear useful; undercutting is heavy.

*The usual HCl etchant was employed in Experiments VI-1, VI-2 and VI-3. An HF: HAc: HNO_3 :: 8:8:84 etchant was used in Experiments VI-4 and VI-5.

Experiment VII

The purpose of Experiment VII was to evaluate effects of spacing width as well as groove width variation on groove geometry. The material was prepared in a manner similar to Experiment VI except that mask 138X was used (Experiment VI explains manner of mask preparation). All steps were identical to Experiment VI (see Table B11 and Figures B17 and B18).

Table B11

Visual Evaluation of Experiment VII.

Experiment*	Run	Slice	Time (min)	Visual Evaluation
VII-1	665	kk60	1	1 mil space deleted at end of groove; oxide intact; spreading of groove indicates that smallest useable surface width is 2 mil; match-stick ends noted.
VII-2	666	kk61	3	Same as kk60 except different degrees of etching noted at intersection; match-stick ends more pronounced.
VII-3	667	kk63	5	2 mil square deleted; oxide relatively intact; some pinholes noted; smallest useable island is 3 mil square (now size is approx. 1 mil square with rounded corners); heavy match-stick effect.
VII-4		kk64	15 sec	1 mil square looks good; oxide intact; bottom locks good; no visible match-stick effect; no deletion of line or spaces.
VII-5		kk62	30 sec	Similar to Test VI-5 (Table 6); however undercutting appears to be greater.

*The usual HCl etchant was employed in Experiments VII-1, VII-2 and VII-3. An HF: HAc: HNO_3 : : 8:8:84 etchant was used in Experiments VII-4 and VII-5.

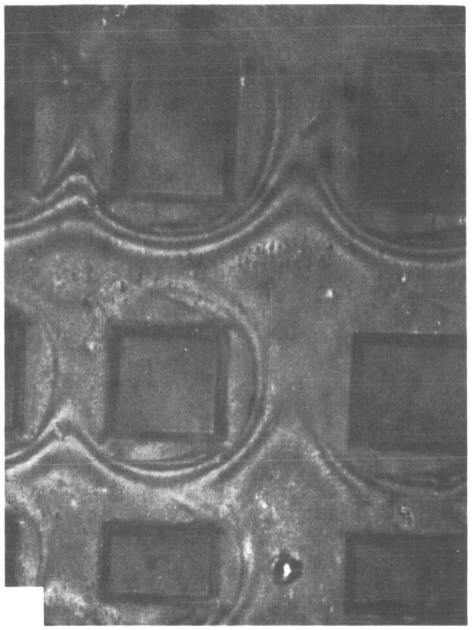


Figure B17—Crossed mask 138 showing depth variation at groove crossings.

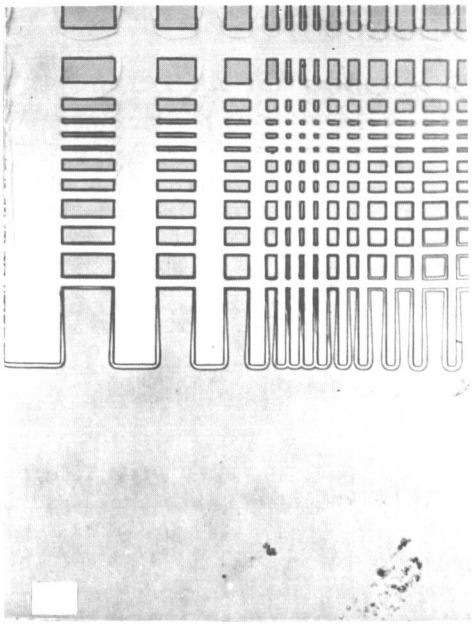


Figure B18—Crossed mask 138.

Table B12

Temperature vs. Etch Rate, Experiment VIII.
(HCl flow rate = 11 cm; H_2 flow rate = 6.5 cm (ca. 4% HCl)

Experiment (Run) /Nominal Temp./	Pyrometer Temperature (°C)	Slice	Resistivity (Ω-cm)		Difference, $\Delta\rho$ (Ω-cm)	Thickness (μ)		Difference, $\Delta X(\mu)$
			Before	After		Before	After	
VIII-1	1105°	α 5	106.3	83.4	-22.9	268	256	-12
(671-4)	1120°	α 6	104	77.5	-26.5	275	256	-19
/1100°C/	1125°	α 7	114	98.1	-16.3	273	267	- 6
	1140°	α 8	104	89.8	-14.2	246	229	-17
VIII-2	1150°	α 9	112	109	- 3	265	256	- 9
(672-4)	1165°	α 10	106	100	- 6	268	257	-11
/1150°C/	1170°	α 11	106	108.2	+ 2.2	260	248	-12
	1190°	α 12	107	115	+ 8	270	256	-14
VIII-3	1210°	α 13	111	109	- 1.3	265	257	- 8
(673-4)	1220°	α 14	110	111	+ 1	267	263	- 4
/1200°C/	1240°	α 15	112.2	97.2	-15	266	260	- 6
	1250°	α 16	109	95	-14	274	266	- 8
VIII-4	1230°	α 17	104	77	-27	242	230	-12
(674-4)	1240°	α 18	104	106	+ 2	262	248	-14
/1250°C/	1255°	α 19	108.2	128.2	+10	271	266	- 5
	1260°	α 20	110.8	133.8	+23	269	259	-10

Experiment VIII

The purpose of Experiment VIII was to check temperature vs. etch rate correlation. A series of tests were run at 1100°C, 1150°C, 1200°C, and 1250°C. Ambient mixture was H_2 at a setting of 6.5 cm and HCl at a setting of 11 cm. Probably because the method of measuring thickness was too gross, results of the test were not clearly understood.

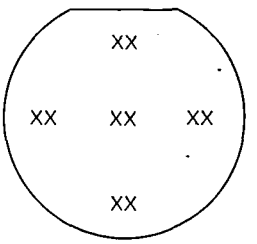


Figure B19—Locations on slices where resistivity and measurements were made.

Slices were measured for both resistivity and thickness parameters at the five places noted on Figure B19. Measurements were then averaged to give the recorded reading. Slices were ordered according to their number, i.e. lowest number was first on the last reading from left to right. Worst possible temperature profiles are shown in Table B12.

Experiment IX

Experiment IX consisted of gas flow and composition tests. Ten slices were used from runs 681-5 and 682-5. All were N -100 Ω-cm material. They were vapor etched 15 minutes at 1200°C. The layer was epitaxially deposited doped with diborane for 10 minutes at 1125°C. Oxide was then grown for 15 minutes; all slices were given 141 mask (not crossed) by standard photoresist processes. Grooves were etched for 3 minutes at 1200°C by the same HCl etch procedure as in prior tests except for variations of concentrations and flow as noted in Table B13. Apparently

Table B13

Visual Evaluation of Gas Flow Make-up, Experiment IX.

Experiment (Run)	HCl Setting (cm)	H_2 Setting (cm)	Slice	Evaluation
IX-1 (685-2)	Twice HCl Concentration 9	6.5	α 24	Oxide badly pitted; undercutting bad; deleted 1 and 2 mil space
			α 25	same as α 24.
IX-2 (686-2)	Half HCl Concentration 6	6.5	α 26	No undercutting; very little match-stick effect;
			α 27	1 mil spacing deleted; pitted oxide.
IX-3 (687-2)	Twice H_2 Concentration 11	12.5	α 28	Oxide slightly pitted; bad oxide.
			α 29	Oxide slightly pitted; bad oxide.
IX-4 (688-2)	Standard Control Run 11	6.5	α 30	1 mil line deleted; bad oxide
			α 31	1 and 2 mil line deleted; bad oxide.
IX-5	Half H_2 Concentration 11	3.5	α 32	1, 2, and 3 mil space deleted; very badly pitted.
			α 33	1, 2, and 3 mil space deleted; very badly pitted.

Note: Slices α 24 through 28 etched for 25 minutes during photoresist window cut; slices α 29 through α 33 for 30 minutes—probably too long for this thick an oxide.

the masking oxide as grown could not withstand the long time etch during photoresist operation as well as the long HCl etch. (Wafers were etched too long in photoresist.)

Inasmuch as total gas flow varied during etch time, results are inconclusive yet they show that etch is dependent on concentration. The erratic nature of the half flow of hydrogen in Test IX-5 was probably due to the erratic flow rate as well as the higher concentration. There is also the possibility that improper mixing added to the degree of deviation from normal flow results (Figures 12 and B20 and Table B14).

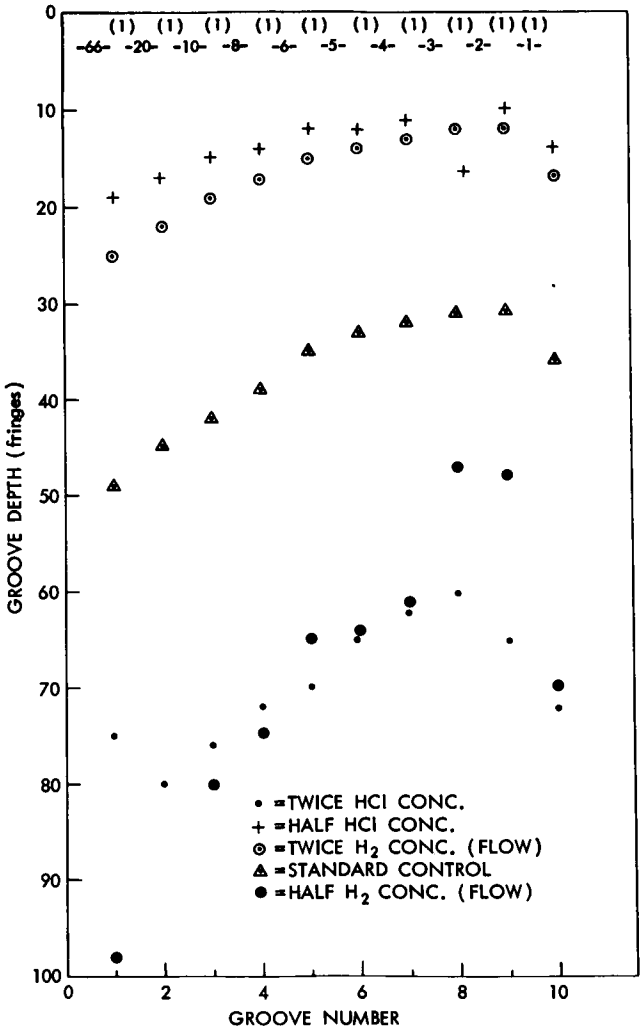


Figure B20—Groove depth vs. groove number, Experiment IX.

Table B14

Groove Depth Measurement of Experiment IX.

Experiment	Run	Slice	Flow HCl (cm)	Flow H_2 (cm)	Groove Number									
					1	2	3	4	5	6	7	8	9	10
	Twice HCl Concentration													
IX-1	685-2	α 24	9st. st.	6.5g	75	80	76	72	70	65	62	60	65	72
	Half HCl Concentration													
IX-2	686-2	α 26	6	6.5g	19	17	15	14	12	12	11	10	10	14
	Twice H_2 Concentration													
IX-3	687-2	α 28	11	12.5g	25	22	19	17	15	14	13	12	12	17
	Standard													
IX-4	688-2	α 30	11	6.5	49	45	42	39	35	33	32	31	31	36
	Half H_2 Concentration													
IX-5	689-2	α 32	11	3.5	98	X	85	80	65	64	61	47	48	70

Experiment X

The purpose of Experiment X was to study the effects, if any, of emissivity on the etch rate of silicon. In this test, wafers prepared as in previous experiments were given mask 141 photoresist treatment to cut windows. Slices were then loaded onto a boat and another boat (envelope and susceptor) was placed over the slices. The upper boat was separated from the lower boat by 1/4" quartz spacers. Slices were heated to 1200°C and HCl and H_2 were introduced to the slices as in previous tests. Groove depth was measured and found to be variable in the same manner as all other mask 141 slices and dependent upon spacing. Comparison of slices from this test and a standard 3 minute test slice kk67 from Test V is given in Table B15.

Table B15

Comparison of Groove Depths of Slices X-34 and kk67.
(groove depth in fringes)

Slice	Groove Number									
	1	2	3	4	5	6	7	8	9	10
X-34	43	36	31	30	27	24	23	22	22	30
kk67	58	51	45	$40\frac{1}{4}$	$38\frac{1}{4}$	$36\frac{1}{4}$	$36\frac{1}{4}$	$35\frac{1}{4}$	36	42

Groove depth of deviations are probably caused by inability to control temperature exactly. Inasmuch as groove depths showed a parallel dependence on spacing in all experiments using mask 141 and assuming that emissivity difference were nullified by the upper boat in Experiment X, there must be some other cause for groove depth variations.

Experiment XI

Experiment XI was conducted to verify emissivity study results from Experiment X and ascertain effects on wide groove bottoms. As in all previous runs, the wide grooves showed an upward curving bottom (Figures B13 and B21). Experiment XI was run exactly as Experiment X except that slices were prepared using mask 138. Groove depths results are shown and a comparison is made with slice ff37 from Experiment 2 given in Table B16.

Table B16

Comparison of Groove Depth of Slices α 38 and ff-37(C).
(groove depth in fringes)

Slice	Groove Number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
α 38	36-18-28	30-20-26	26-19-24	25-21-24	26-23-25	25-24	24	24	25	27	30	34	40	48	60
ff-37(C)	50-22X	36-24X	31-23X	28-22X	27-23	30	29	28	28	30	35	40	45	51	64

Again temperature or concentration variations can explain the differences between the groove depths of the two runs; however, the curved groove bottoms of the runs are similar.

Some similarities detected in all wide groove experiments using mask 138 are: The wider the spacing between grooves, the deeper the edges of grooves; the nearer edges of adjacent wide grooves are of comparable depth, while opposite edges of these adjacent grooves show large comparative differences. This leads us to conclude that the spacing between grooves plays a greater role in depth determination than groove width (Figure B22).

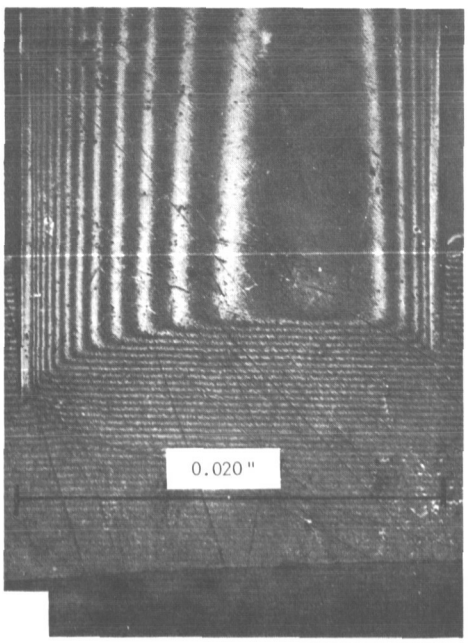


Figure B21—Curved bottoms of wide grooves.

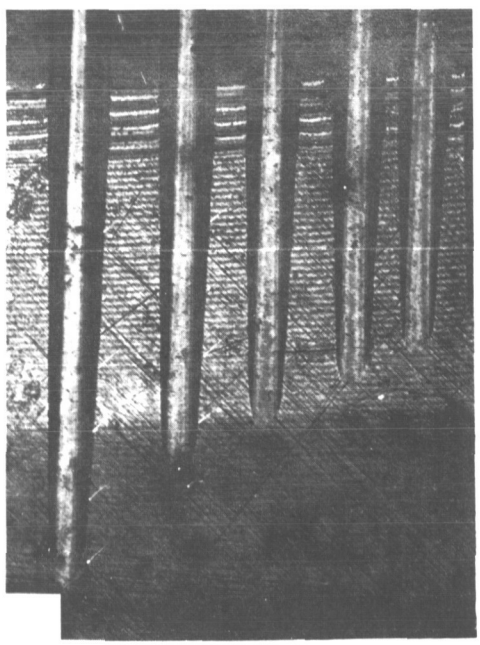


Figure B22—Depth variation of uniform width grooves with different spacing.

Experiment XII

Experiment XII was conducted to verify Experiment X and XI. Slices prepared in standard manner preparatory to groove etching were placed on a quartz boat without an RF susceptor inserted and were covered by a boat with a susceptor as in Tests X and XI. Tests were inconclusive, as only minimal etching was detectable after heating and HCl etch. Apparently a temperature sufficient to activate the etch was not attained.

Mechanisms of Etching

The etching of silicon by HCl is a reversible reaction:

$$Si + 4HCl \rightleftharpoons SiCl_4 + 2H_2 .$$

Glasstone* states, "By means of the equilibrium constant and Van't Hoff's equation it is possible to determine quantitatively the influence of pressure and temperature on the position of equilibrium in a reversible reaction. The same conditions may be reached in a qualitative manner by the principle of *mobile equilibrium* developed independently by H. Le Chatelier (1885) and F. Braur (1886) which may be stated in the following form: If a change occurs in one of the factors, such as temperature or pressure, under which a system is in equilibrium, the system will tend to adjust itself so as to annul, as far as possible, the effect of that change.

If the temperature is raised that reaction will occur in which heat is absorbed, whereas a lowering of temperature will move the equilibrium in the direction of the exothermic reaction. This principle which can be derived from the second law of thermodynamics is of general applicability to all systems in equilibrium and is not restricted to chemical reaction."

The etching reaction is exothermic and temperature will tend to increase at the surface of a slice of silicon:

$$Si + 4HCl \rightleftharpoons SiCl_4 + 2H_2 + 45.12 \text{ Kcal/Mol} .$$

As the temperature increases, the reaction will tend to equilibrate by shifting to the left i.e., slowing down. However at the edges of the wide grooves (Tests I, II, III, IV and XI), we notice that the reaction apparently proceeds at a faster rate than at the middle portion. This is probably caused by heat loss or transfer through the groove wall into that portion of the silicon slice under the oxide mask. The greater expanse of the exposed surface will tend to radiate heat from the silicon slice and keep the temperature of the groove edge lower than the middle portion. This mechanism explains the tendency to etch deeper at the edge than at the middle of a wide groove.

*Glasstone, S., "The Elements of Physical Chemistry," New York: D. Van Nostrand Co., 1946.

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