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SUPERIOR PHOTOENGRAVING PROCESS FOR SEMICONDUCTOR DEVICES

by C. J. Taylor

Prepared by
WESTINGHOUSE ELECTRIC CORPORATION
Baltimore, Md.
for Goddard Space Flight Center

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ABSTRACT

An investigation of the preparation of a silicon wafer surface prior to the application of photoresist to improve the resist adhesion is reported. Several process variations for obtaining oxide surfaces are investigated and correlated with resist adhesion. Methods of mechanically and chemically conditioning the oxide-passivated surface of the wafer to improve the adhesion of resist are investigated. The effects of varying the resist coating thickness and the use of various chelating agents, wetting agents and surfactants to find a linkage to bond the open chain-end of the resist to the surface of the oxide are studied. Procedures are evolved, and those used in the testing program are described. In this report, the use of Kodak Metal Etch Resist as a silicon dioxide masking agent is investigated, and the effects of additives and of a new developer, as well as those of ambient variations are outlined and their importance described.

CONTENTS

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INTRODUCTION

Improvements in techniques for photoengraving of silicon wafers have generally reduced line widths that are useable on a reproducible basis to 0.00025 in. Now, however, more complicated devices are a possibility and the device designer is demanding a means of producing them. Some of the more complicated structures from the photoengraving standpoint include sensors where it is desirable to reduce element size to improve image resolution. Line widths of 0.0001 in. are desirable, as they would also be in high frequency devices.

Although element size is decreasing, the complete device is growing and may cover an area up to the size of a wafer. Not only must the resolution be good across the device but pinholes become more important. A single hole, properly placed in the resist, could ruin a complete section of a device.

Since the number of pinholes is *inversely* related to resist thickness, and resolution is *directly* related to resist thickness, a resist must be selected that will provide good resolution even when it is thick enough to be comparatively pinhole free. The resist must also be capable of withstanding the oxide etch with a minimum of undercutting, i.e., the etch factor (Reference1) must be as large as possible. Etch factor is defined as the distance etched downward divided by the distance etched under the resist. Even if the resolution of the resist is sufficient to meet this requirement, this is of little importance if the line cannot be reproduced through the oxide.

The principal purpose of this investigation is to examine various parameters that might affect adhesion of the resist. This has become necessary because no one has developed a resist for use with semiconductor devices. A number of resists have been used but all have been found lacking in at least one respect (Table 1).

An examination of these resists shows that only two are inherently suitable for semiconductor use. These are Kodak Metal Etch Resist (KMER) and Kodak Thin Film Resist both of which possess better adhesion than other resists.

*Prepared under contract NAS 5-2755.

A method of modifying KMER by the elimination of the globular matter (Appendix A) makes it appear capable of meeting the requirements of high resolution photoengraving. Factors that are beyond the scope of this report, such as wafer flatness, mask quality, alignment and contact printing conditions, etc., have not been examined here. In addition, no consideration has been given to oxides that have been contaminated with dopants.

Table 1

Some Resists and Their Major Defects.

Resist	Principal Defect
Kodak Metal Etch Resist	Contains globular matter, poor resolution
Kodak Photo Resist	Pinholes, poor adhesion
Kodak Ortho Resist	Pinholes, poor adhesion
Kodak Thin Film Resist	Entrained air causing pinholes
Positop	Poor adhesion
Phenol Formaldehyde	Poor adhesion, extended processing time

PROCEDURES

Preparation of the Resist

*Electrophoresis**

Lot 6409-5 of KMER was visually different from other lots of resist in that the color was much lighter, although the viscosity of the untreated resist was the same as other lots. The following tests were run in an attempt to clear the resist.

The resist was mixed 3 parts KMER to 1 part KMER thinner and placed in a 400-ml beaker. A nickel electrode was placed in the bottom of the beaker with a nickel cathode above separated by a 3-inch phenolic insulator. High voltage teflon insulated leads connected the electrodes to the dc power supply. Masking tape covered the beaker to prevent evaporation. A voltage of 8 kvdc was applied for three days. The voltage was increased by 2 kv every third day until 14 kv was reached.

This standard procedure had separated all previous lots of resist but this lot failed to separate. Eight kv was reapplied to the resist for seven days. This separated the resist but the yield of 20 percent was considered too low to be practical. A new batch of resist was mixed one part KMER to one part KMER thinner. It was expected that the thinner resist would allow the sludge to migrate to the bottom of the beaker giving a higher yield. This did not occur so electrophoresis treatment was abandoned in preference to centrifuging, although electrophoresis resist is generally preferred to centrifuged resist, since the amount of KMER thinner required to clean the resist is not as great.

Centrifuging

The resist was mixed one part KMER to one part KMER thinner and placed in four 50-cc pyrex centrifuge tubes. The tubes were covered to prevent evaporation and then loaded into the centrifuge. The resist was centrifuged for 16 hours at 3000 rpm. The tube caps were removed and the

*Electrophoresis treatment of Kodak Metal Etch Resist is a process proprietary to Westinghouse Electric Corporation.

centrifuging was continued until the resist had thickened to the proper viscosity. The resist may also be thickened by heating to 65 °C and allowing the solvent to evaporate without injury to the resist. Past experience has demonstrated there is no difference between electro-resist and centrifuged resist when testing for adhesion, resolution or pinholes.

Preparation of the Wafers

The silicon wafers used for these experiments were one to two ohm-centimeter, n type, 7/8 in. in diameter. The wafers were lapped from a thickness of 0.017 in. to 0.013 in. using 12-micron Al_2O_3 grit. They were lapped to 0.011 in. using 3-micron Al_2O_3 grit and polished to approximately 0.010 in. using one-micron Al_2O_3. The wafers were etched in HCl gas to a thickness of 0.009 in. to remove the sharp edges on the wafers. Rounded edges aid in the prevention of resist buildup at the edge of the wafer during the resist coating operation.

Oxidation

For all oxidations, a furnace was used in which oxygen and nitrogen were supplied so that they could be admitted to the tube either directly or through a controlled temperature water supply. When water was supplied to the tube to act as a carrier, the oxygen and nitrogen were bubbled through the water.

The wafers were cleaned in concentrated sulfuric acid heated to 180 °C, placed in 48 percent hydrofluoric acid to remove any oxide, rinsed in deionized water, and blown dry before being placed in the furnace tube. Dry oxygen was passed through the tube for five minutes to allow the wafer to come to temperature and to help initiate a uniform oxide growth before the desired gases were introduced. Dry gas was also passed through the tube for five minutes before removing the wafers to prevent water condensation in the tube from spattering the wafer. The formula used for the oxidation process was

$$5 \text{ min } O_2 + X \text{ min } (H_2O \text{ @ } T°C + Y \text{ cc/min } O_2 + Z \text{ cc/min } N_2) + 5 \text{ min } (Y \text{ cc/min } O_2 + Z \text{ cc/min } N_2).$$

In addition to the above variables, an oxide series was grown which eliminated the admission of water vapor to the tube. After removal of the wafers from the furnace tube, they were stored at 190 °C at room atmosphere for a minimum of 30 minutes before processing by photoengraving.

Photoengraving

Wafers were processed through photoengraving on the same day that the oxide was grown. Wafers were coated with modified KMER with a viscosity of 85 centipoises. Viscosity measurements were made using a falling ball viscosimeter. The resist was applied through a syringe equipped with a 0.8 micron filter. Spin coating was on the major axis of the wafer at 6000 rpm with a lapsed time to full speed of five seconds. The resist was dried at a temperature of 120 °C for 12 minutes. Exposure of the resist was closely controlled by calibrating the light flux density

using a filter which has approximately the same transmission curve as the sensitivity curve of KMER. Developing was accomplished by spraying on the KMER developer followed by a spray rinse of alcohol-KMER thinner solution. The wafers were post-baked at 180°C for 20 minutes and then etched.

Measurements

Wafers were etched in an ammonium fluoride-buffered hydrofluoric acid solution. A determination of etch rate was made so that the etch factor could be established. One wafer from each of six oxidation runs was dipped for ten seconds in the etch solution before being coated with resist. This created a surface that was a poor adherent for the resist and which caused excessive undercutting (Figure 1). The wafers were aluminized and a fringe measurement was taken (Figure 2). The aluminum was removed and the oxide etched until just removed from the wafer. It was observed that oxides that had been aluminized etched from 15 to 30 seconds sooner than oxides from the same run that had not been aluminized. The average etch rate was established at 750 A per minute for oxides not aluminized. Maximum deviation was 40 A per minute.

Wafers were etched in cooled baths at 19°C and 5°C. The rates of etch for these temperatures were compared to that of the standard etch temperature of 25°C. Figure 3 shows the change in etch rate with change in bath temperature. The etch factor was also compared for the various temperatures. It was found to be constant for all bath temperatures.

The amount of undercut obtained during the time to etch through the oxide was small. The difference between the amount of undercut obtained in etching different oxides was even smaller - on the order of 30 millionths inch. Etch times were arbitrarily extended to increase the amount of undercut so that the measurements made would be more accurate. The method employed was

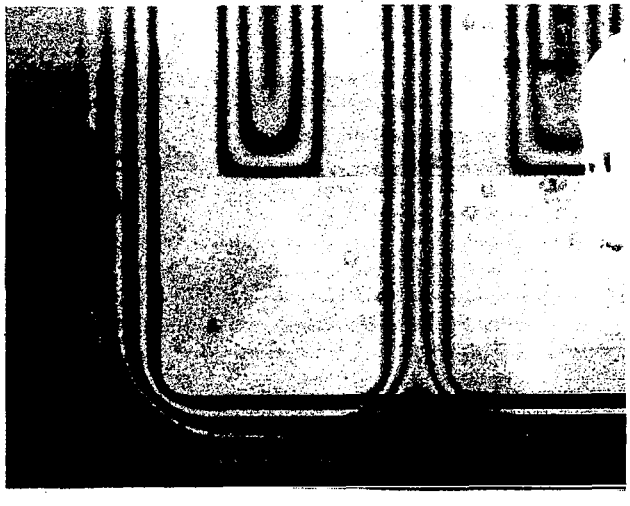

Figure 1—Etched oxide showing undercutting of resist by etch solution (500X).

Figure 2—Aluminized wafer showing thickness of oxide (3600 A) by fringe measurement.

to etch one wafer 20 minutes and a second wafer 30 minutes. Two measurements were taken on each wafer. These four measurements were added together and converted into the amount of undercut equivalent to a 10 minute etch.

A test was made to determine whether the rate of undercut varied with time. For the first fifteen tests, similarly processed wafers were etched for 10 minutes, 20 minutes and 30 minutes. It was found that at 20 minutes the rate of undercut had increased 11 percent and at 30 minutes the rate of undercut had increased by 17.4 percent over a ten minute etch. This factor was used in converting the amount of undercut obtained to that expected for a 10 minute etch.

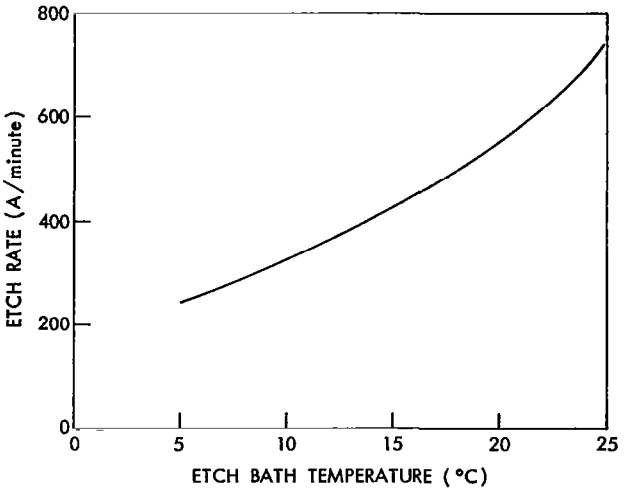

Figure 3—Etch rate of steam-grown silica films in nine percent NH_4F-buffered HF.

Measurements were made at a magnification of 500X using a microscope with a micrometer eyepiece. The resist line width which was 0.0004 inch was first measured and subtracted from the line width as measured in the oxide. Figure 4 shows the resist torn away exposing the oxide line underneath for a wafer which had been etched for thirty minutes.

The proper comparison of resists that differ because of varying viscosities, spin speeds or accelerations requires that the coating thickness be known. To determine coating thickness a wafer was coated on the spinner and baked dry. It was supported with the plane of the wafer vertical and one half submerged in KMER developer for four minutes. The wafer was removed from the developer, rinsed in running water, blown dry with air, and baked at 120 °C for ten minutes. A second bake of 180° C for thirty minutes hardened the remaining resist. A 3000 A coating of aluminum was vacuum deposited over the resist and a fringe measurement was taken (Figure 5). A buildup of the resist occurred at the surface of the developer as shown by the reverse in the fringe line. The measurement of the thickness of the resist was obtained by subtracting the fringes on one side of the buildup from the fringes on the second side. Note that on the surface with resist underneath, the fringe lines break away sharply. The fringe continues across the wafer in a straight line indicating that the resist has not absorbed vapors from

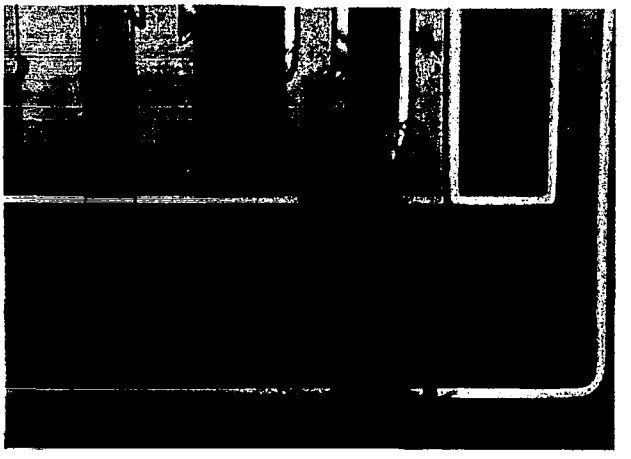

Figure 4—Resist torn away from wafer exposing etched lines (500X).

the developer which would have made it become swollen.

Figure 5—Fringe measurement of resist thickness (16 - 9 = 7 fringes, or 1.7 microns).

DISCUSSION

The discussion is divided into three parts: Thermal Oxides, Epitaxial Oxides, and Resists. The investigations of thermal oxides and epitaxial oxides were conducted using the standard processing specifications for the Westinghouse Aerospace Division, Solid State Systems Technology Laboratory. The resist investigations used the same processing specification except where a notation has been made of the variation. Two wafers processed using the standard process were included with each test conducted under Resists.

Thermal Oxides

The examination of the furnace parameters was made with no attempt to minimize undercutting. It was believed that if an etch factor of 1 were achieved this would be a theoretically minimum undercut, that points on the curve would level out, and that useful information would be lost. Consequently, arbitrary furnace conditions were selected throughout the test to give results somewhat less than optimal.

The curves shown in Figures 6, 7 and 8 compare the adhesive qualities of photoresist to oxides grown at two temperatures. The curves in Figure 6 could have been drawn as a straight line and still have maintained the experimental error of about 7×10^{-6} inches. However, since the direction of these points was consistent and the deviation of the remaining points was very close to the line it is assumed that the case chosen does exist. This same reverse was also observed in the oxide grown in a dry atmosphere (Figure 8).

Data taken comparing gas flow rates at 1050°C and 1200°C indicated that these oxides behaved differently at the two temperatures. No change in adhesion was noted at 1200°C but an increase in adhesion was indicated with a decrease in gas flow at 1050 °C. These tests were rerun to determine if a difference did exist. The new tests were not affected by the gas flow so it was concluded that gas flow did not affect adhesion, but rather that the indication of adhesion was caused only by experimental error.

A new problem arose from these new tests. Although the 1200 °C curve closely followed the original curve, the 1050 °C curve had improved appreciably over the original curve. The 1050 °C tests were run a third time and it again followed the improved curve (Tests 13 through 24, Table 2).

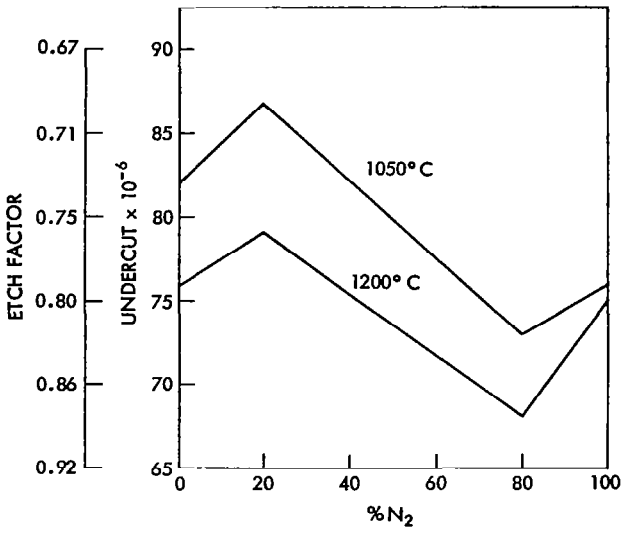

Figure 6–Effect of gas composition (O_2 + N_2) on adhesion of oxide grown in steam atmosphere.

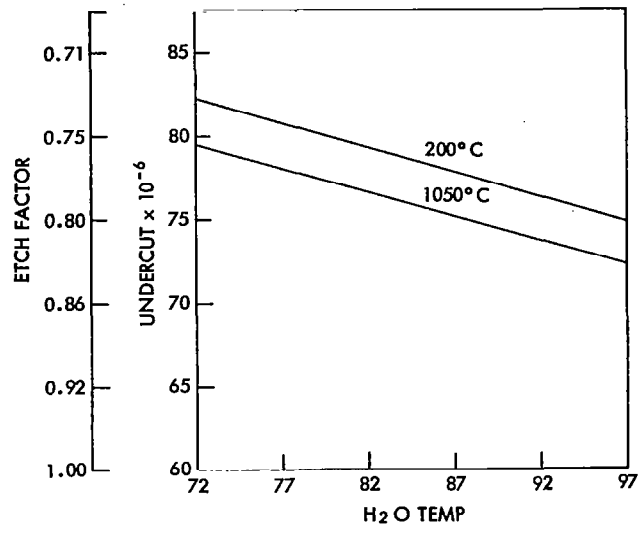

Figure 7–Effect of water temperature on adhesion.

A complete check was made on all photoengraving process steps including etch rate. The only variable that could be found was that the relative humidity in the laboratory had changed from 60 percent to 30 percent. This occurred during the one day period during which the furnace had been changed from 1200°C to 1050°C.

To examine the humidity condition, a humidity chamber was supplied with a supersaturated solution of ammonium chloride and potassium nitrate. This solution gave a relative humidity of 71 percent at 25°C. Two wafers from Test 69 were placed in this chamber for 15 minutes immediately after removal from the oxidation furnace. The wafers were again placed in the humidity chamber for 5 minutes after removal from the 190°C pre-bake oven. They were immediately coated with resist and processed with two other wafers that had received the same oxidation but had not been placed in the humidity chamber. The relative humidity in the room was recorded at 34 percent using a combination hygrometer thermometer. Test 69

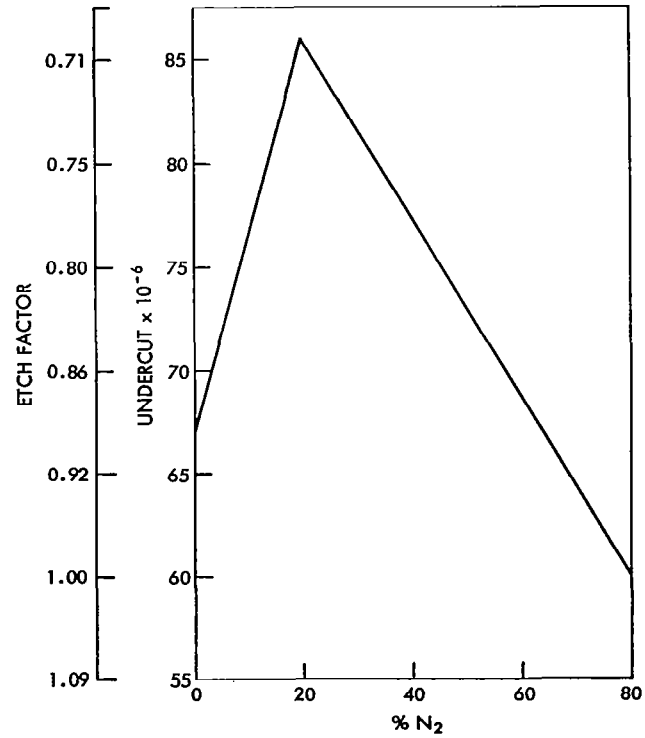

Figure 8–Effect of gas composition (O_2 + N_2) on adhesion of oxide grown in dry atmosphere.

Table 2

Adhesion to Thermal Oxides.

	Test	Oxidation Time (Minutes) "X"*	Furnace Temp. (°C)	Water Temp. (°C) "T"*	Oxygen (cc/min) "Y"*	Nitrogen (cc/min) "Z"*	Oxide Thickness (A)	Undercut For 10 min etch x (10^{-6} inch)
Gas Composition	1	80	1050	92	500	0	5400	82
	2	80	1050	92	400	100	5600	87
	3	80	1050	92	300	200	5600	82
	4	80	1050	92	200	300	5600	77
	5	80	1050	92	100	400	5300	73
	6	80	1050	92	0	500	5300	76
Water Temperature	7	80	1050	72	200	300	1500	76
	8	80	1050	77	200	300	3400	83
	9	80	1050	82	200	300	3800	94
	10	80	1050	87	200	300	4900	73
	11	80	1050	92	200	300	5600	77
	12	80	1050	97	200	300	6400	69
Gas Flow	13	80	1050	92	50	75	4900	69
	14	80	1050	92	100	150	5200	64
	15	80	1050	92	200	300	5600	77
	16	80	1050	92	300	200	6700	80
Gas Flow (Repeat)	17	80	1050	92	50	75		62
	18	80	1050	92	100	150		56
	19	80	1050	92	200	300		58
	20	80	1050	92	300	450		65
	21	80	1050	92	50	75	3800	62
	22	80	1050	92	100	150	4500	56
	23	80	1050	92	200	300	5300	56
	24	80	1050	92	300	450	5300	54
Gas Composition	25	45	1200	92	500	0	7100	64 These Tests
	26	45	1200	92	400	100		110 Thrown Out
	27	45	1200	92	300	200	6000	82 Resist Drying-
	28	45	1200	92	100	400	6400	99 Oven Set
	29	45	1200	92	0	500	6400	90 Too High
Gas Composition (Repeat)	30	45	1200	92	500	0	6400	76
	31	45	1200	92	400	100	6400	79
	32	45	1200	92	300	200	6400	76
	33	45	1200	92	200	300	6000	72
	34	45	1200	92	100	400	6000	68
	35	45	1200	92	0	500	5600	76
Water Temperature	36	60	1200	76	100	400		85
	37	60	1200	84	100	400		73
	38	60	1200	92	100	400		82
	39	60	1200	100	100	400		69
Gas Flow	40	30	1200	92	50	75	4100	83
	41	45	1200	92	100	150	6000	93
	42	45	1200	92	200	300	5600	87
	43	45	1200	92	300	450	6000	83

Table 2 (Continued)

Adhesion to Thermal Oxides.

	Test	Oxidation Time (Minutes) "X"*	Furnace Temp. (°C)	Water Temp. (°C) "T"*	Oxygen (cc/min) "Y"*	Nitrogen (cc/min) "Z"*	Oxide Thickness (A)	Undercut For 10 min etch x (10^{-6} inch)
Gas Flow (Repeat)	44	45	1200	92	50	75		80
	45	45	1200	92	100	150		91
	46	45	1200	92	200	300		80
	47	45	1200	92	300	450		78
	48	45	1200	92	450	675		89
Gas Composition (Dry Oxide)	49	16 hrs.	1200	None	1000	0	7100	105 Thrown Out-Oven Too High
	50	17 hrs.	1200	None	1000	0	7900	67
	51	16 hrs.	1200	None	800	200	6700	86
	52	16 hrs.	1200	None	600	400	5600	76
	53	16 hrs.	1200	None	400	600	5300	73
	54	16 hrs.	1200	None	200	800	4500	56
Oxide Conversion	55	45	1200	92	500	0	5600	82
Wafers From Test 55 Given Additional Treatment	56	4	1200	92	0	250		73
	57	8	1200	92	0	250		76
	58	12	1200	92	0	250		67
	59	16	1200	92	0	250		76
Wafers From Tests 41, 43, 50, 52, 53, 54 Given Additional Treatment	60 Wafer From Test:	5	1050	100	0	100		
	41							67
	43							67
	50							50
	52							60
	53							70
	54							60
	61	60	1050	100	400	100		
Wafers From Test 61 Given Additional Treatment	62	5	1050	100	100	400		99
	63	10	1050	100	100	400		94
	64	15	1050	100	100	400		90
Wafers From Test 65 Given Additional Treatment	66	5	1200	92	100	400		91
	67	10	1200	92	100	400		89
	68	15	1200	92	100	400		93
Effect of Humidity	69	80	1050	92	400	100		69 (34% RH) 67 (71% RH)

*Refers to formula for oxidation process, page 3.

shows there was no difference in resist adhesion between the two sets of wafers. The cause of the change in resist adhesion between the two curves could not be found.

One difference in oxide growth at the two temperatures was that the adhesive quantity of the 1200°C oxide could easily be improved while the 1050°C oxide could not be altered by post-furnace treatment. Special furnace conditions were used. Gas flow rates through water were established before the test began. Wafers were placed immediately in the hot zone of the furnace and immediately withdrawn. The five minute pre-treatment and post treatment used in the standard runs were eliminated. Gas compositions and water temperatures for these conversion tests were chosen to improve the adhesion qualities of the oxide.

Oxides grown at 1200°C were given a conversion treatment at temperatures of 1050°C and 1200°C (Tests 55-60, Table 2). Wafers represented both dry oxidations as well as steam oxidations. All wafers tested improved in adhesive qualities except that wafer from Test 32 which was already at the minimum etch factor of 1. The conversion furnace treatments were run from four to sixteen minutes. All changes taking place had been completed by the end of four minutes.

Oxides grown at 1050°C were given a conversion treatment of 1050°C and 1200°C (Tests 61-68 Table 2). There was no improvement in the adhesive qualities of these oxides after 15 minutes.

Epitaxial Oxides

A group of oxides was deposited on, rather than grown from, silicon wafers using the epitaxial reactor. After the wafers had been gas etched, a light epitaxial layer was deposited to provide a more uniform transition from the silicon to the oxide. The oxide was then deposited over the epitaxial layer. Hydrogen, silicon tetrachloride and carbon dioxide were passed through the epitaxial tube at elevated temperatures to give the following reaction:

$$3H_2 + SiCl_4 + 3CO_2 \longrightarrow SiO_2 + H_2O + 3CO + 4HCl \ .$$

The wafers were then processed in the same manner outlined under "Procedures" in the sections labeled "Photoengraving" and "Measurements."

Two principal problems were examined for solutions. The first was to find a procedure to grow an oxide that would be uniform across the wafer while controlling thickness. The second problem, and the one of major concern here, was to grow an oxide which would be receptive to the photoresist. The first tests consisted of varying the flow rate of silicon tetrachloride. It was found that an increase in the silicon tetrachloride flow increased the oxide thickness. However, there was an increase in oxide growth on the wafer from outside to the center with a heavier deposit on one side than on the opposite. There was no appreciable change in undercut as all wafers showed an undercut about twice that experienced on thermal oxides. A change in the flow rate of carbon dioxide did not appreciably change either the oxide thickness or the adhesive qualities of the oxide.

The temperature of the silicon tetrachloride was changed from room temperature to 4°C in an effort to give a more uniform deposit of the epitaxial oxide. At this reduced temperature, oxides were found to be quite uniform having no more than 300 A thickness variation across the wafer. Adhesion was not improved.

A conversion treatment similar to that given to the thermal oxides to improve adhesion was tried. After the epitaxial oxide was deposited, the hydrogen, silicon tetrachloride, and carbon dioxide were turned off and an atmosphere of nitrogen was supplied at a flow of 1000 cc per minute (Tests 17 and 18, Table 3). Time of nitrogen flow was varied to show the effect of nitrogen on the oxide. It was found that after ten minutes of nitrogen flow, the adhesion was as good as that of thermal-grown oxides.

An experiment involving a ten-micron, one-ohm-cm p-type epitaxial layer followed by an epitaxial oxide and nitrogen treatment, the same as Test 18, was conducted using four wafers. The wafers were coated with wax except for one small area at the edge of the wafer. One drop of 48 percent hydrofluoric acid was placed on the exposed oxide for 45 seconds to expose the epitaxial layer. The wax was then removed from the wafer and a 3000 A aluminum evaporation with the wafer at an elevated temperature was deposited on the oxide. Aluminum pads 3600 square mils in area were etched into the aluminum with one pad over the exposed epitaxial layer.

The aluminum pads were probed using a transistor curve tracer to find if any holes existed in the oxide. A current of 0.01 ma was used while varying the voltage on each capacitor from 0 to 200 volts. Thirty capacitors of each of the four wafers were tested with a yield of 100 percent.

Resists

Coatings and Exposures

The curves shown in Figure 9 give resist coating thickness for wafers coated on two spinners. These curves show that the time for a spinner to come to full speed is as important as the speed itself in determining resist thickness. The standard spinner represented by the solid lines had a lapsed time to the pre-set speed of from five to fifteen seconds depending on the pre-set speed. The special spinner had a lapsed time to the pre-set speed of less than one second.

The resist on all wafers that were coated using the special spinner was marked by globules of resist about 0.002 inch in diameter. These spots of resist would not print and gave imperfections in the etched line as shown in Figure 10. The resist was otherwise acceptable and the wafers were used to determine resist thickness and adhesion qualities. A comparison of the adhesion showed that the special spinner gave no appreciable change to the adhesive qualities of the resist over the standard spinner.

The effect of resist thickness on adhesion for two viscosities was examined. It was found that there was an improvement in adhesion for both viscosities especially as the resist thickness decreased. It was also observed that pinholes were etched in the oxide through the very thin (1.6

Table 3

Adhesion to Epitaxial Oxides.

Test	Epitaxial Growth				Oxide Growth					Oxide Thickness (A)	Undercut for 10 min. etch (x 10^{-6} inches)	N_2 Flow @ 1215°C (min.)
	EPI. Temp. (°C)	Dopant	Time (Min.)	H_2 Carrier Flow (1/min)	$SiCl_4$ H_2 Flow (cc/min)	$SiCl_4$ Flow (cc/min)	CO_2 Flow (cc/min)	Temp. (°C)	Time (Min.)			
1	1125	Boron	1	18.5	225	47.5 @ 15°C	338	1215	4	5000	150	
2	1125	Phos.	1	18.5	225	47.5 @ 15°C	338	1215	4	6400	140	
3	1125	Phos.	1	18.5	225	47.5 @ 15°C	338	1215	4	6700	130	
4	1125	Phos.	1	18.5	435	91.5 @ 15°C	338	1215	3	9000	140	
5	1125	Phos.	1	18.5	640	134 @ 15°C	338	1215	3	12000	120	
6	1125	Phos.	1	18.5	820	172 @ 15°C	338	1215	3	13000	110	
7	1125	Phos.	1	18.5	225	47.5 @ 15°C	475	1215	3	6000	150	
8	1125	Phos.	1	18.5	225	47.5 @ 15°C	612	1215	3	5600	160	
9	1125	Phos.	1	18.5	225	47.5 @ 15°C	738	1215	3	5600	120	
10	1125	Phos.	1	18.5	225	47.5 @ 15°C	1025	1215	3	6600	110	
11	1125	Phos.	1	18.5	225	47.5 @ 15°C	1855	1215	3	6400	110	
12	1125	Phos.	1	18.5	225	47.5 @ 15°C	2375	1215	3		120	
13	1125	Phos.	1	5.5	25	5.1 @ 15°C	413	1215	10	1900	240	
14	1125	Phos.	1	18.5	225	47.5 @ 15°C	1025	1000	4		300	
15	1125	Phos.	1	18.5	820	172 @ 15°C	263	1215	3	19500	120	
16	1125	Phos.	1	18.5	380	49 @ 4°C	413	1215	3	5300	120	
17	1125	Phos.	1	18.5	380	49 @ 4°C	413	1215	3	5300	99	5
18	1125	Phos.	1	18.5	380	49 @ 4°C	413	1215	3	5300	72	10

micron) resist coating. Differences in the adhesion between the 65 cp resist and the 85 cp resist were traced to a change in relative humidity (Tests 2 and 3, Table 4). Comparison of readings taken from Test 2, Table 4 and readings from Table 2 whose tests were performed in a relative humidity of 60 - 65 percent indicate that there is no difference in adhesion between 65 cp and 85 cp resist of equal thickness.

The effect on exposure of the resist to ultraviolet light indicated that with a reduction of 25 percent from standard exposure, narrow lines became somewhat wavy but adhesion was not affected. Exposures of 250 percent of standard exposure had no appreciable effect on resist adhesion. Excessive heat from the exposure lamp due to the long exposures was overcome by passing the light through a layer of water which absorbed the infrared energy.

It can easily be demonstrated that the hydrophilic nature of silicon dioxide will cause absorption of enough moisture in a humid atmosphere to affect adhesion of KMER. A 200°C pre-bake for 30 minutes removes this troublesome moisture. This condition was partially examined in the discussion of thermal oxides. It was shown that the short time required to remove the wafer from the furnace and coat it was not enough time for the oxide to absorb moisture. Since there appeared to be a direct correlation between humidity and adhesion even when pre-bake was used, the effect of humidity on the resist was examined. Wafers were processed in an atmosphere having less than 30 percent relative humidity except for the time that they were being spin-coated. Air at a humidity of about 60 percent was passed over the spinner as the coating process was being carried out. These wafers were compared to wafers that were processed

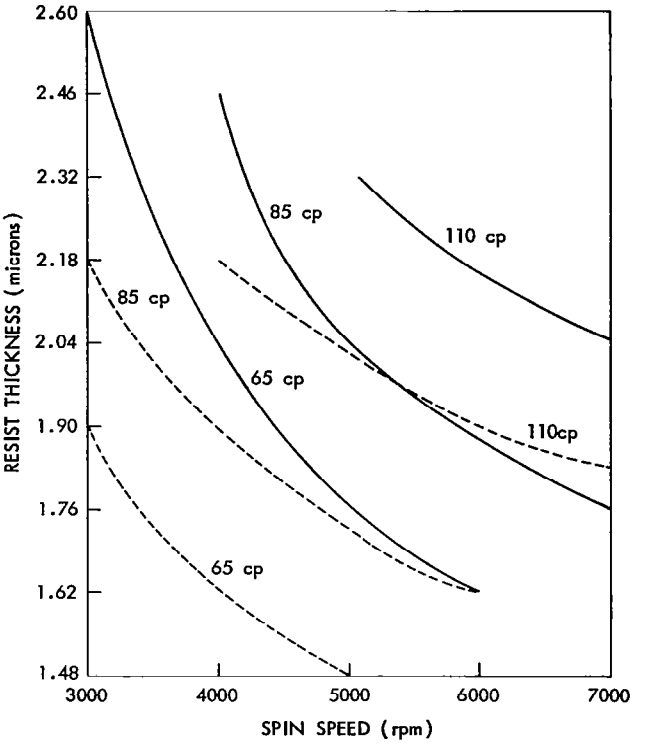

Figure 9—Coating thickness for modified KMER with KMER thickness in microns as a function of spin speed showing viscosity of resist; ----- shows resist coated on spinner with lapsed time to full speed of less than one second; _____ shows resist coated on spinner with lapsed time to full speed of five to fifteen seconds.

Figure 10—A defect caused by improper coating of the resist.

Table 4

Effect of Process Change on Adhesion.

Test	Oxidation Time (minutes) "X"*	Furnace Temp. (°C)	Water Temp. (°C) "T"*	Oxygen (cc/min) "Y"*	Nitrogen (cc/min) "Z"*	Undercut (10^{-6} inches)	Remarks
1	80	1200	92	400	100		
						86	Standard Spinner 85 Cp Resist 6000 RPM
						94	Special Spinner 65 Cp Resist 4000 RPM
						94	Special Spinner 85 Cp Resist 5000 RPM
						87	Special Spinner 110 Cp Resist 7000 RPM
2	80	1200	92	400	100		RH = 65%
						74	Thin Resist had Pinholes; 65 Cp Resist 6000 RPM
						86	5000 RPM
						83	4000 RPM
						91	3500 RPM
3	80	1050	92	400	100		RH = 35%
						55	85 Cp Resist 8000 RPM
						59	7000 RPM
						65	6000 RPM
						63	5000 RPM
							Resist Thick, Lines Poor; 4000 RPM
4	80	1050	92	400	100		
							85 Cp Resist 6000 RPM
						79	Narrow Lines where Wavy; Exposure Time: 15 sec.
						83	17-1/2 sec.
						76	Standard Exposure, 20 sec.
						78	22-1/2 sec.
						71	25 sec.
5	80	1050	92	400	100		RH = 33%
							85 Cp Resist
						63	Standard Exposure; Exposure Time: 20 sec.
						57	30 sec.
						61	40 sec.
						58	50 sec.

Table 4 (Continued)

Effect of Process Change on Adhesion.

Test	Oxidation Time (minutes) "X"*	Furnace Temp. (°C)	Water Temp. (°C) "T"*	Oxygen (cc/min) "Y"*	Nitrogen (cc/min) "Z"*	Undercut (10^{-6} inches)	Remarks
6	80	1050	92	400	100		
							85 Cp Resist
						64	Wafers Coated in RH of 28%
						75	Wafers Coated in RH of 55%
	7	80	1050	92	400	100	
							85 Cp Resist
						51	RH of 22%
						75	RH of 62%
8	45	1200	92	400	100	96	
						133	Wafers Coated with Aluminum & Stripped
9	45	1200	92	400	100	94	Localized Undercutting
						143	Extreme Undercutting; 5% Benzoic Acid (Surface Adherent); 10% 1 Phenyl - 1, 3 Butanedine (Chelating Agent)
						99	100% Octanoic Acid (Surface Adherent)
						99	100% Acetyl Acetone (Chelating Agent)
10	80	1050	92	400	100	61	RH = 20%
						330	Wafers cleaned with Cotton Swab
						228	Wafers cleaned with Ultrasonic Agitation
11	80	1050	92	400	100	64	RH = 22
							Extreme Undercutting, Wafers Ultrasonic In Detergent
						79	Wafers cleaned in Chemicals
12	80	1050	92	400	100	77	
							Developer Rinses:
						70	Dipropyl Carbonate
						78	Methyl Ethyl Carbonate
						80	Dimethyl Carbonate
						77	Diethyl Carbonate

Table 4 (Continued)

Effect of Process Change on Adhesion.

Test	Oxidation Time (minutes) "X"*	Furnace Temp. (°C)	Water Temp. (°C) "T"*	Oxygen (cc/min) "Y"*	Nitrogen (cc/min) "Z"*	Undercut (10^{-6} inches)	Remarks
13	80	1050	92	400	100	61	Developer - Developer Rinses
						78	50% KMER Developer; 80% Isopropyl Alcohol 50% Dipropyl Carbonate; 20% Dipropyl Alcohol
						58	50% KMER Developer; 80% Isopropyl Alcohol 50% Dipropyl Carbonate; 20% KMER Thinner
14	80	1050	92	400	100	72	Additive to the Resist:
						78	0.01% Modaflow
						79	0.1% Modaflow
							Resist full of holes; 1.0% Modaflow
15	80	1050	92	400	100	89	RH = 50%
							Additive to the Resist:
						87	0.01% Linolenic Acid
						77	Rough lines; 0.1% Linolenic Acid
						71	Rough lines; 1.0% Linolenic Acid
16	80	1050	92	400	100	60	RH = 20%
							Resist lines poorly defined; 0.01% Crotonic Acid
							Resist lines poorly defined; 0.1% Crotonic Acid
							Resist lines poorly defined; 1.0% Crotonic Acid
17	80	1050	92	400	100	66	Additive to the Resist:
						64	0.6% Amoco 18
						57	1.2% Amoco 18
						66	2.5% Amoco 18
18	45	1200	92	400	100	89	Additive to the Resist:
						81	Holes in Resist; 0.1% Oiticica Acid
						73	Holes in Resist; 1.0% Oiticica Acid

*Refers to formula for oxidation process, page 3.

only in the atmosphere having lower relative humidity. It was found that the resist adhesion was degraded by the humid atmosphere (Table 4, Tests 6 and 7). Only one half the expected change in undercut was noted, as the undercut should have been about 90×10^{-6} inches at a relative humidity of 60 percent. The cause of the complete amount of undercut could not be demonstrated.

Oxide Conditioning

The possibility of altering the surface of the oxide prior to coating with resist was examined in an effort to improve adhesion. Oxidized wafers were aluminized and placed in a 190°C furnace to allow the aluminum to form a controlled, thin oxide layer (Reference 2) at the aluminum-silicon interface. The aluminum was then removed by soaking the wafer in 180° C sulfuric acid for five minutes. It was found that adhesion was degraded by the action between the aluminum and the oxide (Table 4, Test 8).

A group of chemicals that should aid in giving a polarized monomolecular orientation to the bonds between the resist and oxide, or act as a chelating agent, was tried as a means of improving the adhesion. Solutions were made by dissolving these chemicals in KMER thinner where necessary. The wafers were soaked in the solution for twenty minutes, sprayed with KMER thinner to remove the excess solution and dried at 180°C for thirty minutes before being coated with resist. Table 4, Test 9 shows that little effect was obtained with octanoic acid or acetyl-acetone and that benzoic acid and 1-phenyl - 1, 3-butanedone caused severe undercutting.

A cleaning procedure was examined (Reference 3) to determine what effect was obtained on adhesion of a modified KMER solution on silicon dioxide by the cleaning process. Wafers were processed immediately from the oxidation furnace in the following manner:

1. Using a cotton swab, scrub the wafer with a detergent solution. (One group of wafers was scrubbed using the detergent and ultrasonic agitation.)
2. Rinse the wafer with water and place in a 50 ml beaker which has also been scrubbed with cleaning compound and rinsed.
3. Flush the beaker with water five times.
4. After pouring off the last water, cover the wafer with methyl alcohol and ultrasonically agitate for 30 seconds.
5. Pour off the methyl alcohol and cover the wafer with trichloroethylene.
6. Heat gently until boiling has been evident for 30 seconds.
7. Pour off the trichloroethylene and repeat step 6 with fresh trichloroethylene.
8. Pour off the trichloroethylene and cover with methyl alcohol for 60 seconds.
9. Pour off the methyl alcohol and flush beaker with water five times.
10. Half fill the beaker with nitric acid.
11. Heat at about 80°C for 20 minutes.

12. Pour off the hot nitric acid and flush with water five times

13. Rinse wafer with methyl alcohol for 30 minutes.

14. Pour off methyl alcohol and store in trichloroethylene.

The wafers were processed through photoengraving. Undercutting was severe on both the wafers that had been scrubbed with a cotton swab and those which had been ultrasonically agitated (Table 4, Test 9). This undercutting was not caused by wafers that were not clean, but rather by excessive mechanical abrasion on the oxide. A second group of wafers was processed where the ultrasonic agitation of step one and step four was separated from the remainder of the cleaning process. The two wafers cleaned by the mechanical action undercut severely, while those receiving only chemical cleaning showed little deterioration. Mechanically cleaned wafers were even worse in Test 11 than the cleaned wafers in Test 10 because removal of all of the contaminates (the detergent) was incomplete. Wafers chemically cleaned in Test 11 were worse than the control wafers because of the excessive handling.

Developing

The ability of carbonates to react with rubber products led to the testing of a group of these chemicals as rinses in the developing of KMER. While isopropyl alcohol is an excellent rinse in producing clean lines in the exposed resist (with both KMER and KPR) its reaction with the resist causes localized undercutting in etches requiring extended etch times. Since this problem is reduced by the addition of KMER thinner to the alcohol, it seemed reasonable to assume the possibility of further enhancing the adhesion by the complete elimination of the alcohol. Table 4, Test 12 shows that all carbonate rinses were effective but that dipropyl carbonate gave the best results.

The dipropyl carbonate was then examined as a possible developer. Although in itself dipropyl carbonate would not develop KMER, a mixture of 50 percent dipropyl carbonate and 50 percent KMER developer was found to be superior to KMER developer alone. The new developer combination would develop lines of 0.0001 in. when the resist thickness was 1.7 microns and line widths of 0.0002 in. when the resist thickness was 2.2 microns. The improved resolution appeared to be a result of minimizing the swelling action of the resist. Resist line edges did not bridge the line width, thereby permitting the rinsing step to clean out the line. An examination of resist adhesion showed that the dipropyl carbonate - KMER developer was as good as 100 percent KMER developer. Figure 11 is of three lines, 0.0001 in., 0.00025 in. and 0.0005 in. printed in a resist 1.7 microns thick. Figure 12 is of the line etched in 6000 A oxide after the resist has been removed.

Additives

MODAFLOW, designed to increase adhesion of polymer films and to assist leveling and flow was added to the resist in varying amounts from 0.01 percent to 1.0 percent. No improvement was noted in the uniformity of the resist thickness as visually noted by the color fringes in the coated resist, nor in adhesion as recorded in Table 4, Test 15.

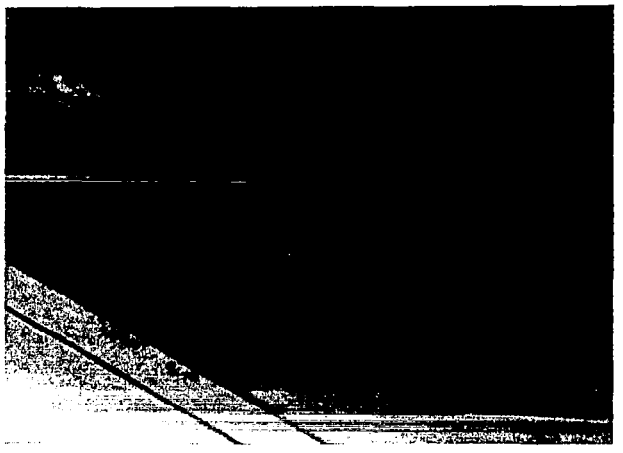

Figure 11—Line widths of 0.0001, 0.00025, and 0.0005 inch printed in 1.7 micron resist (550X).

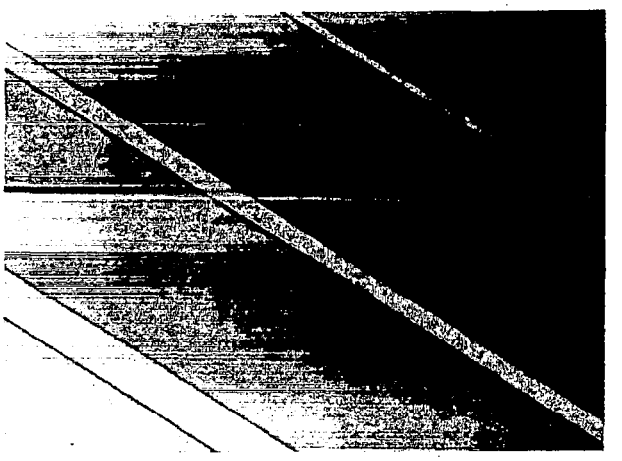

Figure 12—Lines etched in 6000 A oxide with resist removed (550X).

Linolenic acid and crotonic acid were investigated as a possible means of strengthening the polymerized bond of KMER. These chemicals are unsaturated double bond-containing molecules which could be expected to copolymerize with the resist monomer. Test 15 indicates that linolenic acid *did* copolymerize with the KMER, since with an increase of the additive the adhesion of the resist improved. Further work with this chemical was not undertaken because a roughness of the developed resist lines was objectionable. The crotonic acid failed to be of value in that it caused the resist to flow into the developed-out regions.

Amoco resin 18-210 was selected for testing because of its compatibility with styrenebutadiene copolymers which are believed to be similar to KMER. This material is used to control hardness, toughness and strength. Adhesion of the resist improved the most with the addition of 1 percent Amoco 18. Further testing of this additive was undertaken where weights of 12, 6, 3, 1.5 and 0.75 grams of Amoco 18 were added to individual 100 cc amounts of KMER thinner. Each individual mixture was then placed in a jar and stirred for 15 minutes using a magnetic stirrer. The mixture was then filtered through a 1.2 micron filter using a stainless steel hydrosol filter and a vacuum filtering flask. The solution was then mixed with an equal volume of untreated and undiluted KMER. This mixture was centrifuged to produce modified KMER containing Amoco 18. Viscosity was adjusted to 85 centipoise.

Three wafers were coated with resist from each of the five lots of resist containing Amoco 18. The wafers were processed through resist developing and then examined for resolution and general surface conditions.

All of the resists containing Amoco 18 with the exception of the 0.75 gram lot showed signs of resist imperfections such as droplets as shown in Figure 13. The remaining four lots of Amoco 18 resist were considered unsuited for further processing and were rejected.

Oiticica fatty acid was examined because it is a highly unsaturated molecule (conjugated double bonds) which should copolymerize with any compatible photoresist. This chemical required special filtration after dissolving in KMER thinner to remove the particulate matter held in suspension. The solution was then mixed with KMER to obtain the desired concentrations. Although an improvement was noted in the adhesion of the resist, holes were noted in the oxide of the etched wafer.

Capacitor Test for Pinholes

A number of methods has been devised for testing oxides for pinholes. These tests include passing chlorine or hydrogen chloride gas across the wafer at elevated temperatures; driving in an impurity for an extended period of time, stripping the oxide and staining the wafer; or evaporating a metal across the oxide and checking electrically to see if the metal has penetrated any holes in the oxide, making contact with the silicon base (capacitor test). The third method was preferred here as it was much easier to relate the defects in terms of failures per unit area. The evaporated metal can be etched into areas of controlled sizes and tested individually. Also, the severity of the test may be regulated by controlling the oxide thickness and time of oxide etch.

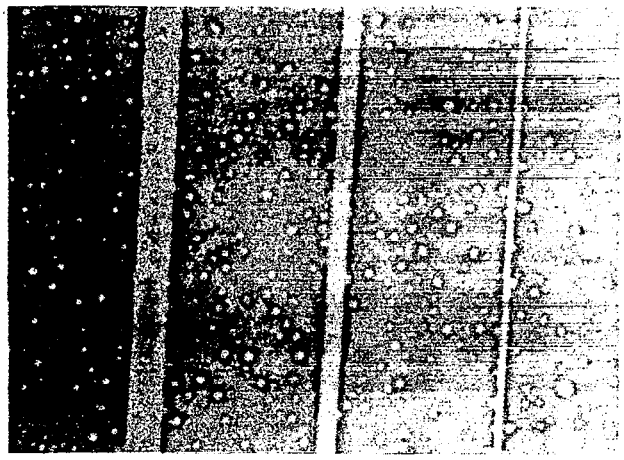

Figure 13—Undissolved Amoco 18 in Kodak Metal Etch Resist.

Tests made previously had shown that in controlling pinholes, consideration must not only be given to the etch time but also to the time between completion of etch and removal of the resist. Due to the permeability of the resist to hydrofluoric acid, etching can continue under the resist after the wafer has been rinsed and dried. It was found that for resist thickness of 1.9 microns, a twenty minute delay in resist removal caused an increase of 15 percent in defective 3600 square mil capacitors. A significant test for pinholes must therefore consider what oxide thickness, and consequently what required etch time, is necessary for the devices for which the test is being conducted. Since 7000 A is a good general oxide thickness, a 10 minute etch was selected for this set of tests. It was desired that all pinholes giving weak points would show up in this test, even those that normally are etched only partially through the oxide. To accomplish this, the oxide thickness was grown to a thickness of only 4000 A. Normally this thickness of oxide would require less than 5-1/2 minutes etch so a ten minute etch would open any holes that had started after 5-1/2 minutes of etching.

Photographic masks were not used in exposing the resist to ultraviolet light except in Test 4, Table 5. It was desired to know the pinhole density attributed to the resist without having the results clouded with possible faults caused by imperfections in the photographic mask. Test 4 was included to show that with clean masks (an intangible quality at best) it is possible to obtain the

Table 5

Capacitor Pinhole Tests.

Test	Oxide Thickness (A)	Resist Lot	Viscosity (Cp.)	Spinner Speed (rpm)	Exposure Time (sec.)	Developer	Total Capacitors Tested	Capacitors Tested Good	Percent Good Capacitors	Remarks
1	4000	6308	85	8000	20	50% KMER Developer 50% Dipropyl Carbonate	77	61	74	
	4000	6308	85	8000	40	"	78	51	65	
	4000	6308	85	6000	20	"	76	62	82	
	4000	6308	85	6000	40	"	75	61	82	
	4000	6308	115	6000	40	"	155	138	89	
	4000	6308	85	6000	20	100% KMER Developer	75	62	83	
	4000	6308	85	6000	40	"	75	63	84	
2	4000	6308	115	6000	40	50% KMER Developer 50% Dipropyl Carbonate	313	290	93	
3	4000	6308	85	8000	20	50% KMER Developer 50% Dipropyl Carbonate	235	88	38	
4	5600	6402	115	6000	40	50% KMER Developer 50% Dipropyl Carbonate	119	111	93	Photomask Used for Exposure
	5600	6402	115	6000	60	"	119	116	97	Photomask Used for Exposure
5	4000	6308	85	8000	20	50% KMER Developer 50% Dipropyl Carbonate	314	191	61	1% Amoco 18 Added to Resist
6	4000	6402	85	8000	20	50% KMER Developer 50% Dipropyl Carbonate	310	124	40	
	4000	6402	85	7500	20	"	317	145	46	

same yield as experienced without masks. Increased exposure times were included in these tests to show that pinholes were not increased with the longer exposure. This would permit certain types of mask defects such as translucent gelatin particles (not silver particles) to be present without causing pinholes in the acid resist.

The aluminum pads were formed on the oxide and tested in the same manner used for the epitaxial oxides.

Test 1, Table 5 was conducted to examine the effect of doubling the exposure time on pinholes. This test also included a comparison of the standard KMER developer and the 50 percent KMER - 50 percent dipropyl carbonate developer. No change in either of these factors could be detected between the standard condition and the new developer or the increased exposure time.

Test 2, Table 5 was conducted to indicate that the probability of obtaining a 3600 square mil area that was pinhole free when protected by a 2.2 micron thick resist (0.0002 in. line capability) was 93 percent. Test 3, Table 5 shows that a 1.7 micron thick resist (0.0001 in. line capability) had an acceptance probability of 38 percent.

The addition of 1 percent Amoco 18 to the resist improved the pinhole rate from 38 percent (Test 3, Table 5) to 61% (Test 5, Table 5). Some question arises as to why wafers from Test 1 that were processed similarly to Test 3 had a yield of over 60 percent. More extensive testing of Amoco 18 suggested that the shift in pinhole rate must have been due to other variables. Final test results showed no difference in pinholing between those resists using Amoco 18 and those without it.

Test 5 and 6, Table 5 were included to give a comparison between KMER Lots 6308 which was extensively used in this program and KMER Lot 6402. Little difference in the density of pinholes was noted.

PROCESSING OPERATIONS

The operation of photoengraving for functional electronic blocks is critical, as the activity of the fluoride ion used in etching the oxide tends to separate the resist from the oxide at the interface for all but the most exacting bonds. Experience over the past four years has evolved procedures which are a compromise between the various functions which must be considered, i.e., clean lines, resolution, adhesion, and pinholes. The process given here is a combination of these findings and the investigations conducted for this report.

Oxide Bakeout

All wafers received into the photoengraving area are given an inspection at a magnification of 60X. The wafers receive a strong sprayoff of trichloroethene to remove any dust particles. Metalized wafers are immediately coated with electro-resist. Oxidized wafers are placed into a covered petri dish and placed into a 190 °C oven for a minimum of thirty minutes. This bakeout is

necessary because oxides are hydroscopic and good adhesion cannot be obtained without first removing the mechanically held moisture in the oxide.

Resist Coating

Two viscosities of resist are used in wafer processing. Viscosities are measured using a falling ball viscosimeter. The thicker resist has a viscosity of 120 cp and is used for etching isolation diffusion masks where minimizing pinholes is of primary importance. The thinner resist has a viscosity of 85 cp and is used for all maskings other than isolation diffusion.

A syringe equipped with a 0.8 micron filter and a prefilter is filled with resist. A number 17 hypodermic needle is attached to the filter. Resist is dispensed onto the wafer which has been placed onto the spinner. The wafer is spun at 6000 rpm for 20 seconds. A slight down draft of air around the spinner head will remove any "strings" of resist that form while the resist is being spun from the wafer.

Resist Pre-bake

The wafer is placed on a teflon boat and placed into an oven at 110-120° C for 12 minutes for 85 cp resist and 15 minutes for the 120 cp resist. A teflon boat is preferred since sticking of the wafer to the boat will not occur if the resist flows to the under side of the wafer.

Exposure

The wafer is aligned with the photographic mask and brought into contact. Light fringes must be seen at two points on the wafer or good contact will not be made and poor resolution will result. Wafer flatness must be within twenty light fringes as measured with an optical flat before application of the resist, or resolution will not be uniform across the wafer. It is necessary that a radius of 0.005 inch be present at the edge of the wafer or a buildup of resist at the periphery of the wafer will prevent intimate contact.

This process requires that a light mechanical pressure be used to make contact, or resolution will not be satisfactory. An examination of resolution obtainable in a resist 1.9 microns thick consistently gave 0.0001 in. spacings at the edge of the wafer, but this spacing was often incompletely developed out in the center of the wafer. Examination showed that the thickness of the resist was constant from the center of the wafer to the edge of the wafer. Better wafer-mask contact was sought to examine the variation in resolution. A vacuum fixture was constructed to hold the mask against the wafer. It was found that although fringes were extended over a greater portion of the wafer, resolution of spaces developed out of the resist were degraded from 0.0001 in. on the mechanical contacted wafer to 0.0005 in. on the vacuum contacted wafer (Figure 14 and Figure 15). Lines of resist on the order of 0.0001 in. were much stronger and easier to produce in vacuum exposed resist.

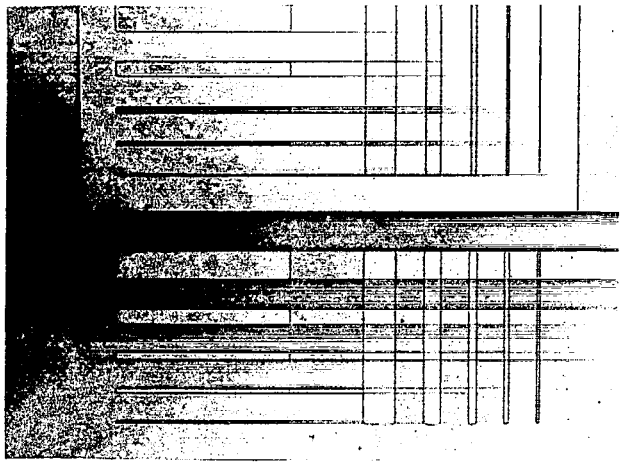

Figure 14—Resolution pattern in mechanically contacted wafer showing line widths and spacings of 0.0001, 0.00025, 0.0005, 0.001 and 0.002 inch.

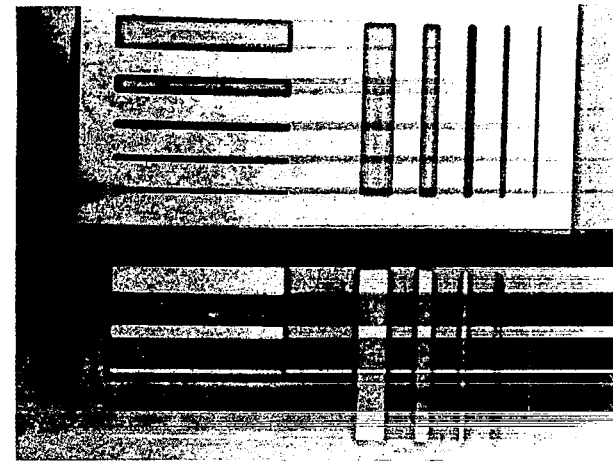

Figure 15—Resolution pattern in vacuum contacted wafer.

The evidence indicated that vacuum exposed resist was thicker than mechanically contacted resist. A series of coated, exposed, and developed wafers was coated with aluminum. A fringe measurement was made with the variations in resist thickness recorded in Figure 16. It was seen that the wafer coated with a 1.9 micron resist had a coating thickness of only 1.1 microns in the vacuum contact while the mechanical contact had reduced the coating thickness to only 0.72 microns.

A test was set up to determine why the two methods of contact printing gave different thicknesses of resist. Wafers were placed in a vacuum jar and the air evacuated down to 30 in Hg. A gas was then admitted to the jar until atmospheric pressure was regained. Atmospheres used were nitrogen, hydrogen, argon, carbon dioxide, and oxygen. All atmospheres with the exception of oxygen gave the same result as vacuum printing. The resist when exposed in an oxygen atmosphere completely dissolved from the wafer leaving no pattern at all. A series of exposures was made while varying the proportions of oxygen and nitrogen. The resist thickness was measured and recorded in Figure 17. It was concluded that oxygen present during exposure prevented complete polymerization of the resist.

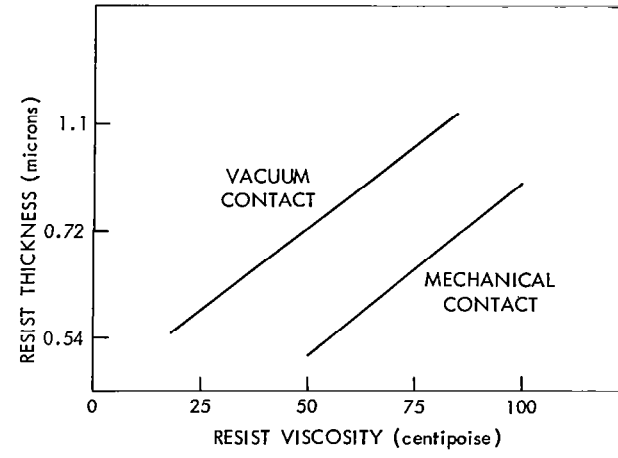

Figure 16—Comparison of coating thickness of vacuum and mechanical contact printing.

Developing

Standard Developing

The wafers are held on a vacuum chuck in a vertical plane. KMER developer is sprayed at the wafer from a distance of three to four inches for 30 seconds using an air gun at a pressure of forty psi. Immediately after

developing, a rinse of 80 percent isopropyl alcohol - 20 percent KMER thinner is sprayed onto the wafer for 15 seconds. The wafer is then blown dry and is ready for inspection.

High Resolution Developing

With the addition of 40 percent dipropyl carbonate to the KMER developer, an improvement in resolution was obtained. Where the standard developing process would resolve 0.0002 in. lines when 85 cp resist was used, it was found possible to resolve 0.0001 in. lines with the dipropyl carbonate developer. Table 6 gives a comparison of obtainable resolution for the two developing processes.

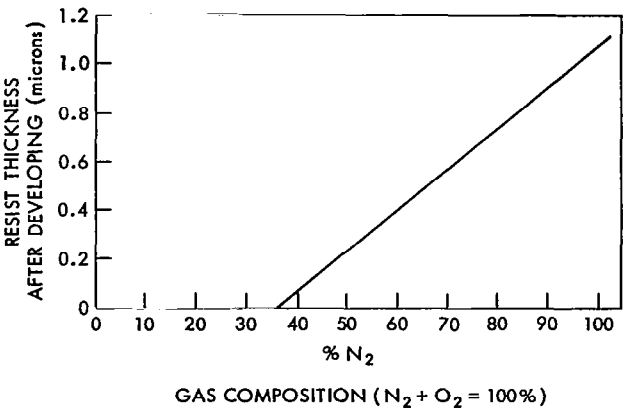

Figure 17—Effect of gas composition on resist thickness.

Other developer combinations were tried but met with little success since either the resolution was degraded or the developer caused excessive undercutting. These developers are included in Table 7.

Post Bake

Wafers are placed on a teflon boat and placed into an oven at 180°C for twenty minutes. It is important that the time for temperature *not* be increased, because the resist will run, and resolution will be decreased. Lower temperatures or shorter times tend to degrade the adhesive qualities of the resist and undercutting may occur.

Table 6

Effect of Dipropyl Carbonate on Resolution.

Test	Developer System					Resist Thickness Before Developing (microns)	Resolution (inches)
	Developer		Rinse Isopropyl Alcohol (percent)	KMER Thinner (percent)	Dipropyl Carbonate (percent)		
	KMER Developer (percent)	Dipropyl Carbonate (percent)					
1	100	-	80	20	-	1.7	0.0002
2	75	25	80	20	-	1.7	0.0001
3	60	40	80	20	-	1.7	0.0001 (Smoothest)
4	50	50	80	20	-	1.7	0.0001
5	40	60	80	20	-	1.7	would not develop
6	70	30	80	15	5	1.7	0.0001
7	100	-	80	20	-	2.2	0.0005+
8	60	40	80	20	-	2.2	0.0002

Table 7

Effect of Developers on Adhesion.

Test	Developing System			Isopropyl Alcohol (percent)	KMER Thinner (percent)	Special Rinses (percent)	Undercut (10^{-6} inches)	Remarks
	KMER Developer (percent)	Dipropyl Carbonate (percent)	Special Developers (percent)					
1	100			80	20		81	
		50	50 Stoddard Solvent	80	20		76	Poor Resolution
		50	50 Stoddard Solvent	80		20% Dipropyl Carbonate	108	
2	100			80	20			
		50	50 Stoddard Solvent	80	20		62	
		50	50 Stoddard Solvent	80		20% Dipropyl Carbonate	88	
3	100			80	20		90	
	60	40(175)*				100T Butanol	135	
	60	40(175)				100 Diacetone	135	
	60	40(175)		80		20% Dipropyl Carbonate (175)	135	
4	100			80	20		64	
	50	50		80	20		82	
	60	40		80	20		70	
5	100			80	20		57	
	100			80	20		62	Amoco 18 Added
	60	40(345)		80	20		59	Amoco 18 Added
6	100			80	20		67	Amoco 18 added to resist
	60	40(175)		80	20		78	Amoco 18 added to resist
7	100			80	20		55	
	60	40(175)		80	20		78	
	60	40(345)		80	20		59	
	50	50(345)		80	20		60	
8	100			80	20		71	
	50	50(175)		80	20		80	
	50	50(345)		80	20		67	
9	100			80	20		62	
	70	30(345)		80	20		65	
	60	40(345)		80	20		56	
	50	50(345)		80	20		67	

Table 7 (Continued)

Effect of Developers on Adhesion.

Test	Developing System			Isopropyl Alcohol (percent)	KMER Thinner (percent)	Special Rinses (percent)	Undercut (10^{-6} inches)	Remarks
	KMER Developer (percent)	Dipropyl Carbonate (percent)	Special Developers (percent)					
10	100			80	20		59	Dipropyl Carbonate
	60	40(345)		80	20		64	Was shaken in an
	50	50(345)		80	20		67	open bottle
	70	30(345)		80	20		63	5 minutes to remove carbonater
11	100			80	20		59	
	60	40(345)		80	20		62	
	60	40(345)		80	20		66	(1%) α β, β, tri-fluorostyrente added to resist
	60	40(345)		80	20		88	(4%) α β, β, tri-fluorostyrene added to resist
12	100			80	20		81	
	60	40(345)		80	20		89	
	60	40(345)		80	20		110	
13	100			80	20		74	
	60	40(345)		80	20		65	
	60	40(425)		80	20		63	

*(175) Laboratory Produced Lot of Dipropyl Carbonate
(345) and (425) Pilot Line Lots of Dipropyl Carbonate

Etching

The etch solution is composed of:

1000 cc H_2O Solution I
1 pound NH_4F
48 percent HF Solution II

Ten parts of solution I are added to one part of solution II. The etch rate of this solution is 750 A per minute for a neutral oxide. Since all doped portions of oxides from boron and phosphorus diffusion are stripped before drive-in, this etch rate is good for all oxide etching. Wafers are etched for a time determined by etch rate and oxide thickness.

Undercutting during etching was reflected by the developing process used. An examination of the effects of changing the developing solution on undercut during etching is shown in Table 7. Particular attention was paid to dipropyl carbonate. It was found that the two lots of dipropyl carbonate produced in a new pilot line facility did not affect adhesion but that a previous lot produced in the laboratory increased undercutting. Comparisons of these lots of dipropyl carbonate are given in Table 7.

Resist Cleanup

The wafer is placed in sulfuric acid heated to 180°C for five minutes. The acid is decanted and the wafer soaked in fresh 180°C sulfuric acid for five minutes. The acid is cooled, decanted, and the wafer rinsed five times in deionized water and then blown dry.

Pinholes

Four processes were tested for their effects on pinholes. These were

1. Standard Process
2. 0.75 gm Amoco 18 added to the resist
3. 40 percent dipropyl carbonate in the developer
4. 0.75 gm Amoco 18 added to the resist and 40 percent dipropyl carbonate in the developer.

The wafers were oxidized with 4000 A oxide. A resist coating of 1.9 microns was spun on, dried, and exposed without a photographic mask. The pads of 3600 square mils were placed on the oxide and the metal-oxide-silicon capacitors were electrically tested for holes in the oxide. The results of these tests are shown in Table 8.

Little difference was noted between the process changes. Run number 226 showed a degrading effect from dipropyl carbonate but the other three runs gave no indication of this condition. One lot of wafers, 277, was processed using vacuum printing techniques to examine its effects on

Table 8

Capacitor Pinhole Tests
(Mechanically Exposed Resist).

Run	Process	Capacitors Tested	Capacitors Tested Good	Percentage of Good Capacitors
217	Standard	157	127	81
	Amoco 18	158	137	87
	Dipropyl Carbonate	157	118	75
	Amoco 18 + Dipropyl Carbonate	157	123	78
228	Standard	156	116	74
	Amoco 18	158	120	76
	Dipropyl Carbonate	157	116	74
	Amoco 18 + Dipropyl Carbonate	157	124	79
240	Standard	157	131	83
	Amoco 18	157	135	86
	Dipropyl Carbonate	156	131	84
	Amoco 18 + Dipropyl Carbonate	156	119	76
226	Standard	157	124	79
	Amoco 18	156	122	78
	Dipropyl Carbonate	158	56	35
	Amoco 18 + Dipropyl Carbonate	156	45	29

pinholes. Resist viscosities of 25 cp, 50 cp, and 75 cp were spun onto the wafers at 6000 rpm. The wafers were exposed through a clean, clear glass plate at a vacuum of 26 inHg. Dipropyl carbonate was used in the developer.

An examination of Figure 13 will show that vacuum-exposed resist with a viscosity of 50 cp is comparable to the resist of 85 cp when processed using standard procedures. The vacuum-exposed resist of 50 cp had a higher density of pinholes (Table 9) than could be expected using 85 cp resist processed by standard techniques (Table 8). No advantage could be found to using vacuum-exposed resist.

Table 9

Capacitor Pinhole Tests
(Vacuum Exposed Resist).

Run	Resist Viscosity	Capacitors Tested	Capacitors Tested Good	Percentage of Good Capacitors
227	25	155	36	23
	50	159	98	62
	75	156	132	85

CONCLUSIONS AND RECOMMENDATIONS

Modified KMER is capable of maintaining an etch factor of one for ammonium fluoride-buffered hydrofluoric acid etches of silicon dioxide. This rate of undercut can be maintained for oxide thickness of at least 20,000 A and for etching times of thirty minutes. Parameters of oxide growth affected adhesion at higher relative humidity but this variation was overcome as the humidity dropped below 40 percent. Very low relative humidity, below 30 percent, is not recommended, since static charges on the wafer tend to attract particulate matter. Changes in the resist as the relative humidity dropped appeared to cause a roughness to the line edges that was not present at higher humidities. This roughness may have been caused by acutance of the photographic mask (acutance is the transition distance from transparent to opaque perpendicular to a photographic line).

Extensive cleaning procedures degrade adhesion of the resist for the oxide. In particular, mechanical action used in cleaning oxides causes extensive undercutting. Spray cleaning with trichloroethylene or a five minute soak in 180°C sulfuric acid does not affect adhesion and is recommended as a cleaning method. The adhesive qualities of oxides grown at 1200°C can be restored by a furnace treatment of less than four minutes.

Investigations of epitaxially grown oxides demonstrated that a treatment of nitrogen flow following the growth of the oxide improved the adhesive qualities of the oxide for the resist. An examination of pinholes in the epitaxial oxide showed that the quality of the oxide was sufficiently

good for use in molecular electronic devices. The use of this type oxide would eliminate the extra operation of oxidation.

A developer solution of 50 percent KMER Developer - 50 percent dipropyl carbonate illustrated that a resist thickness of 2.2 microns could be used while producing line widths of 0.00025 in. and an acceptance of 93 percent of 3600 square mil capacitors free of pinholes. Reproducible 0.0001 in. lines were a reality using 1.7 micron resist thickness. For maskings where pinholes were considered of paramount importance, a thicker resist, 2.2 microns, was found to yield line widths of 0.0002 in. Previously the minimum line width had been 0.0005 in. Dipropyl carbonate is recommended for use only where the higher resolution is needed. The stronger solvency action of this solution tends to accumulate under the resist in droplet form and at times causes rework.

The addition of 1 percent Amoco 18 resin improved resist adhesion but gave no indication of an improved resist. No effect was seen in the resolution of the developed resist, and the pinhole count was no better than resists without this additive.

One major problem area associated with the use of this resist and its resolution capability is alignment and contact of the resist coated wafer to the photographic plate. The reliability of reproducing 0.0001 in. lines is highly dependent on good contact between the wafer and the photographic plate. Experience has shown that a flexible wafer stage such as a rubber mat will give better contact than will a rigid one. The apparent problem with the flexible stage is that close alignment is difficult since the wafer must be held farther from the photographic mask during alignment to prevent an inadvertent scraping of the resist coating the wafer. A study program of this problem would aid in photoengraving of semiconductor devices.

The process specification for photoengraving given here will etch silica with resolution and freedom from defects at least equal to the state of the art today. Line widths of 0.0002 in. are easily reproduced and a method of producing acceptable line widths of 2.5 microns is given. Pinholes reproduced in the oxide from the resist have not been eliminated but are acceptable for the moment.

The direct effect of oxygen on the polymerization of KMER shows that the exclusion of oxygen from the resist ambience during exposure increases the resist thickness after developing but decreases resolution. The viscosity of the resist had to be decreased by 35 percent to achieve comparable resolution but this introduced a pinhole problem. Vacuum exposure is not recommended.

Eastman Kodak Company recently placed on the market a resist, Kodak Thin Film Resist, which was designed for use with circuits containing micron-wide lines. This resist was not designed especially for silicon dioxide etching. However, it has properties that make the resist look appealing for the masking of silicon wafers. The cleanliness of the resist coupled with its resolving capability while possessing the same rubber base systems as KMER warrants an investigation into the performance of the resist as compared to the electrophoresis KMER.

(Manuscript received December 3, 1965)

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Appendix A

High Resolution Photoengraving for Semiconductor Devices

One of the major deterrents to producing high resolution devices has been the limited ability to reproduce very fine lines in an acid resistant film capable of meeting all the processing requirements of producing an etched semiconductor device. All the commonly known resists are deficient in one or more of the following essential characteristics:

1. Capability of withstanding low surface tension, highly corrosive etches such as buffered hydrofluoric acid without undercutting or lifting at edges of the film.
2. Possessing a resolution capability of 0.0001 in. while maintaining smooth line edges (to give minimum electrical noise).
3. The absence of pinholes in the resist (a mandatory requirement to prevent defective devices).

A long investigation into methods to achieve these characteristics through modification of an existing resist has resulted in a material which does in fact satisfactorily meet the above requirements.

Kodak Metal Etch Resist was selected as the most promising material as it had previously exhibited reasonable resistance to undercutting and had sufficient solids content to prevent pinholing. The principal problem with KMER was its lack of uniformity from lot to lot and its apparent inability to resolve fine lines. Resolution tests conducted over a period of two years showed that the resolution capability of KMER when thinned three parts to one part KMER thinner ranged between line widths of 0.0008 inch (lot 6304) with unusually rough edges and 0.0004 inch (lot 6209), when using KMER developer to bring out the pattern. The density of pinholes was apparently related to the resolution capability of the resist. While resolution was better in the more highly thinned KMER, the solids content was lower. The use of isopropyl alcohol as a spray rinse following developing resulted in the resolution being consistent from lot to lot with a capability of 0.00025 inch line width. Small particles of matter could be seen protruding from the body of the exposed resist into the developed areas. There was no change in the number of pinholes existing in the resist film.

The edge roughness and blobs of gelatinous-appearing particulate matter indicated certain things about the character of the resist. One implication was that the KMER was not homogeneous, that it had several species of material in suspension, and also that these were polymerized to varying degrees and were of different reactivity to light.

Since the nature of these materials was unknown, the first task was to carry out a spectrophotometric analysis of the various batches of KMER. The results are shown in the following figures. A correlation between good performance of the KMER and the spectrophotogram was attempted and gave some hint of being meaningful. Comments are shown on the curves of Figure A1.

Samples of KMER were dissolved in toluol at a concentration of 0.66 g/100 ml. Below 400 millimicrons the concentration was reduced to 0.165 g/100 ml (Figure A1). Readings were carried out between 335 and 580 millimicrons on four sample lots of KMER.

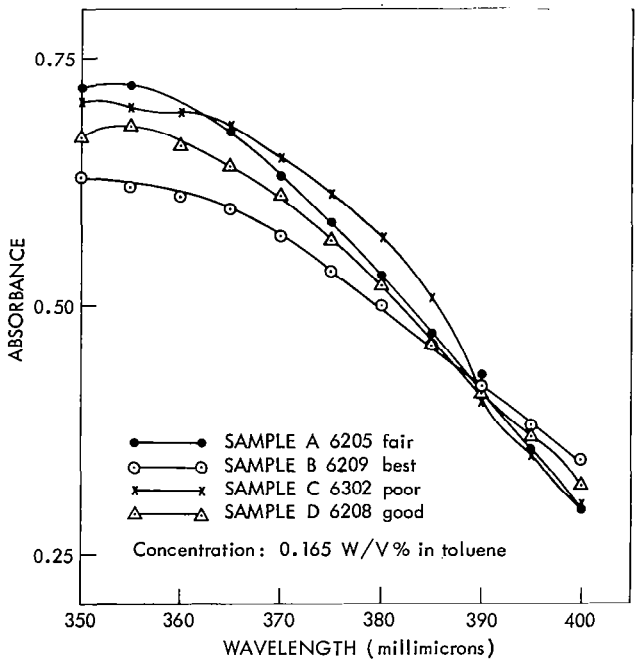

Figure A1—Transmission of four KMER samples.

There was an attempt made to establish a relation between the in-plant performance and the position of the absorbance curves. Between 365 and 385 millimicrons there did seem to be a relationship. However in the light of the small number of samples, no strong conclusion could be drawn. The results are suggestive rather than conclusive.

After an attempt at centrifugal separation which partially removed high molecular weight polymerized material, ball milling was tried. This produced a somewhat smoother resist and to some extent reduced the size of the gelatinous matter but resulted in a serious pinholing problem. Filtration was not practical because eight micron filters blocked at once. Since the resist film thickness as used was on the order of one micron, no effective purpose could be seen in filtration that could not remove less than one micron particles.

Improvement in the resist was obtained when it was found that the particulate matter protruding into the developed area could be removed from the resist prior to use by the application of a strong electric field. The application of a high voltage electric field to the resist caused unwanted material in the KMER to collect as a sludge layer on the bottom of the beaker. The resulting resist, which is called electro-resist was 75 percent of the volume of the original resist. It was light amber in appearance and visually uniform as contrasted to the original brown, viscid gelatinous blob-containing KMER. The modified resist was now capable of passing through an 0.8 micron filter without clogging. The original resist would not pass through a filter smaller than 10 microns without clogging the pores.

The transmission curves of KMER before high voltage treatment and of the sludge and clarified material after treatment are shown in Figures A2, A3 and A4. The implication to be drawn

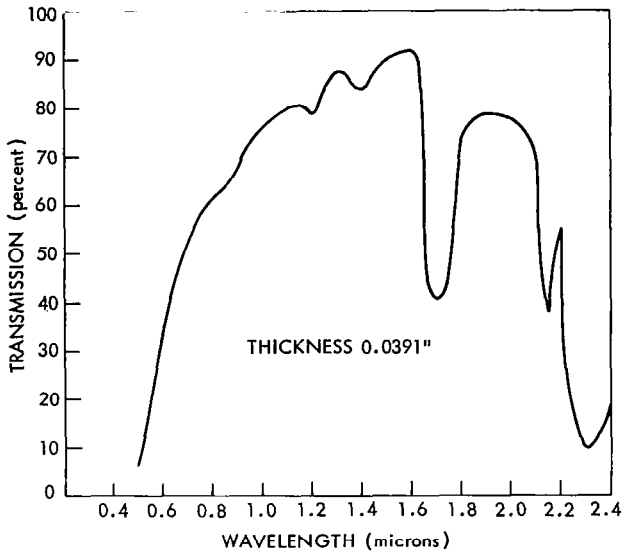

Figure A2—Transmission of normal KMER not subjected to high voltage.

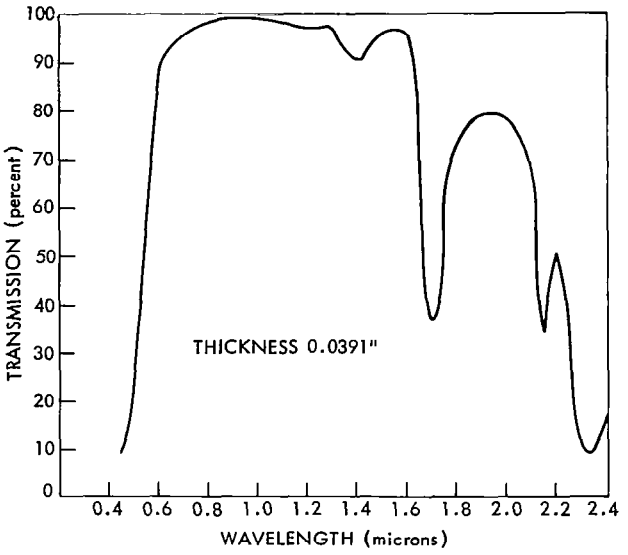

Figure A3—Transmission of supernatant KMER after application of high voltage.

from these curves is that the supernatant clarified component of KMER has a much higher transmission in short wavelengths, and that the sludge of polymerized gelatinous material is the source of the undesired characteristics of the untreated KMER. This sludge has undesirable characteristics, prime among them rendering the clean up more difficult than necessary by leaving adherent carbonaceous residues on wafers. These do not appear when the treated resist is used. Two immersions in hot sulfuric acid for about 5 minutes result in clean surfaces.

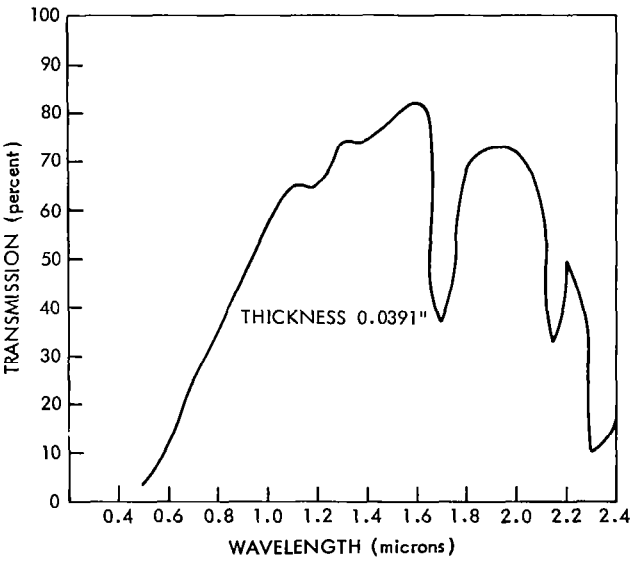

Figure A4—Transmission of KMER sludge after application of high voltage.

Tests conducted on electro-resist have shown that it is capable of resolving line widths of 0.0001 in. and can withstand a hydrofluoric acid etch through 10,000 angstroms of silicon dioxide with no measureable amount of undercutting for a time of up to 15 minutes. A pinhole study made on 200 capacitors formed on silicon using 3000 A of oxide as the dielectric and a vacuum-deposited aluminum pad as the top electrode showed that 91 percent of the 3600 square mil capacitors were pinhole free when tested at 60 volts potential. Capacitors were tested up to 200 volts before indications of breakdown were evident.

The mechanism of the removal of the sludge in the KMER is at present obscure. One hypothesis is that the electric charge on the unwanted colloidal matter is neutralized and that it then coagulates. Another hypothesis is that there is an actual migration of the unwanted matter to one of the electrodes and that it then deposits on the bottom of the beaker. One interesting observation was that the sludge material fell to the bottom of the beaker even when the plates were suspended horizontally well above the bottom of the beaker. In some cases the supernatant resist fluid was observed to migrate along the positive lead and out of the beaker. We are not ready to venture an explanation of these phenomena at this time. The attached photograph, (Figure A5) taken at 500X, shows electro-resist as exposed to the standard Air Force target array.

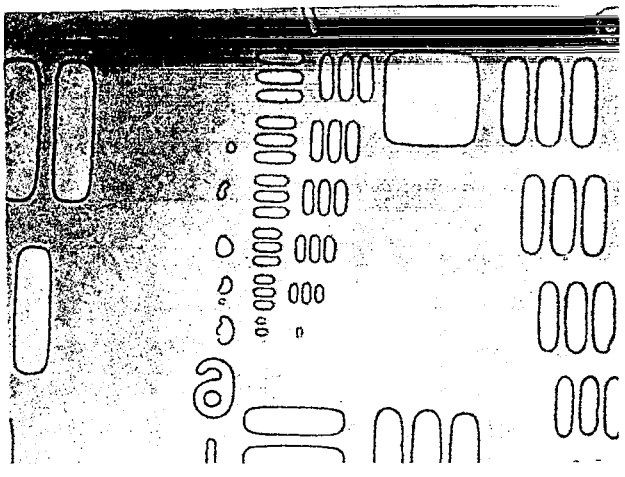

Figure A5—Pattern showing WSR printed and developed on a silicon dioxide surface (500X).

The efforts described above have resulted in a highly satisfactory technique for overcoming some of the difficulties with a product vital in the semiconductor industry and have thereby resulted in a step forward in semiconductor block processing.