Westinghouse

ELECTRIC CORPORATION

FINAL REPORT

FOR

SEMICONDUCTOR WAFER IMPROVEMENT THROUGH PHOTOENGRAVING

1 MARCH - 1 JULY 1965

Contract No. NAS 5-3758
Procurement No. 670-W46

Prepared By

WESTINGHOUSE ELECTRIC CORPORATION
DEFENSE AND SPACE CENTER
AEROSPACE DIVISION
GENERAL ORDER NO. 51248ASA

For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

FINAL REPORT

FOR

SEMICONDUCTOR WAFER IMPROVEMENT THROUGH PHOTOENGRAVING

1 MARCH - 1 JULY 1965

Prepared By

WESTINGHOUSE ELECTRIC CORPORATION
DEFENSE AND SPACE CENTER
AEROSPACE DIVISION

For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

Prepared By C. J. Taylor
C. J. Taylor

Approved By William S. Corak
W. S. Corak

SUMMARY

15986

This investigation discusses the use of Kodak Metal Etch Resist as a silicon dioxide masking agent. The photoengraving process is described such that the results achieved can be duplicated. Process capability is described in terms of:

1. Good resolution
2. Good etch resistance, and
3. Pinhole count

Amoco 18 which is an additive to the resist and dipropyl carbonate, a new developer, were examined to determine their effects on the process. Amoco 18 was found to have little effect. Dipropyl carbonate improved the resolution of the resist from 100 lines per millimeter to 200 lines per millimeter.

Resist exposed in a vacuum, i.e. vacuum printing, was found to be thicker than resist exposed by mechanical contact pressure. An adjustment in resist thickness to give equal resolution created more pinholes in the vacuum exposed resist than could be expected in the mechanically contacted resist.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

This report is in logical sequence with the report, Semiconductor Wafer Improvement Through Photoengraving, completed in January 1965, under contract NAS 5-2755, Procurement No. 670-W90602. The findings of the January report indicated two avenues that might be followed to improve photoengraving for functional electronic blocks.

The first of these findings was that dipropyl carbonate when added to the Kodak Metal Etch Resist developer produced higher resolution than could be obtained otherwise. The second finding was that Amoco 18 when added to KMER improved the permeability of the resist to hydrofluoric acid. These conclusions were based on a cursory examination of both dipropyl carbonate and Amoco 18. The January report recommended that further study be given to the use of dipropyl carbonate as a developing solvent and Amoco 18 as an additive to the resist. A study of these changes to the presently used process coupled with an investigation into possible improvements that evidenced themselves during the study were to establish a complete process that would be acceptable for the photoengraving of semiconductor wafers.

This report in addition to an examination of avenues of possible improvements was to detail a process specification that would provide a reproducible process for those wishing to photoengrave silicon semiconductor wafers. A need for a detailed process specification is appreciated by those who in learning to photoengrave wafers find that many hours and weeks are required to establish a process that is "tuned" to the marginal capabilities of present day resists.

Further information is given for methods used to prepa e the Kodak Metal Etch Resist for use with the process described here. The resist as received from Kodak varies considerably and a variation in the procedure to clear the resist must be used. This was found to be especially true on the lot received and prepared for use with this study. Although the resist cleared the yield was low enough to warrant the use of other procedures to clean the resist.

2.0 RESIST PREPARATION

2.1 Electrophoresis*

Kodak Metal Etch Resist Lot 6409-5 was used to conduct the investigations in this report. This lot of resist 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 clearify 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 KV d.c. 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% was considered to 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.

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

2.2 Centrifuging

Electrophoresis resist is generally preferred to centrifuged resist as the amount of KMER thinner required to clean the resist is not as great for the electrophoresis resist. 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 loaded into an International Clinical Centrifuge. The resist was centrifuged for 16 hours at 3000 rpm. The tube caps were removed and the 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 experiences has demonstrated there is no difference between electro-resist and centrifuged resist when testing for adhesion, resolution or pinholes.

2.3 Amoco 18

Improper preparation of resist containing Amoco 18 will yield an abnormally high pinhole count. In a first attempt to add Amoco 18 to the resist, the Amoco 18 was added directly to the modified resist. The resulting visual pinholes, especially in the more concentrated solutions, demonstrated the need for further preparation of the resist. The following procedure was developed for blending the Amoco 18 into the resist.

Weights of 12, 6, 3, 1.5 and .75 grams of Amoco 18 were added to individual 100cc 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 Millipore 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 examined for resolution and general surface conditions.

All of the resists containing Amoco 18 with the exception of the .75 gram lot showed signs of resist imperfections such as droplets as shown in Figure 1. The remaining four lots of Amoco 18 resist were considered unsuited for further processing and were rejected.

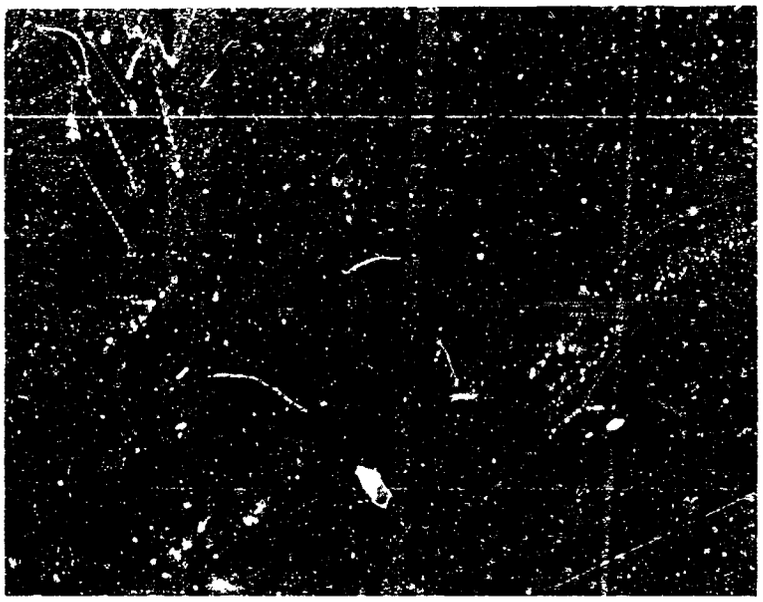


Figure 1

Undesolved Amoco 18 In
Kodak Metal Etch Resist

3.0 PROCESSING OPERATIONS AND DISCUSSIONS

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.

3.1 Oxide Bakeout

All wafers received into the photoengraving area are given an inspection at a magnification of 60. The wafers receive a strong spray-off of trichloroethene to remove any dust particles. Metallized 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.

3.2 Resist Coating

Two viscosities of resist are used in wafer processing. Viscosities are measured using a National Instrument Company 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 Millipore sweeney, a 0.8 micron filter and a prefilter is filled with resist. A number 17 hyperdermic needle is attached to the sweeney. Resist is dispensed onto the wafer which has been placed onto the spinner. The spinner used is an International Clincal centrifuge equipped with a head which receives the wafer. 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.

3.3 Resist Prebake

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.

3.4 Exposure

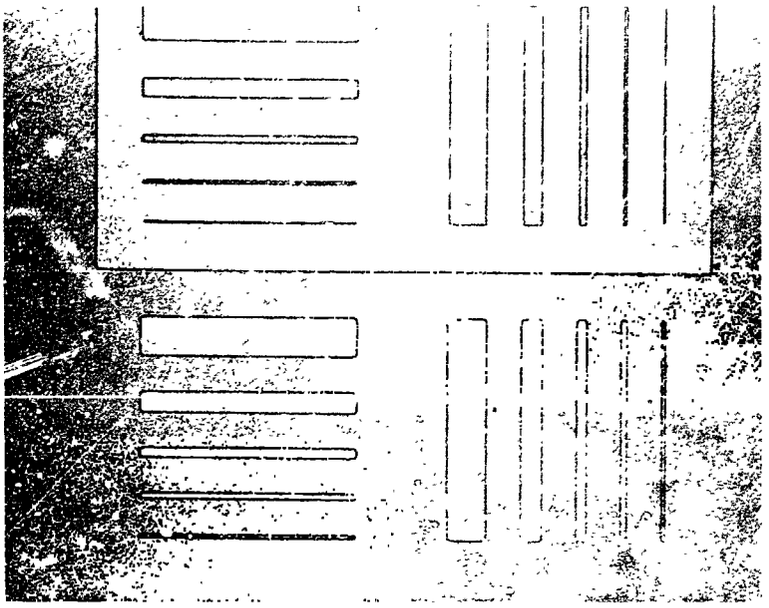
The wafer is aligned with the photographic mask and brought into contact. Light fringes must be seen at two points on the wafer or good contact will not be made and poor resolution will result. Wafer flatness must be within twenty light fringes as measured with an optical flat before application of the resist or resolution will not be uniform across the wafer. It is necessary that a radius of .005" is 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 1.9 micron thick resist (see previous photoengraving

report, Semiconductor Wafer Improvement Through Photoengraving, 17 June 1964 through 11 January 1965, contract NAS 5-2755, Procurement No. 670-W90602) consistently gave .0001" spacings at the edge of the wafer but often this spacing was 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 .0001" on the mechanical contacted wafer to .0005" on the vacuum contacted wafer. (Figure 2 and Figure 3) Lines of resist on the order of .0001" were much stronger and easier to produce in vacuum exposed resist.

The evidence was that vacuum exposed resist was thicker than mechanically contacted resist. A series of coated, exposed and developed wafers were coated with aluminum. A Tolansky fringe measurement was made with the variations in resist thickness recorded in Figure 4. 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 .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" of Hg. A gas was then admitted to the jar until the pressure was back to atmospheric. Atmospheres used were nitrogen, hydrogen, argon, carbon dioxide and oxygen. All atmospheres with the exception of oxygen gave the same result as



Resolution Pattern In Mechanically Contacted Wafer
Line Widths and Spacings of .0001, .00025,
.0005, .001, .002 inches

Resolution Pattern In Vacuum Contacted Wafer

COMPARISON OF COATING THICKNESS
VACUUM and MECHANICAL CONTACT PRINTING

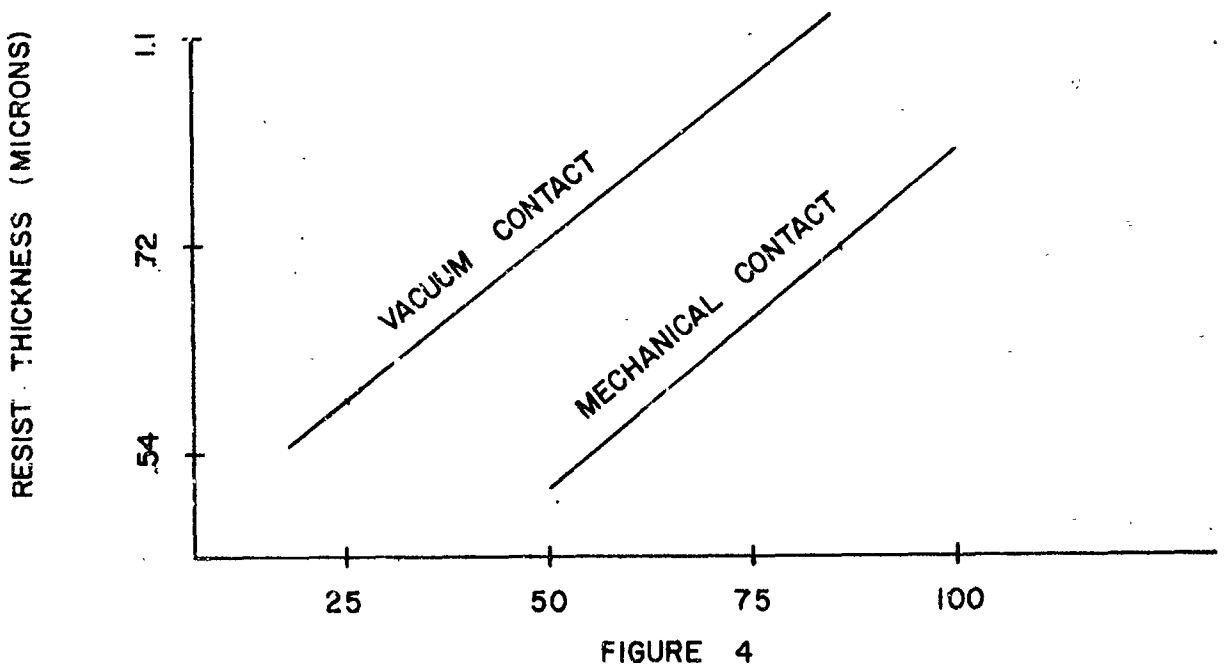


FIGURE 4

vacuum printing. The resist when exposed in an oxygen atmosphere completely dissolved from the wafer leaving no pattern at all. A series of exposures were made varying the proportions of oxygen and nitrogen. The resist thickness was measured and recorded in Figure 5. It was concluded that oxygen present during exposure prevented complete polymerization of the resist.

3.5 Developing

3.5.1 Standard Developing

The wafers are held on a vacuum chuck in a vertical plane. KMER developer is sprayed at the wafer for 30 seconds using a Paasche air gun, Model VL 5, and a number 5 tip. Air pressure is set at forty pounds. Spray distance is from three to four inches. Immediately after developing a spray rinse of 80% Isopropyl Alcohol - 20% KMER thinner is given the wafer for 15 seconds. The wafer is blown dry and is ready for inspection.

3.5.2 High Resolution Developing

With the addition of 40% dipropyl carbonate to the KMER developer, an improvement in resolution was obtained. Where the standard developing process would resolve .0002" lines when 85 cp resist was used, it was found possible to resolve .0001" lines with the dipropyl carbonate developer. Table I gives a comparison of obtainable resolution for the two developing processes.

Other developer combinations were tried but meet with little success as either the resolution was degraded or the developer caused excessive undercutting. These developers are included in Table 2.

EFFECT OF GAS COMPOSITION ON
RESIST THICKNESS

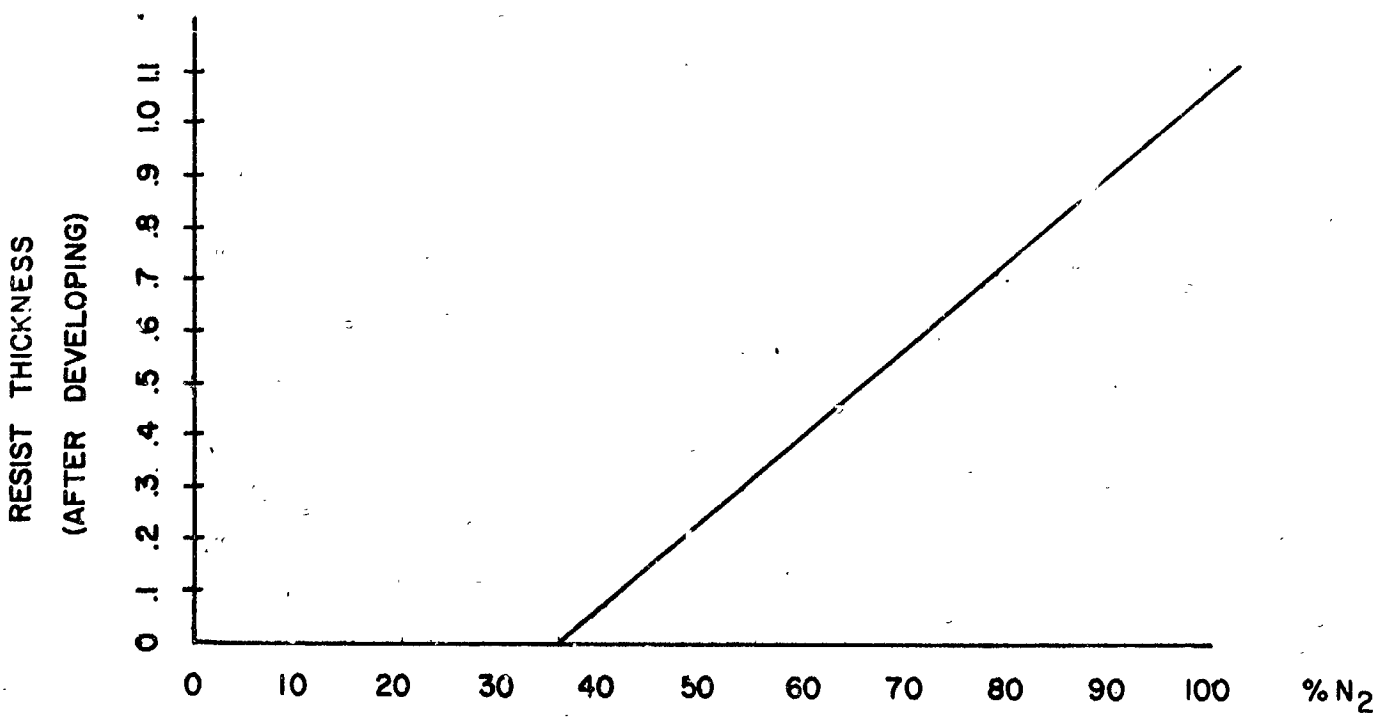


FIGURE 5

GAS COMPOSITION ($N_2 + O_2 = 100\%$)

3.6 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 or running of the resist will occur and resolution will be decreased. Lower temperatures or shorter times tend to degrade the adhesive qualities of the resist and undercutting may occur.

3.7 Etching

The etch solution is composed of:

1000 cc H_2O	Solution A
1 lb. NH_4F	
48% HF	Solution B

Ten parts of solution A is added to one part of solution B. The etch rate of this solution is 750 Å 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 2. Particular attention was paid to dipropyl carbonate. It was found that the two lots of dipropyl carbonate produced by Chemetron Chemical Company in their 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 2.

3.8 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 blown dry.

3.9 Pinholes

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

1. Standard Process
2. .75 gm Amoco 18 added to the resist
3. 40% dipropyl carbonate in the developer
4. .75 gm Amoco 18 added to the resist and 40% dipropyl carbonate in the developer.

The wafers were oxidized with 4000 Å oxide. A resist coating of 1.9 micron 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 3.

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 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 in of Hg. Dipropyl carbonate was used in the developer.

An examination of Figure 2 will show that vacuum exposed resist with a viscosity of 50 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 4) than could be expected using 85 cp resist processed by standard techniques (Table 3). No advantage could be found to using vacuum exposed resist.

TABLE 1

EFFECT OF DIPROPYL CARBONATE ON RESOLUTION

Test No	Developer System					Resist Thickness (Before Developing) μ	Resolution Inches
	Developer		Rinse				
	KMER Developer %	Dipropyl Carbonate %	Isopropyl Alcohol %	KMER Thinner %	Dipropyl Carbonate %		
1	100	-	80	20	-	1.7	.0002
2	75	25	80	20	-	1.7	.0001
3	60	40	80	20	-	1.7	.0001 (Smoothest)
4	50	50	80	20	-	1.7	.0001
5	40	60	80	20	-	1.7	would not develop
6	70	30	80	15	5	1.7	.0001
7	100	-	80	20	-	2.2	.0005+
8	60	40	80	20	-	2.2	.0002

TABLE 2

EFFECT OF DEVELOPERS ON ADHESION

Test No	Developing System KMER Developer %	Dipropyl Carbonate %	Special %	Isopropyl Alcohol %	KMER Thinner %	Special %	Undercut $\times 10^{-6}$ Inches	Remarks
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

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

Test No	Developing System						Undercut x10^{-6} Inches	Remarks
	KMER Developer %	Dipropyl Carbonate %	Special Developers %	Isopropyl Alcohol %	KMER Thinner %	Special Rinses %		
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	
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, trifluorostyrente added to resist

Test No	Developing System: KMER Developer %	Dipropyl Carbonate %	Special Developers %	Isopropyl Alcohol %	KMER Thinner %	Special Rinses %	Undercut x10^{-6} Inches	Remarks
	60	40(345)		80	20		88	(4%) α β,β, trifluorostyrene 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	

TABLE 3

CAPACITOR PINHOLE TESTS

Run #	Process	Capacitors Tested	Capacitors Tested Good	% 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

TABLE 4

CAPACITOR PINHOLE TESTS

(VACUUM EXPOSED RESIST)

RUN #227

Resist Viscosity	Capacitors Tested	Capacitors Tested Good	% Good Capacitors
25	155	36	23
50	159	98	62
75	156	132	85

4.0 NEW TECHNOLOGY

A method of using dipropyl carbonate in the developing system has been defined in this report. An Industrial Application Flash Sheet has been submitted on the innovation to the standard processing techniques.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Two procedures have been given for modification of Kodak Metal Etch Resist, electrophoresis and centrifuging. Electrophoresis is preferred as the resist doesn't have to be thinned to the extent required for centrifuging. Experience has shown that those lots which will not clean by electrophoresis also do not clean completely by centrifuging. However, the small globular particles which remain do not materially effect resolution or pinholes.

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 width of .0002" 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 has not been eliminated but is at an acceptable level for the moment.

The direct effect of oxygen on the polymerization of KMER was examined. Exclusion of oxygen from the resist ambient during exposure increased the resist thickness after developing but decreased resolution. The viscosity of the resist had to be decreased by 35% to achieve comparable resolution but this introduced a pinhole problem. Vacuum exposure is not recommended.

Dipropyl carbonate was examined as an additive to the developer to improve resolution. Line widths of .0001" could be obtained in the resist using this developer. For maskings where pinholes were considered of paramount importance, a thicker resist, 2.2 microns, was found to

yield line widths of .0002", previously the minimum line width was .0005". Dipropyl carbaonate 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 use of Amoco 18 resin in KMER gave no indication of an improved resist. No effect was seen in the resolution of the developed resist and the pinhole count of resist with Amoco 18 was no better than the resist without Amoco 18.

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 should warrent an investigation into the performance of the resist as compared to the electrophoresis KMER