FINAL REPORT

for

SEMICONDUCTOR WAFER IMPROVEMENT THROUGH PHOTOENGRAVING

17 June 1964 - 11 January 1965

Contract No. NAS 5-2755

Prepared by

WESTINGHOUSE ELECTRIC CORPORATION
DEFENSE AND SPACE CENTER
AEROSPACE DIVISION

For

NASA GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

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Prepared By C J Taylor
C. J. Taylor

Approved By William S Corak
W. S. Corak

SUMMARY

An investigation into the preparation of the surface of a silicon wafer prior to the application of photoresist to improve the resist adhesion is reported. The following process variations for obtaining oxide surfaces were investigated and correlated with resist adhesion:

1. Effect of changing oxidation temperature.
2. Variation of gas flow rates and furnace ambient composition.
3. Comparison of steam oxidation and thermal oxidation.
4. Preparation of oxide with silicon tetrachloride and carbon dioxide.

Methods of mechanically and chemically conditioning the oxide passivated surface of the silicon wafer to improve the adhesion of resist were investigated. The effects of varying the resist coating thickness through changing spin speed, acceleration and dilution of solutions were also studied. 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 were studied. Procedures were evolved and those used in the testing program are described.

Humidity was found to adversly effect resist adhesion especially above 40%. An additive to the developer was found that allowed line widths of .00025" to be etched while maintaining a yield in pinhole free areas of 3600 square mils of 93%. It was also found that line widths of .0001" could be reproducibly etched in silicon dioxide.

TABLE OF CONTENTS

1.0 INTRODUCTION

2.0 PROCEDURES

3.0 DISCUSSION

4.0 CONCLUSION AND RECOMMENDATIONS

5.0 REFERENCES

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

Improvements in techniques for photoengraving of silicon wafers have generally reduced line widths that are useable on a reproducible basis to .00025". This capability has satisfied the device designer as he has been kept busy learning the effects of integrating molecular electronic components. Now that more complicated devices are a possibility, the device designer is demanding a means of producing these devices. 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 .0001" 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 are inversely related to resist thickness and resolution is directly related to resist thickness, a resist must be selected that will provide good resolution in the resist 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[1] must be as large as possible. Etch factor is defined as

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[1] Photosensitive Resists for Industry, Eastman Kodak, p. 17.

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 was to examine various parameters that might affect adhesion of the resist. The necessity of this work has been brought about 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.

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

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

A method of modifying KMER[2] by the elimination of the globular matter makes it appear capable of meeting the requirements of high resolution photoengraving. Factors that are beyond the scope of this report (wafer

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[2] High Resolution Photoengraving for Semiconductor Devices, Westinghouse Aerospace Division, March 25, 1964, Unpublished - attached. (Note: This work was not performed as part of the present contract and is being included for information purposes only. A patent application has been filed by the Westinghouse Electric Corporation.)

flatness, mask quality, alignment and contact printing conditions etc.) have not been examined here. Also, no consideration has been given to oxides that have been contaminated with dopants.

2.0 PROCEDURES

2.1 Preparation of Wafers

The silicon wafers used for these experiments were one to two ohm-centimeter, n type, 7/8" in diameter wafers purchased from Monsanto Chemical Company. The wafers were lapped from a thickness of .017" to .013" using 12 micron Al_2O_3 grit. They were lapped to .011" using 3 micron Al_2O_3 grit and polished to approximately .010" using one micron Al_2O_3. The wafers were etched in HCl gas to a thickness of .009" to remove the sharp edges on the wafers more than to remove the mechanical strains. Rounded edges aid in the prevention of resist buildup at the edge of the wafer during the resist coating operation.

2.2 Oxidation

The furnace used to run all oxidations was a Hevi-Duty Glo-Bar furnace. Oxygen and nitrogen were supplied such that they could be admitted to the tube either directly or through a controlled temperature water supply. When water was supplied to the tube, the oxygen and nitrogen were bubbled through the water to act as a carrier.

The wafers were cleaned in concentrated sulfuric acid heated to 180°C, placed in 48% hydrofluoric acid to remove any oxide, rinsed in deionized water and blown dry before being placed in the furnace tube. Dry oxygen was flowed 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 splatter on the wafer from condensation in the tube. The following formula was used for the oxidation process:

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

In addition to the above variables, an oxide series was grown which elminated 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 through photoengraving.

2.3 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 National Instruments Company falling ball viscosimeter. The resist was applied through a syringe equipped with a .8 micron millipore 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 Dow Corning filter, CS5-58, which has approximately the same transmission curve as the sensitivity curve of KMER. Developing was by spraying KMER developer followed by a spray rinse of alcohol-KMER thinner solution. The wafers were post-baked at 180°C for 20 minutes and etched.

2.4 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 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 Å per minute for oxides not aluminized. Maximum deviation was 40 Å 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 is even smaller - on the order of 30 millionths inch. Etch times were arbitrarily extended to increase the amount of undercut so that measurements made would be more accurate. The method employed was 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 if the rate of undercut varied with time. For the first fifteen tests similarly processed wafers were etched for 10 [illegible] at 20 minutes the rate of undercut had increased 11% and at 30 minutes the rate of undercut had increased by 17.4% over a ten minute etch. This factor was used in converting the amount of undercut obtained to that expected for a 10 minute etch.

Measurements were made at a magnification of 500X using a Leitz Panphot Microscope and a Filar Micrometer eyepiece. The resist line width which was .0004" 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 has been etched for thirty minutes.

The proper comparison of resists that differ because of varying viscosities, spin speeds or accelerations require that the coating thickness be known. Coating thickness was determined in the following manner. 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 Å coating of aluminum was vacuum deposited over the resist and a fringe measurement was taken (Figure 8). A buildup of the resist occurred at the surface of the developer as shown by the reverse in the fringe line. 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 the developer and become swollen.

3.0 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 Section 3.3.

3.1 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 and points on the curve would level out and useful information would be lost. Consequently, arbitrary furnace conditions were selected throughout the test to give results somewhat less than the best condition.

The curves shown in Figures 5, 6 and 7 compare the adhesive qualities of photoresist to oxides grown at two temperatures. The curves in Figure 5 could have been drawn as a straight line and still maintain the experimental error of about 7 x 10^{-6} inches. However, since the direction of these points were consistant and the deviation of the remaining points were 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 7).

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 effected by the gas flow so it was concluded that gas flow did not effect adhesion but that the indication of adhesion was caused only by experimental error.

A new problem arose from the 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 (see Tests 13 thru 24, Table I). A complete check was made on all photoengraving process steps including etch rate. The only variable that could be found was the relative humidity in the laboratory had changed from 60% to 30%. This occured during the one day period the furnace had been changed from 1200°C to 1050°C.

To examine the humidity condition, a humidity chamber was supplied with a super-saturated solution of ammonium chloride and potassium nitrate. This solution gave a RH of 71% at 25°C.[3] 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 prebake oven. They were immediately coated with resist and processed with two other

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[3] Handbook of Chemistry and Physics - Fortieth Edition, p. 2497.

wafers that had received the same oxidation but had not been placed in the humidity chamber. The room humidity was recorded at 34% RH using a Honeywell combination hygrometer thermometer, series 612 X 21 EL 87. Test 69 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 pretreatment 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 I). 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 I). There was no improvement in the adhesive qualities of these oxides after 15 minutes.

3.2 Epitaxial Oxides

A group of oxides were 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:

$$H_2 + SiCl_4 + CO_2 \longrightarrow SiO_2 + H_2O + CO + HCl \text{ - - -}$$

(Unbalanced equation)

The wafers were then processed in the same manner outlined in paragraph 2.3 and 2.4.

Two principal problems were examined for solutions. The first was to find the proper 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 $SiCl_4$ 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 the opposite. There was no appreciable change in undercut, all wafers having 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. Oxides were found to be quite uniform having no more than 300 Å 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, 18 and 19). Time of N_2 flow was varied to show the effect of nitrogen on the oxide. It was found that an improvement in the adhesion was achieved. After ten minutes of nitrogen flow, the adhesion was as good as found on thermal grown oxides.

An experiment involving a ten micron, one Ω cm p-type epitaxial layer followed by an epitaxial oxide and nitrogen treatment the same as Test 19 was conducted using four wafers. The wafers were coated with Apiezon wax except for one small area at the edge of the wafer. One drop of 48% hydrofluoric acid was placed on the exposed oxide for 45 seconds to expose the epitaxial layer. The wax was removed from the wafer and a 3000 Å 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 Tektronix Type 575 transistor curve tracer to find if any holes existed in the oxide. A current of .01 ma was used while varying the voltage on each capacitor from 0 - 200 volts. Thirty capacitors of each of the four wafers were tested with a yield of 100%

3.3 Resists

3.3.1 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 in determining resist thickness. The standard spinner represented by the solid lines had a lapsed time to the preset speed of from five to fifteen seconds depending on the preset speed. The special spinner had a lapsed time to the preset 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 .002" in diameter. These spots of resist would not print and gave imperfections in the etched line as shown in Figure 10. The resist otherwise was 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 became very thin. It was also observed that pinholes were etched in the oxide through the very thin (1.6 micron) resist thicknesses. Differences in the adhesion between the 65 cp resist and the 85 cp resist was traced to a change in relative humidity, Table III, Test 2 and 3. Comparison of readings taken from Test 2, Table III and readings from Table I whose tests were performed in a humidity of 60 - 65% RH 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 U.V. light indicated that with a reduction of 25% from standard exposure narrow lines became somewhat wavy but adhesion was not effected. Exposures of 250% 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 absorbing out 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 effect adhesion of KMER. A 200°C prebake for 30 minutes will remove this troublesome moisture. This condition was partially examined in Section 3.1. 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 abosrb moisture. Since there appeared to be a direct correlation between humidity and adhesion even when prebake was used, the effect of humidity on the resist was examined. Wafers were processed in an atmosphere of less than 30% RH except for the time that they were being spin-coated. Air at a humidity of about 60% was passed over the spinner as the coating was being carried out. These wafers were compared to wafers that were processed only in the lower RH atmosphere. It was found that the resist adhesion was degraded by the humid atmosphere (Table III, Test 6 and 7). Only one half the expected change in undercut was noted as the undercut should have been about 90 x 10^{-6} inches at a RH of 60%. The cause of the complete amount of undercut could not be demonstrated.

3.3.2 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[4] 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 III, 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 were tried as a means of improving the adhesion. Solutions were made by dissolving the chemical in KMER thinner where necessary. The wafers were soaked in the solution for twenty minutes, sprayed off with KMER thinner to remove the excess solution and dried at 180°C for thirty minutes before coating with resist. Table III, Test 9 shows that little effect was obtained with octanoic acid or acetyl-acetone and that benzoic acid and 1-phenyl - 1, 3-butanedine caused severe undercutting.

A cleaning procedure outlined by Research Triangle Institute[5] was examined to determine what effect was obtained on adhesion

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[4] "A New Approach to Surface Chemistry and to Hetrogeneous Catalysis" by W. A. Weyl, Pennsylvania State College Mineral Industries Experiment Station, Bulletin #57, 1951.

[5] Research Triangle Institute, "Integrated Silicon Device Technology, Volume III - Photoengraving", ASD-TDR-63-316.

of modified KMER 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 solution of Alconox. (One group of wafers were scrubbed using Alconox 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 sec.
5. Pour off the methyl alcohol and cover the wafer with trichloroethylene.
6. Heat gently until boiling has been evident for 30 sec.
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 wafers that had been scrubbed with a cotton swab and those ultrasonically agitated as shown in Table III, Test 9. This undercutting was not caused by wafers that were not clean, but by excessive mechanical abrasion on the oxide. A second group of wafers were 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 were reasonably good. Mechanically cleaned wafers were even worse in Test 11 than the cleaned wafers in Test 10 because removal of all of the contaminates (Alconox) was incomplete. Wafers chemically cleaned in Test 11 were worse than the control wafers because of the excessive handling.

3.3.3 Developing

The ability of carbonates to react with rubber products led to the testing of a group of these chemicals as rinses in 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 the possibility of further enhancing the adhesion by the complete elimination of the alcohol was reasonable. Table III, 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% dipropyl carbonate and 50% KMER developer was found to be superior to KMER developer alone. The new developer combination would develop out lines of .0001" when the resist thickness was 1.7 microns and line widths of .0002" when the resist thickness was 2.2 microns. The improved resolution appeared to be as a result of minimizing the swelling action of the resist. Resist line edges did not bridge the line width 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% KMER developer. Figure 11 is of three lines, .0001", .00025" and .0005" printed in 1.7 micron thickness resist. Figure 12 is of the line etched in 6000 Å oxide after the resist has been removed.

A Patent Disclosure was submitted on the use of dipropyl carbonate as an aid in developing KMER.

3.3.4 Additives

MODAFLOW, Monsanto Chemical Company defoamer # PC 1344, designed to increase adhesion of polymer films and assist leveling and flow was added to the resist in varying amounts from 0.01% to 1.0%. No improvement was noted in the uniformity of the resist thickness as visually noted by the color fringes in the coated resist or in adhesion as recorded in Table III, Test 15.

Linolenic acid and crotonic acid were investigated as a possible means of strengthing 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 would indicate that linolenic acid did copolymerize with the KMER as with an increase of the additive the adhesion of the resist improved. Further work with this chemical was not undertaken as a roughness of the developed resist lines was objectionable. The crotonic acid failed to be of value as it caused the resist to flow into the developed-out regions.

Amoco resin 18-210 was selected because of its compatability 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 with the addition of the resin. Adhesion appeared to be best with the addition of 1% Amoco 18. A good evaluation of the additive was hampered by the low humidity. Further testing of this additive was withheld for an examination by electrical test of pinholes in the oxide.

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.

3.3.5 Capacitor Test for Pinholes

A number of methods have 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 electrically checking to see if the metal has penetrated any holes in the oxide making contact to the silicon base. (Capacitor Test). The third method was perferred here as it is 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 controlled by controlling the oxide thickness and time of oxide etch.

Tests previously made under a Westinghouse Military Research and Development Program had shown that in controlling pinholes consideration must not only be given to the etch time but 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 dryed. It was found that for resist thickness of 1.9 microns a twenty minute delay in resist removal caused an increase of 15% in defective 3600 square mil capacitors. A significant test for pinholes must therefore consider what oxide thickness, (consequently the required etch time)is required for the devices for which the test is being conducted. Since 7000 Å is a good general oxide thickness a 10 minute etch was selected for this set of tests. It was desired that all pinholes, even those that normally are etched only partially through the oxide giving weak points would show up in this test. To accomplish this, the oxide thickness was grown to a thickness of only 4000 Å. Normally this thickness of oxide would require less than 5½ minutes etch so a 10 minute etch would open any holes that had started after 5½ minutes of etching.

Photographic masks were not used in exposing the resist to ultraviolet light except in Table IV, Test 4. 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!) it is possible to obtain the 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 in Section 3.2.

Test 1 Table IV was conducted to examine the effect of doubling exposure time on pinholes. This test also included a comparison of the standard KMER developer and the 50% KMER developer - 50% 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 IV 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 (.0002" line capability) was 93%. Test 3 shows that a 1.7 micron thick resist (.0001" line capability) had an acceptance probability of 38%.

The addition of 1% Amoco 18 to the resist improved the pinhole rate from 38% (Test 3) to 61% (Test 5). Some question arises as to why wafers from Test 1 that were processed similarly to Test 3 had a yield of over 60%. More extensive testing of Amoco 18 would be needed to completely evaluate this resin. A Patent Disclosure was submitted on the use of Amoco 18 as an additive to KMER to improve adhesion and reduce pinholes.

Test 5 and 6 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.

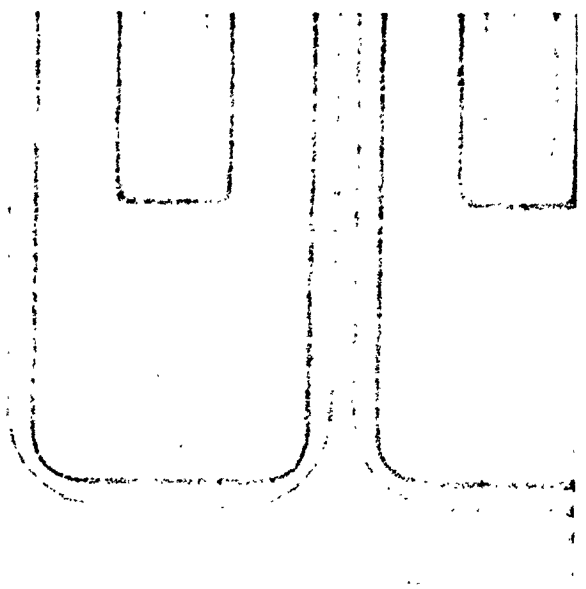
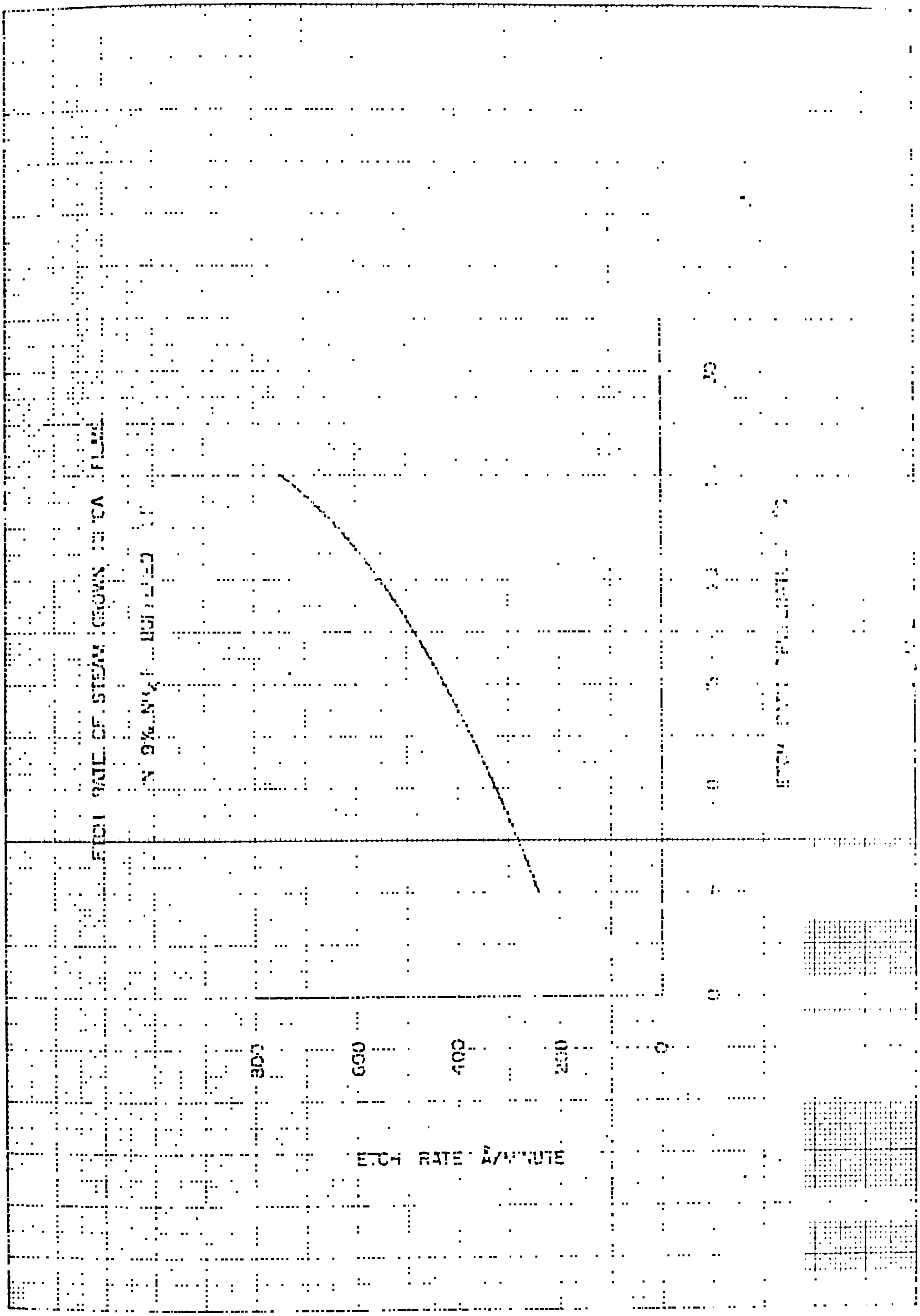


FIGURE 1

Etched Oxide Showing Undercutting Of Resist By Etch Solution. 500X

FIGURE 2

Aluminized Wafer Showing Thickness Of Oxide (3600 A) By Fringe Measurement


ETCH RATE OF STEAM GROWN SILICA FILM
IN 9% NH4F BUFFERED HF
800
600
400
200
0
ETCH RATE Å/MINUTE

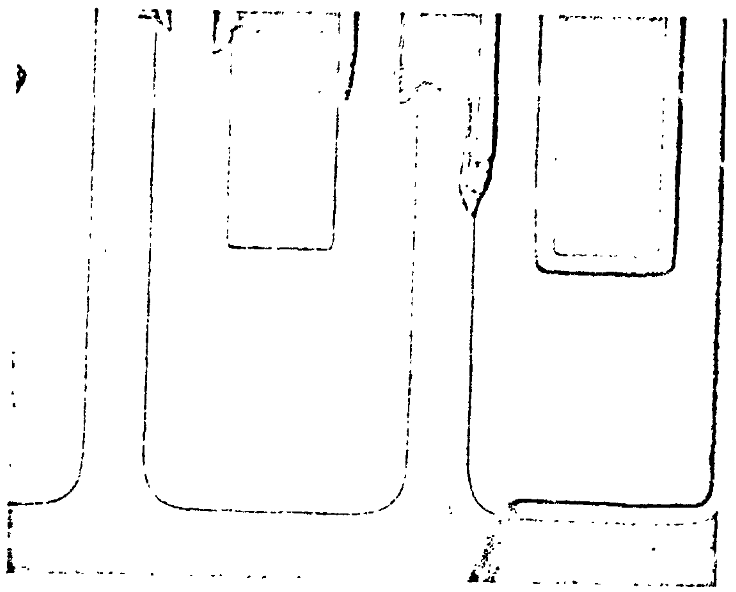
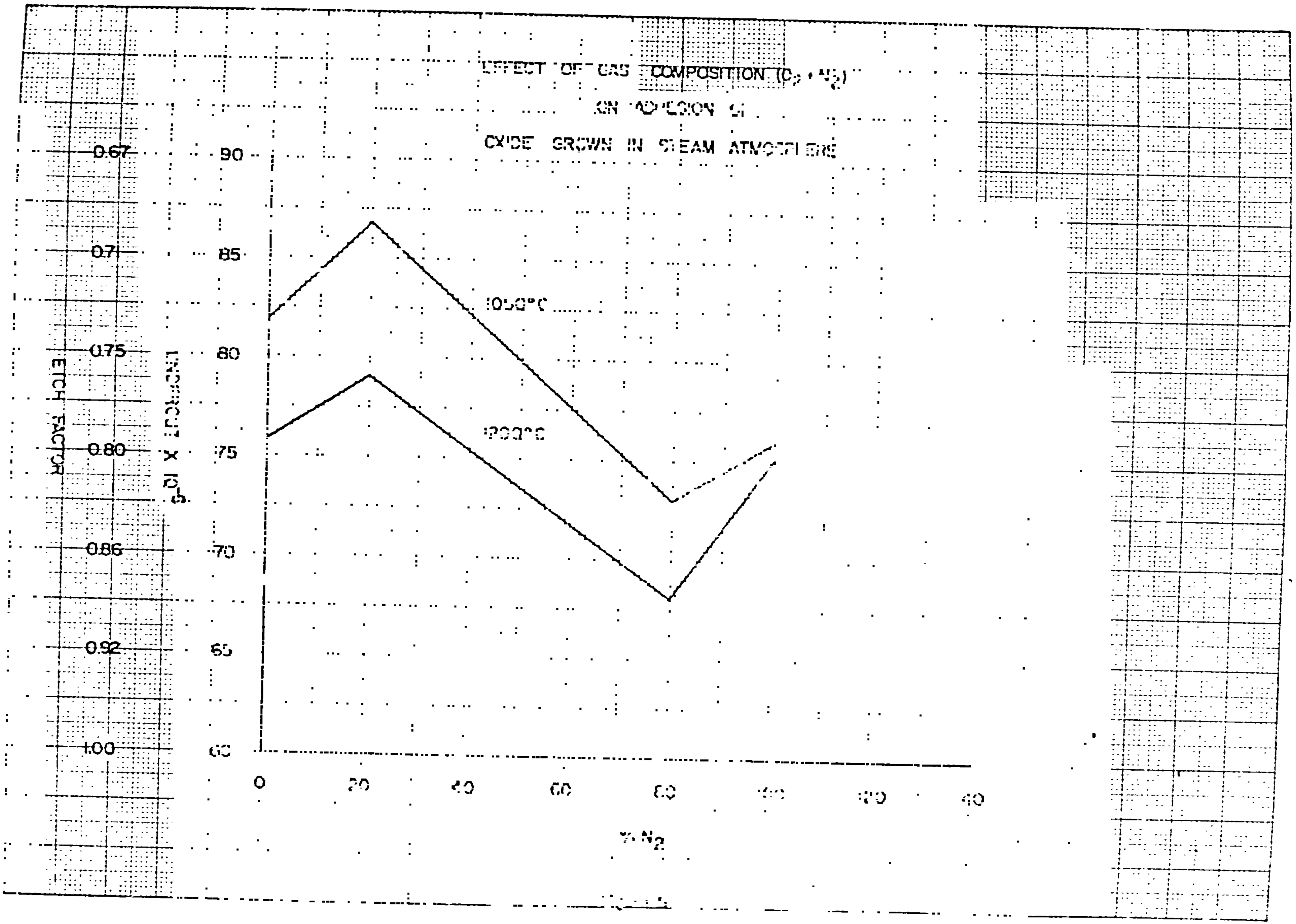
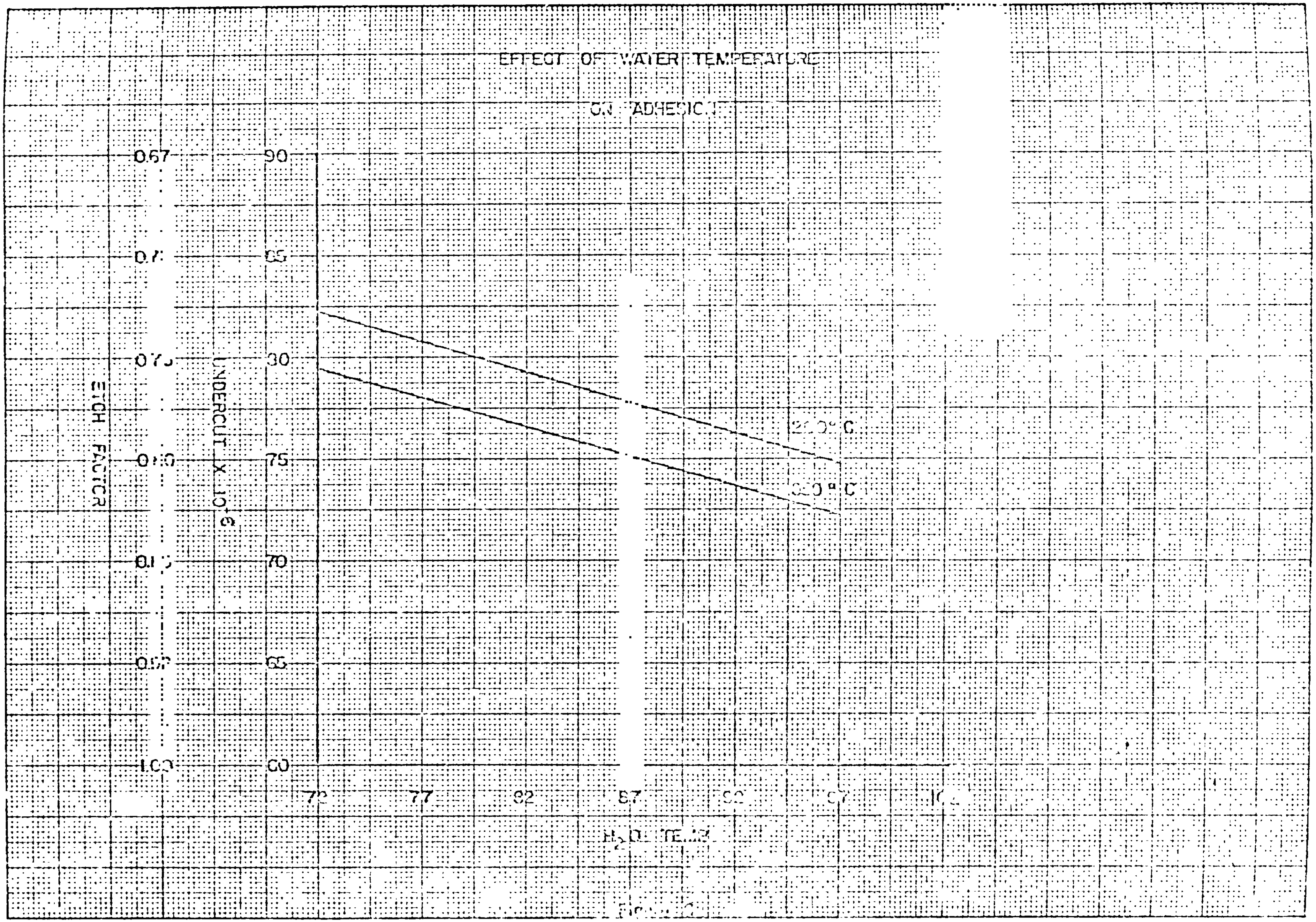
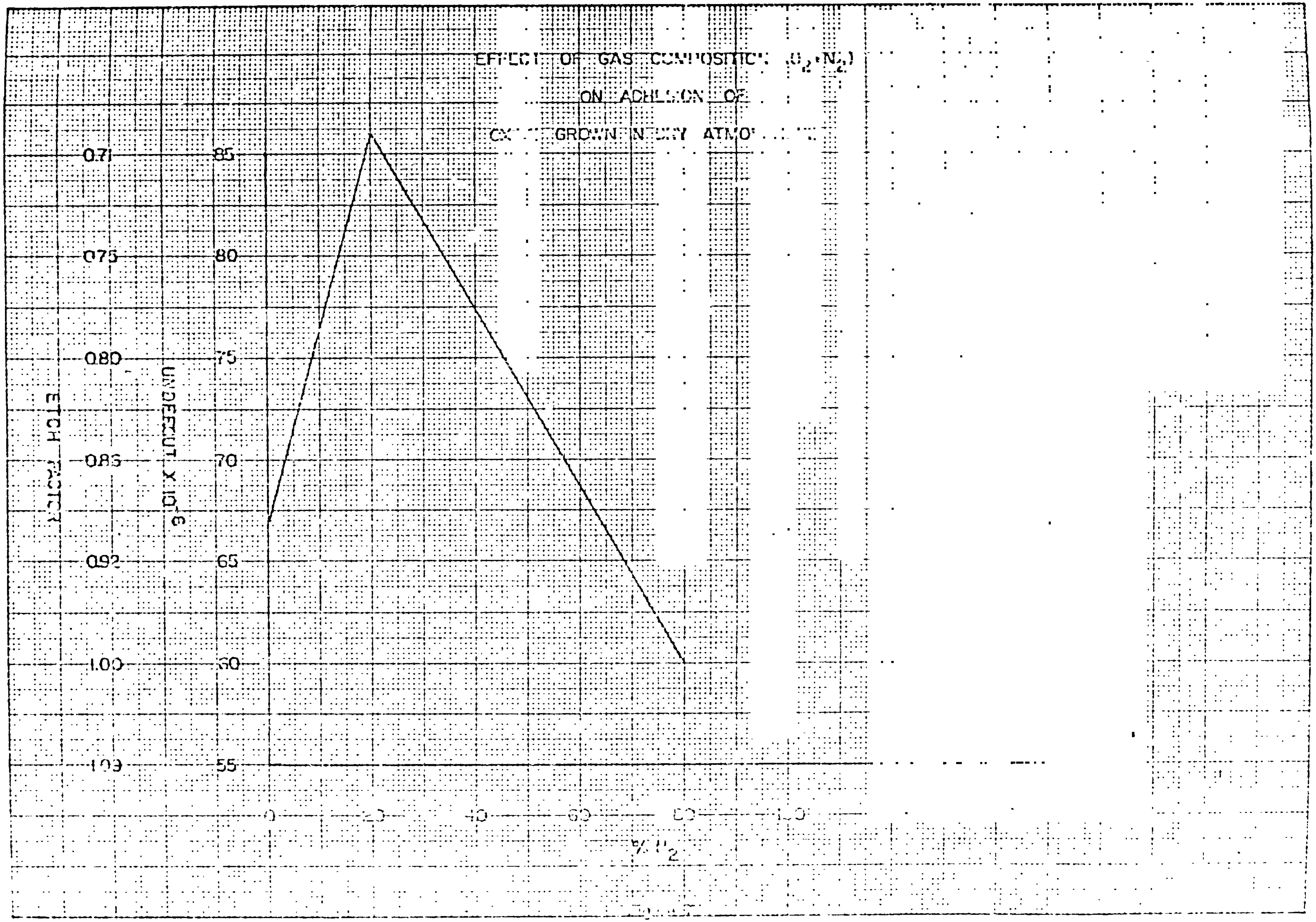


FIGURE 4

Resist Torn Away From Wafer
Exposing Etched Lines. 500X


EFFECT OF GAS COMPOSITION (O_2 + N_2)
ON ADHESION OF
OXIDE GROWN IN STEAM ATMOSPHERE
1050°C
1200°C
UNDERCUT X 10^{-5}
90
85
80
75
70
65
60
ETCH FACTOR
0.67
0.71
0.75
0.80
0.86
0.92
1.00
0
20
40
60
80
100
120
140
% N_2


EFFECT OF WATER TEMPERATURE
ON ADHESION
ETCH FACTOR
0.67
0.7
0.75
0.80
0.8
0.9
1.00
UNDERCUT X 10-6
90
85
80
75
70
65
60
200° C
300° C
72
77
82
87
92
97
102
H2O TEMP



EFFECT OF GAS COMPOSITION (H_2, N_2) ON ADHESION OF OX GROWN IN DRY ATMO

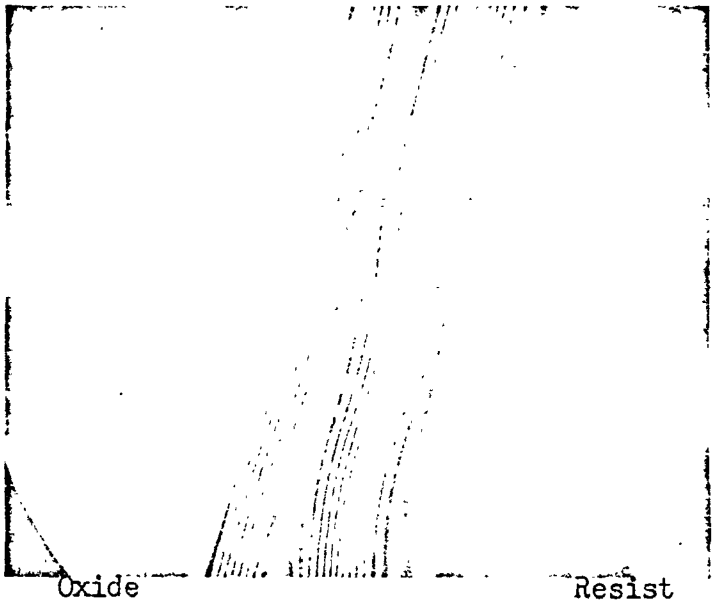


FIGURE 8

Fringe Measurement of Resist Thickness
(16-9=7 fringes or 1.7 microns)

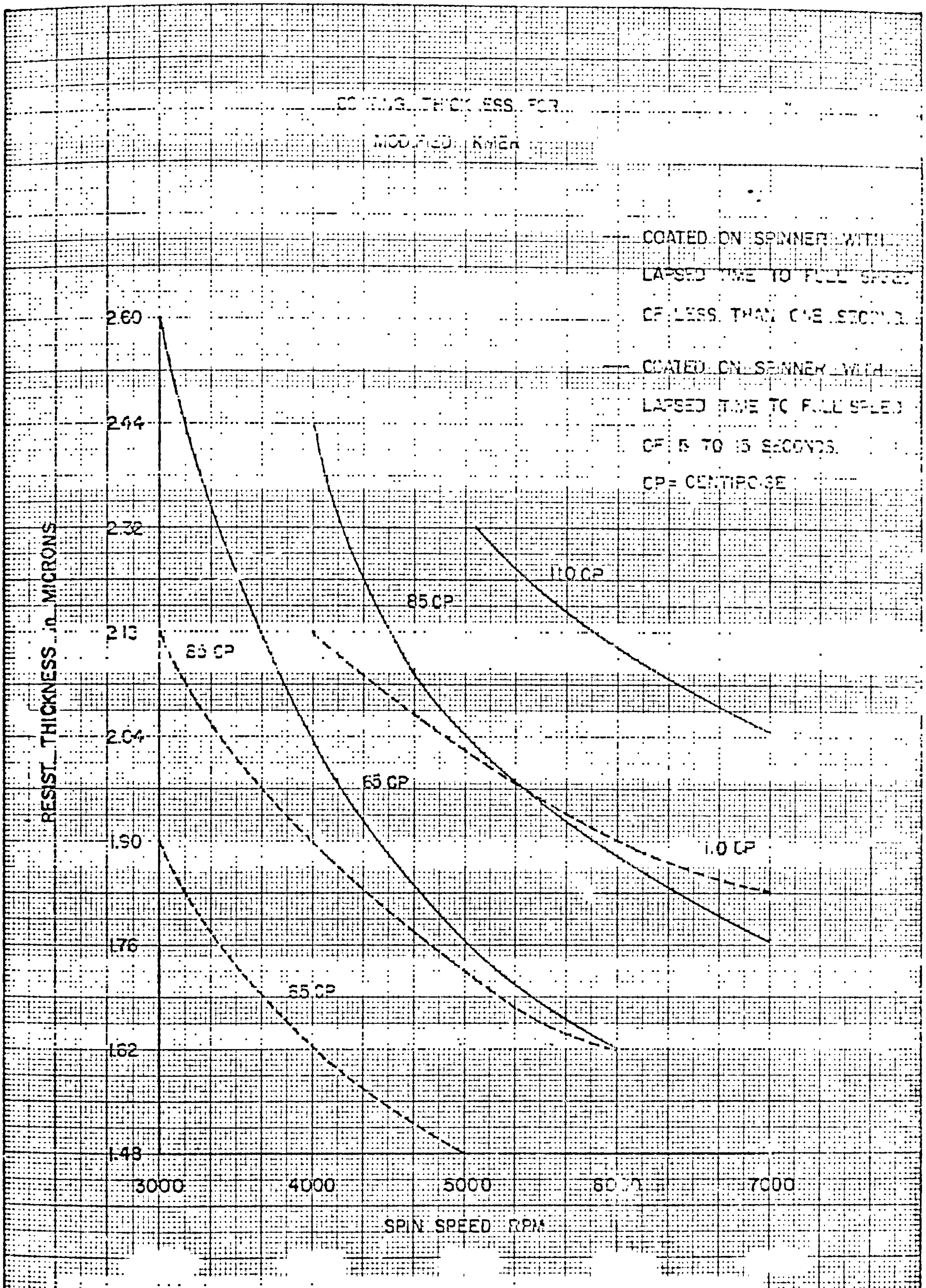

COATING THICKNESS FOR
MODIFIED KMER
COATED ON SPINNER WITH LAPSED TIME TO FULL SPEED OF LESS THAN ONE SECOND.
COATED ON SPINNER WITH LAPSED TIME TO FULL SPEED OF 5 TO 15 SECONDS.
CP= CENTIPOISE
RESIST THICKNESS in MICRONS
2.60
2.44
2.32
2.18
2.04
1.90
1.76
1.62
1.48
110 CP
85 CP
85 CP
65 CP
110 CP
65 CP
3000
4000
5000
6000
7000
SPIN SPEED RPM

Figure 9

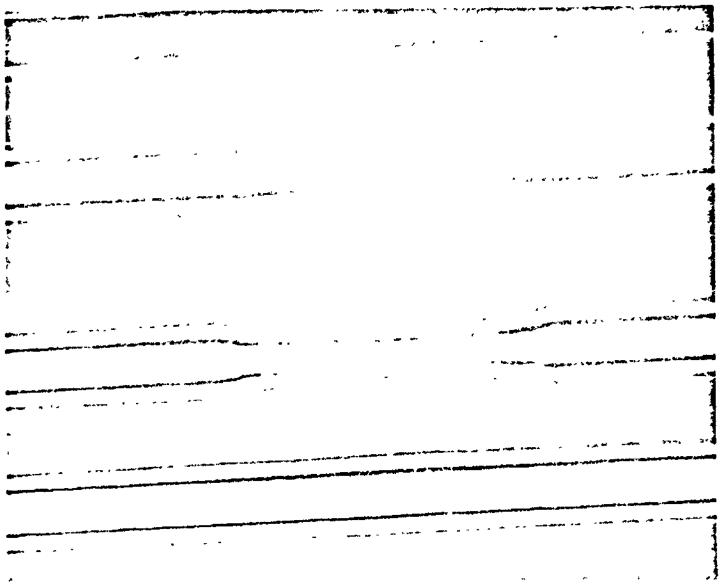


FIGURE 10

A Defect Caused By Improper
Coating of the Resist

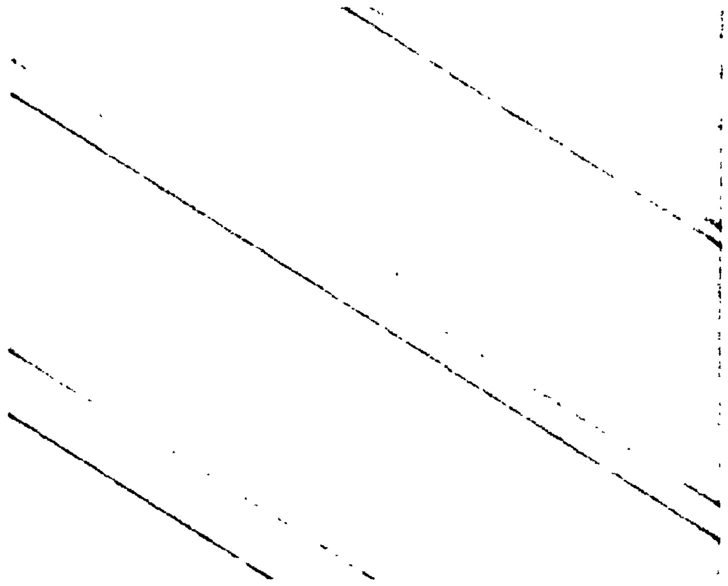


FIGURE 11

Line Widths Of .0001, .00025 and .0005 Inches
Printed In 1.7 Micron Resist 550X

FIGURE 12

Lines Etched In 6000 Å Oxide
Resist Removed. 550X

TABLE I

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 Å	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

Test #	Oxidation Time (Minutes) "X"	Furnace Temp. °C	Water Temp. °C "T"	Oxygen cc/min "Y"	Nitrogen cc/min "Z"	Oxide Thickness Å	Undercut (For 10 min etch) x 10^{-6} inch	
			GAS FLOW (REPEAT)					
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	

Test #	Oxidation Time (Minutes) "X"	Furnace Temp. °C	Water Temp. °C "T"	Oxygen cc/min "Y"	Nitrogen cc/min "Z"	Oxide Thickness Å	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 50,41,43,52,53,54 GIVEN ADDITION TREATMENT			
60	5	1050	100	0	100		
					Wafer from Test:	50	50
						41	67
						43	67
						52	60
						53	70
						54	60
61	60	1050	100	400	100		

Test #	Oxidation Time (Minutes) "X"	Furnace Temp. °C	Water Temp. °C "T"	Oxygen cc/min "Y"	Nitrogen cc/min "Z"	Oxide Thickness Å	Undercut (For 10 min etch) x 10-6 inch
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)

TABLE II

ADHESION TO EPITAXIAL OXIDES

	EPITAXIAL GROWTH			OXIDE GROWTH								
Test #	EPI. Temp °C	Dopant	Time Min.	H_2 Carrier Flow-l/min	$SiCl_4$ H_2 Flow-cc/min	$SiCl_4$ Flow-cc/min	CO_2 Flow cc/min	Temp °C	Time Min.	Oxide Thickness Å	Undercut for 10 min. etch x 10^{-6} inches	N_2 Flow @ 1215°C-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	13.5	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

TABLE III

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 x 10^{-6} inches	Remarks
1	80	1200	92	400	100		
		Standard Spinner	85 Cp	Resist	6000 RPM	86	
		Special Spinner	65 Cp	Resist	4000 RPM	94	
		Special Spinner	85 Cp	Resist	5000 RPM	94	
		Special Spinner	110 Cp	Resist	7000 RPM	87	
2	80	1200	92	400	100		RH = 65%
			65 Cp	Resist	6000 RPM	74	Thin Resist had Pinholes
					5000 RPM	86	
					4000 RPM	83	
					3500 RPM	91	
3	80	1050	92	400	100		RH = 35%
			85 Cp	Resist	8000 RPM	55	
					7000 RPM	59	
					6000 RPM	65	
					5000 RPM	63	
					4000 RPM	—	Resist Thick - Poor Lines
4	80	1050	92	400	100		
			85 Cp	Resist	6000 RPM		
				Exposure Time:	15 sec.	79	Narrow Lines where Wavy
					$17\frac{1}{2}$ sec.	83	
					20 sec.	76	Standard Exposure
					$22\frac{1}{2}$ sec.	78	
					25 sec.	71	

Test #	Oxidation Time (Minutes) "X"	Furnace Temp. °C	Water Temp. °C "T"	Oxygen cc/min "Y"	Nigrogen cc/min "Z"	Undercut x 10^{-6} inches	Remarks
5	80	1050	92	400	100		RH = 33%
			85 Cp Resist				
			Exposure Time:		20 sec.	63	Standard Exposure
					30 sec.	57	
					40 sec.	61	
					50 sec.	58	
6	80	1050	92	400	100		
			85 Cp Resist				
		Wafers Coated in RH of 28%				64	
		Wafers Coated in RH of 55%				75	
7	80	1050	92	400	100		
			85 Cp Resist				
			RH of 22%			51	
			RH of 62%			75	
8	45	1200	92	400	100	96	
		Wafers Coated with Aluminum & Stripped				133	
9	45	1200	92	400	100	94	
		5% Benzoic Acid (Surface Adherent)				143	Localized Undercutting
		10% 1 Phenyl - 1, 3 Butanedine (Chelating Agent)				Extreme Undercutting	
		100% Octanoic Acid (Surface Adherent)				99	
		100% Acetyl Acetone (Chelating Agent)				99	
10	80	1050	92	400	100	61	PH = 20%
		Wafers cleaned with Cotton Swab				330	
		Wafers cleaned with Ultrasonic Agitation				228	
11	80	1050	92	400	100	64	RH = 22
		Wafers Ultrasonic In Alconox				Extreme Undercutting	
		Wafers cleaned in Chemicals				79	
12	80	1050	92	400	100	77	
		Developer Rinses:					
		Dipropyl Carbonate				70	
		Methyl Ethyl Carbonate				78	
		Dimethyl Carbonate				80	
		Diethyl Carbonate				77	

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

CAPACITOR PINHOLE TESTS

Test #	Oxide Thickness	Resist Lot	Viscosity Cp.	Spinner Speed R	Exposure Time sec.	Developer	Total Capacitors Tested	Capacitors Tested Good	% 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	

4.0 CONCLUSIONS AND RECOMMENDATIONS

Modified Kodak Metal Etch Resist 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 Å and for etching times of thirty minutes. Parameters of oxide growth effected adhesion at higher relative humidity but this variation was overcome as the humidity dropped below 40%. Very low relative humidity, below 30%, is not recommended as static charges on the wafer tend to attract particulate matter. Changes to 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 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 effect 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% KMER Developer - 50% dipropyl carbonate illustrated that a resist thickness of 2.2 microns could be used while producing line widths of .00025" and an acceptance of 93% of 36000 square mil capacitors free of pinholes. Reproducible .0001" lines were a reality using 1.7 micron resist thickness.

The addition of 1% Amoco 18 resin not only improved resist adhesion but improved the pinhole acceptance of the etched oxide. An extensive testing program for this additive would be required to completely prove its acceptability.

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 phtographic plate. The reliability of reproducing .0001" lines is highly dependant on good contact between the wafer and the photographic plate. The experience of this laboratory has been that a flexible wafer stage such as a rubber mat will give better contact than a rigid one. The apparent problem with the flexible stage is that close alignment is difficult as the wafer must be held further 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.

5.0 REFERENCES

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Unpublished - Attached

3. "Handbook of Chemistry and Physics", Fortienth Edition, p. 2497

4. "A New Approach to Surface Chemistry and to Heterogeneous Catalysis", By W. A. Weyl, Pennsylvania State Mineral Industries Experiment Station, Bulletin # 57,1951

5. Research Triangle Institute, "Integrated Silicon Device Technology, Volumn III, Photoengraving", ASD-TDR-63-316

Molecular Systems Engineering

Technical Memorandum No. 17

HIGH RESOLUTION PHOTOENGRAVING FOR SEMICONDUCTOR DEVICES

March 25, 1964

WESTINGHOUSE ELECTRIC CORPORATION
Air Arm Division
Baltimore, Maryland

By

C. J. Taylor
I. F. Barditch

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. Capable of withstanding low surface tension, highly corrosive etches such as buffered hydrofluoric acid without undercutting or lifting at edges of the film.
2. Possess the resolution capability of .0001" 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 previously exhibited reasonable resistance to undercutting and 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 .0008 inches (lot 6304) with unusually rough edges and .0004 inches (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 .00025" 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 and 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 this material 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 1.

Samples of KMER were dissolved in toluol and a concentration of .66 g/100 ml was most convenient. Below 400 millimicrons the concentration was reduced to .165 g/100 ml (see Figure 1). Readings were carried out between 335 and 580 millimicrons on four sample lots of KMER.

There was an attempt 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 light of the small number of samples no strong conclusion could be drawn. The results are suggestive rather than conclusive.

After an attempt at centrifugation 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 millipore 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 the original brown, viscid gelatinous blob containing KMER. The modified resist was now capable of passing through an .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 2, 3 and 4. The implication to be drawn from these curves is that the supernatant clarified component of KMER has a much higher transmission in short wavelengths and 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 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 H_2SO_4 for about 5 minutes results in clean surfaces.

Tests conducted on ER has shown that it is capable of resolving line widths of .0001" and is capable of withstanding 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 Å 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 concept is that the electric charge on the unwanted colloidal matter is neutralized and it then coagulates. Another concept is that there is an actual migration of the unwanted matter to one of the electrodes and 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 explaination of these phenomena at this time. The attached photograph, taken at 500X, shows WSR as exposed to the standard Air Force target array.

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 has thereby resulted in a step forward in semiconductor block processing.

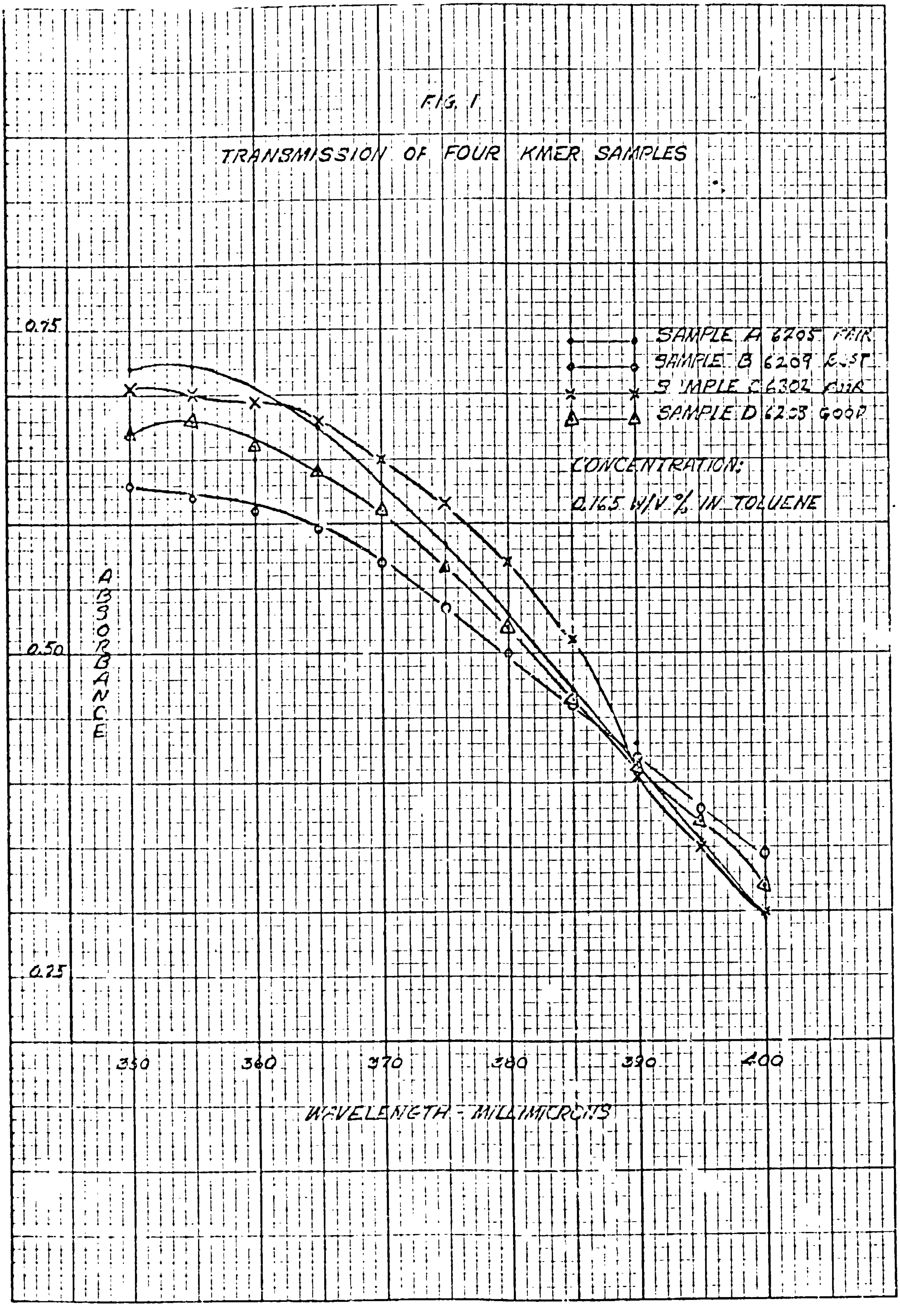


FIG. I

TRANSMISSION OF FOUR KMER SAMPLES

FIG 2

TRANSMISSION OF NORMAL KIMER

not subjected to high voltage

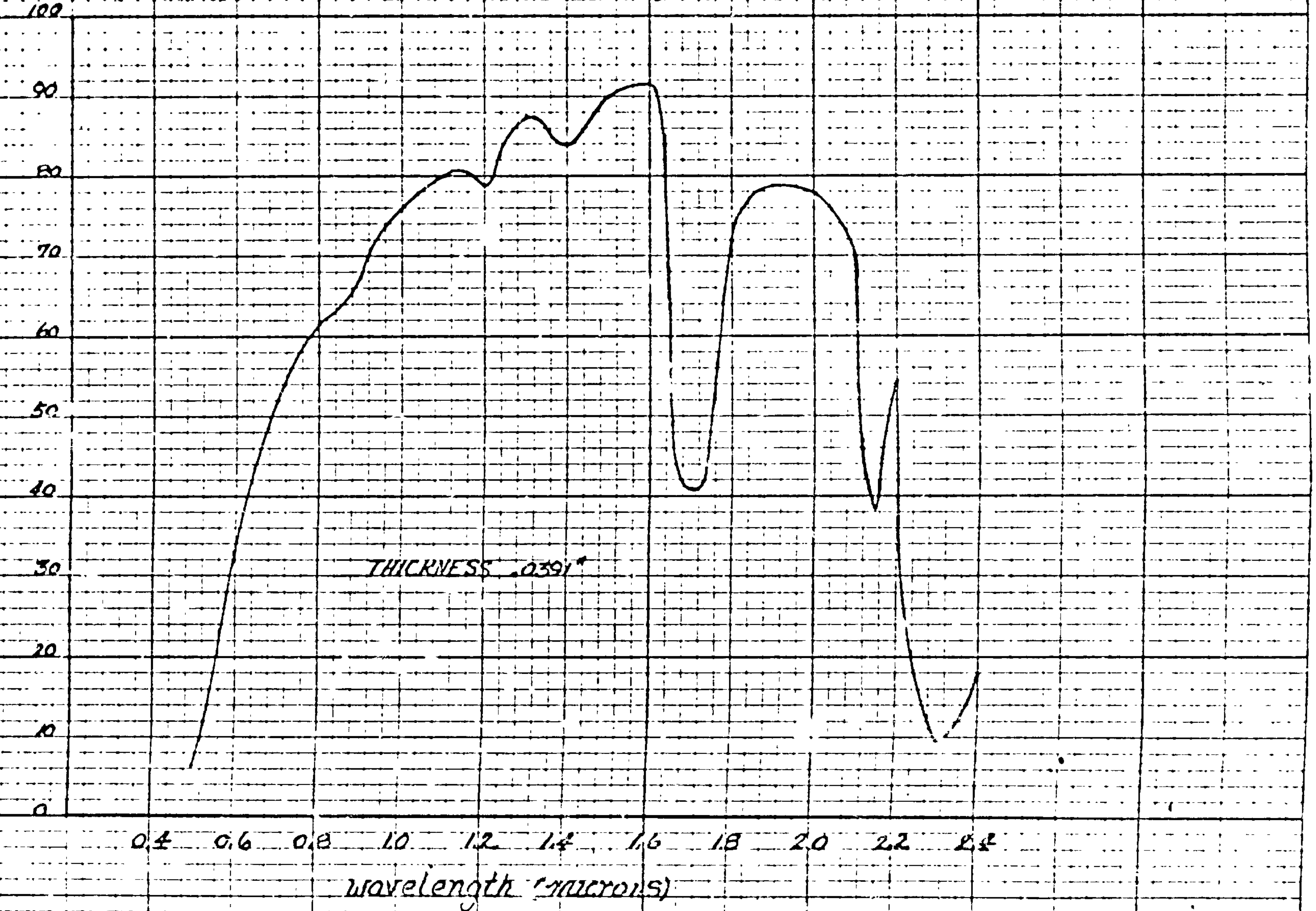
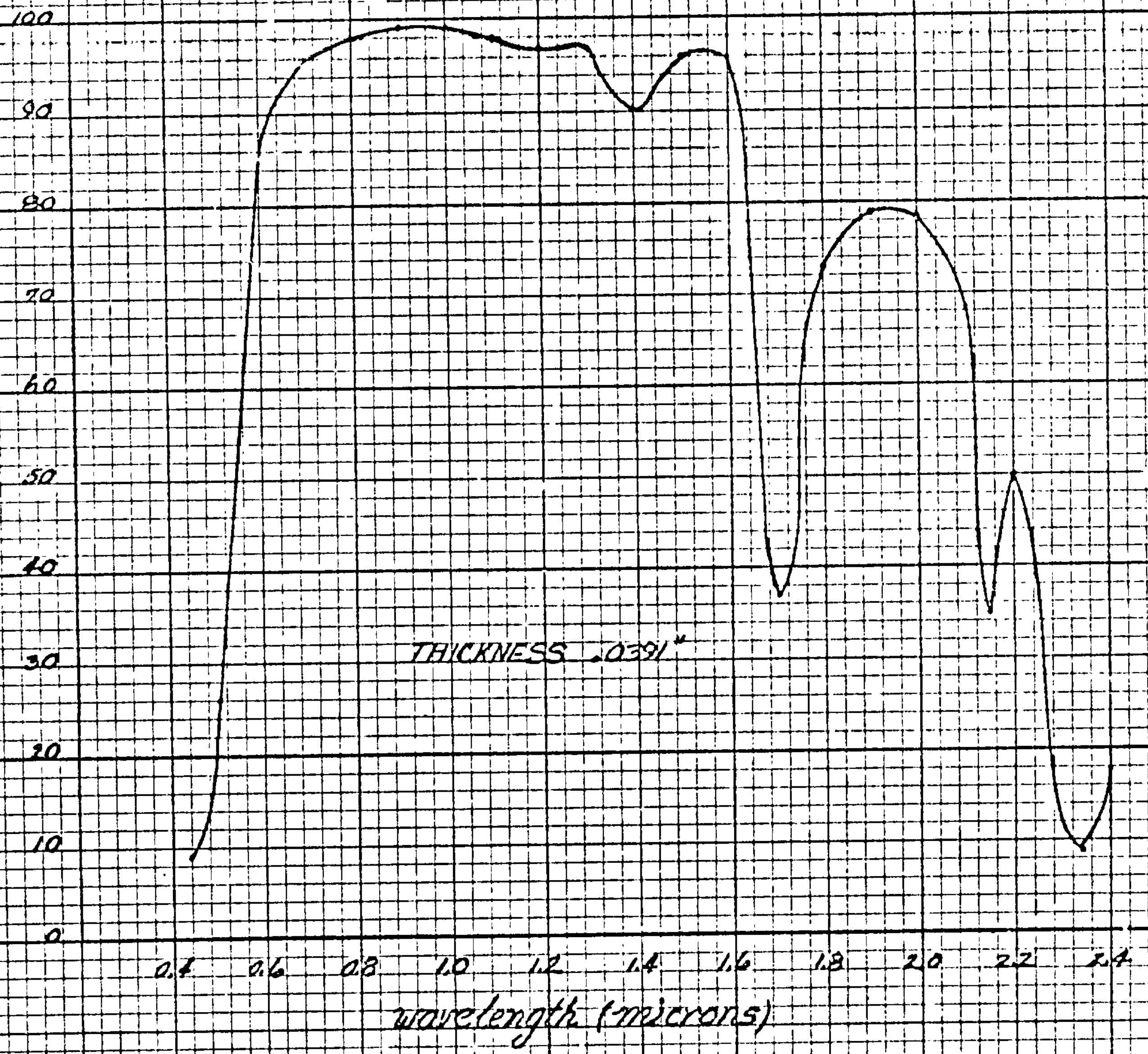


FIG.3

TRANSMISSION OF SUPERNATANT KMER
AFTER APPLICATION OF HIGH VOLTAGE



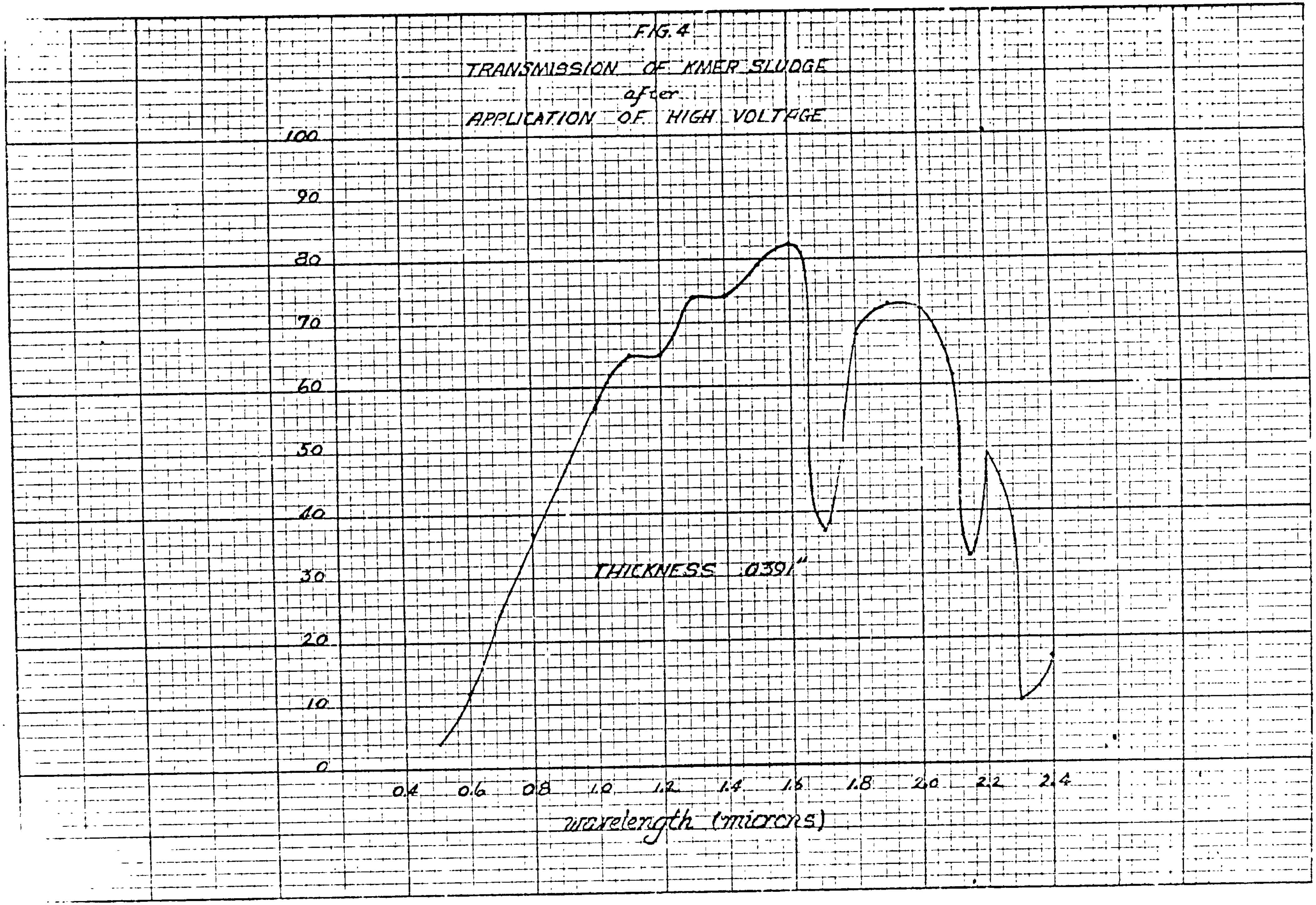


FIG. 4

TRANSMISSION OF KMER SLUDGE
after
APPLICATION OF HIGH VOLTAGE

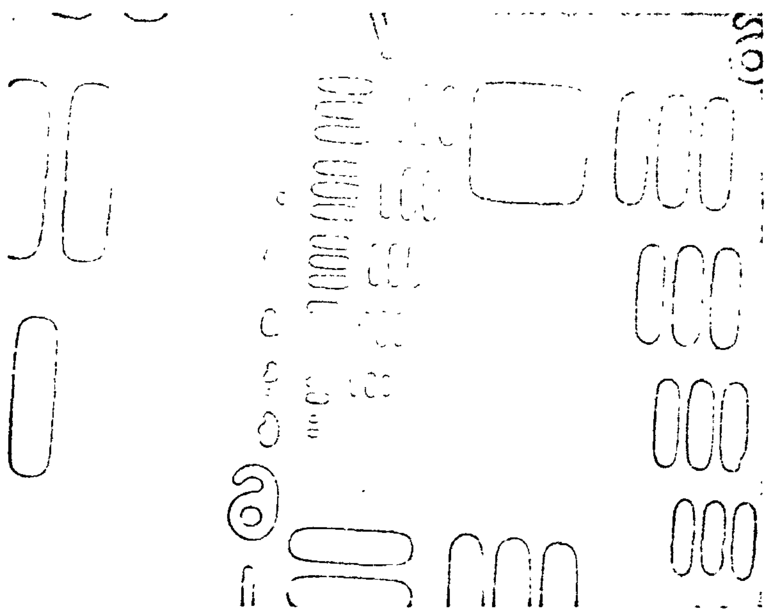


FIG 5 500 X

PATTERN SHOWING WSR PRINTED AND DEVELOPED ON A SILICON DIOXIDE SURFACE.