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RESEARCH AND DEVELOPMENT
FOR
SURFACE PROTECTION
FOR
SILICON DEVICES

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RESEARCH AND DEVELOPMENT
FOR
SURFACE PROTECTION FOR SILICON DEVICES

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FOREWORD

Work during the past quarter was directed toward chemical surface treatments and their efforts on breakdown voltages, studies on the formation of thermal oxides of silicon, and the electrical evaluation of passivating coatings on silicon.

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A. CHEMICAL SURFACE TREATMENTS AND THEIR EFFECTS ON BREAKDOWN VOLTAGES

Author: M. A. Hall

ABSTRACT

Wet chemical treatments which can shift surface potential in devices, and alter their current-voltage characteristics to produce higher voltages for specified currents have been demonstrated, the nature of the oxidizing material studies, the effective concentration of chemical in the treatment solution investigated, and the most effective desiccant to preserve the effect of the surface modification has been proposed.

1.0 Introduction

With emphasis on device parameter control to produce higher reliability devices, the important role of the surface has been written about at great length in the literature. Study in this group has been concentrated upon the effects of surfaces on observed PN junction breakdown voltages in alloyed germanium devices.

As has already been reported from this laboratory, certain chemical surface treatments have been found that significantly raise the apparent breakdown voltages in P+N junctions in alloyed devices. The experimental procedure used to produce this effect was to dip completely fabricated, electrolytically etched, but unsealed devices into a freshly prepared dilute solution of strong oxidizing agent, to blot and bake them dry in an oven, and then seal each with a desiccant in its encapsulation. Observed PN junction breakdowns were more than doubled in most cases by this technique .

Investigations have continued into the important variables in this surface oxidizing treatment technique.

2.0 The Oxidizing Agent Utilized

The chemical oxidizing agents first used to produce increased junction breakdown voltages in this laboratory were permanganates, dichromates and vanadates. Observing the location of the principal elements of these materials - that is, vanadium, chromium and manganese in the periodic arrangement of the elements, it was noted that they occur in groups V, VI, and VII of the table. With this in mind, an attempt was made to secure the corresponding compounds of other elements above and below in the periodic table the three already tried and found effective. These materials were: molybdates, tungstates, rhenates, niobates, etc. No attempt was made to find an optimum concentration or aging temperature for each material investigated, but it has been ascertained that treatment of alloyed germanium devices with dilute solutions of salts of any of the group V, VI, and VII elements (as described in Scientific Report No. 2 for dichromates and permanganates) produces to varying degrees, a significant change in observed PN junction breakdown voltage. A control (untreated) group was always processed with each group of test devices.

3.0 The Concentration of Oxidant in Solution

It was found early in our work that a very high concentration of oxidizing agent in the aqueous dipping solution could produce damage to devices so treated, because such strong oxidants attacked exposed metals and solders in the fabricated devices, and often crystallized objectionably over the surfaces of the treated devices when they were dried.

To find, then, the lowest effective concentration of the oxidizing material in solution, has been one of our objectives. Concentrations of oxidizing solutions varying from 10 percent by weight of oxidant down to as little as 0.01 percent were investigated. It appears that the optimum concentration of oxidizing materials for producing significant increases in breakdown voltages is not precisely the same for all materials tried. However, in most cases, the best results were obtained with solutions in the range 0.03 to 0.1 percent by weight of oxidizing material in solution.

4.0 The Desiccant Used to Encapsulate Devices Which Have Been Surface Treated with Oxidizing Solutions

A desiccant is added to the encapsulations of many devices to produce the driest possible ambient conditions. In this ambient the device usually is most stable.

In the case of high voltage devices produced by the solution treatment previously described, barium oxide, a very strong desiccating material was added to the encapsulations of all test and control devices. Previous study in this laboratory had shown that barium oxide-encapsulated devices were stable, and that the variance in distributions of the surface-dependent parameters in these devices was small. Hence, the choice of barium oxide.

To know, however, whether other desiccating materials might be used as effectively with the surface-oxidized devices, was deemed important. Experiments were run using oxides of the other alkaline earth metals besides barium, and it was found that they, too, possess strong enough desiccating power to maintain a stable surface-oxidized, high voltage device.

Other materials tried, such as molecular sieve and some silicone varnishes, did not seem to be active enough to preserve the stability of these high voltage devices, whereas in a standard device, these materials are adequate desiccants.

It has been shown, therefore, that for high voltage devices produced by the chemical surface treatment in this laboratory, only barium oxide, or its drying equivalent, seems the most suitable desiccant for use in the encapsulation.

5.0 Other Variables Which Will Be Investigated

To complete this phase of study on the variables active in the production and maintenance of high breakdown voltage levels in germanium alloyed devices by the surface oxidation-treatment technique, the effect of varying the post-treatment baking temperature will be studied further. An attempt will be made to apply the technique to other devices, and the aging studies already begun will be continued for a longer period of time so that data will be available for as long a period as is reported in most device reliability studies (5000 hours or more).

B. FORMATION OF THERMAL OXIDES OF SILICON

Authors: H. C. Evitts
H. W. Cooper
S. S. Flaschen

ABSTRACT

Oxidation growth rates of SiO_2 have been studied using as variables Si conductivity types, crystal growing methods, and bulk resistivity. Rates were determined in closed systems of both dry O_2 and steam over a temperature range of 800° to 1300°C.

The conclusion is drawn that the only factors controlling oxide growth rate were time, temperature, and ambient. Results reported include a study of the optical properties of the oxide films.

Because of the increased importance that oxide films have in the diffusion masking and surface passivation of planar silicon devices, we have felt it highly desirable to know with precision the oxidation kinetics for silicon under various conditions of conduction type, resistivity, and ambient atmospheres.

Our work was a two-fold one; first, to find better ways to measure these oxide films, and second, to obtain more information about the growth rate as a function of properties.

We also attempted to orient our work as much as possible, and whenever possible, to the methods that were being used, or could be easily adapted to production facilities. Therefore, some of the exacting laboratory conditions that could have been imposed were circumvented in one way or another so that we would have techniques that the device fabrication lines could use. The oxidation system used was a closed one, as shown in Figure 1, consisting of a high temperature diffusion furnace, with all of the accompaning glassware constructed of high-purity quartz. On the left-hand side of the schematic is the ambient introduction area. For our "dry" system, line O_2 was passed through suitable drying chambers to get the moisture content below 1 ppm and then through a sub-

CLOSED OXIDATION SYSTEM

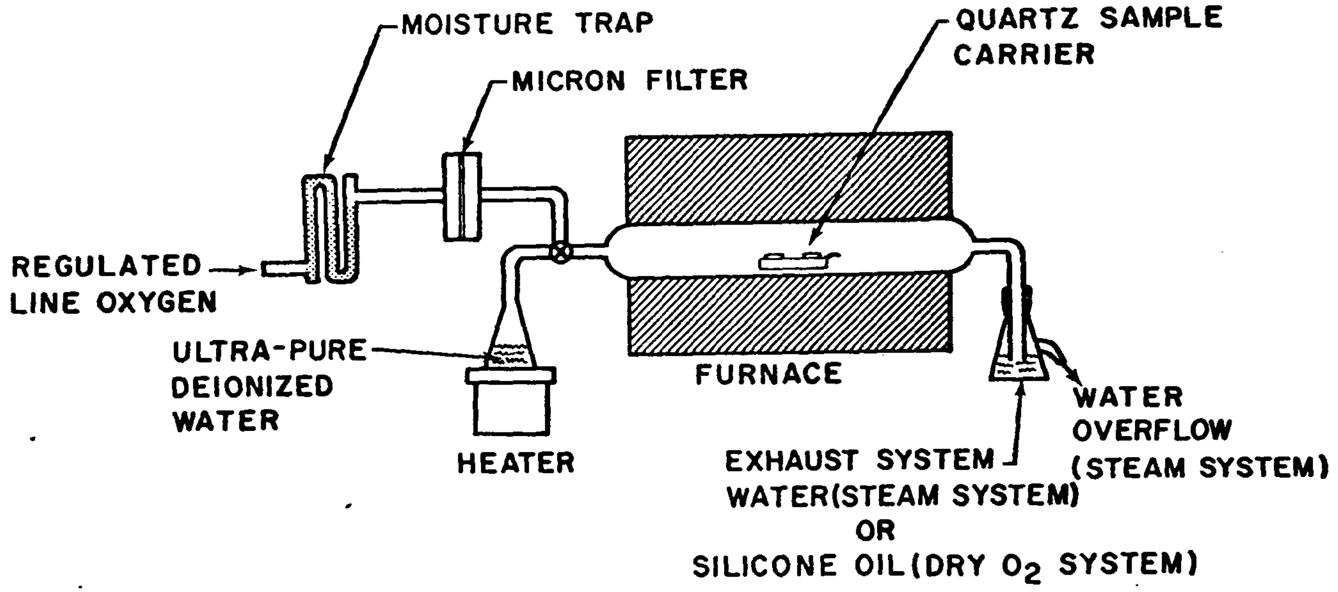

FIGURE 1

micron filter to remove any contaminating particles picked up in the line or in the drying columns, and hence, into the furnace itself. At the exhaust end of the system the gas passes into a trap of silicone oil, which was chosen because of its very low vapor pressure.

The alternate system was for steam. In this case, the oxygen was not used, but instead, the generator was filled with ultra-pure water, and the steam was passed through the furnace tube to a water-filled trap. Since the amount of water vapor formed by this trap is insignificant when compared to the greater amount of steam introduced by the generator, the backflow can again be disregarded. An overflow syphon is used here to remove the condensed steam, and to keep the liquid level constant. As can be seen for both of these methods, the entire system is sealed from the outside atmosphere, insuring a high degree of purity. The pressure inside the furnace is kept as near to one atmosphere as possible, however, by maintaining as small a liquid head as practical in the tubes leading into the exhaust traps.

The materials used varied over the following parameters: Two bulk conduction-types (N or P), crystal fabrication method (either Czochralski or float-zoned material), and bulk resistivities ranging from a low value of .01 Ω cm for each of the four above combinations, 1 Ω cm of each, and a high value of 100 Ω cm of each, giving a total of twelve wafers in each run. As has been stated, the ambient gases used were clean, dry oxygen, <u>or</u> steam, in a sealed system over a temperature range of 800° to 1300°C, maintained at ± 1°C throughout the experiments. The polished wafers were placed on a quartz boat, either flat or on edge since we found experimentally that their positioning was immaterial to the growth rate, as long as the furnace was sufficiently stable and the temperature well controlled.

Our method of measuring the grown silicon dioxide films consisted of the usual technique of removing a section of the oxide with HF, metallizing the entire surface to obtain a sharper, clearer image, and placing the resulting "step" into a monochromatic interferometer. Since most interferometers do not have a sufficiently fine reticle scale, and the reading is often one of more guesswork than of accuracy, we photographed the image and then further magnified it, while employing a suitable measuring scale such as a wide-field filar micrometer eyepiece on a low-powered microscope.

After a number of runs at various times and temperatures had been completed, we subjected the data to extensive statistical analysis to study the effects of the variables, as well as their interactions with each other. At this time we came to the conclusion that there was no difference statistically between N or P type materials; that there was no difference between the material grown by either the Czochralski or the float-zoned methods, and further, over the resistivity range used, there was no difference due to this parameter either. Therefore, we concluded that it was not necessary to use all twelve wafers for each data point, although we did continue to read at least four wafers from each of the runs as a check on our accuracy and reproducibility.

The resulting data points, after completion of some seventy-five runs, were plotted, as in the next figures. The first of these is for the dry oxygen, with time in seconds versus the measured thicknesses for the various temperatures from 900° to 1300°C. Temperatures below 900°C were not investigated in this case since the oxides grown are not of particular use, time-wise, in fabricating most of our devices. Figure 3 is a similar one for the steam system.

In calculating the activation energies and related equations, one is faced with somewhat of a dilemma. At lower temperatures a different slope than those for the higher temperatures is obtained, indicating a definite change in activation.

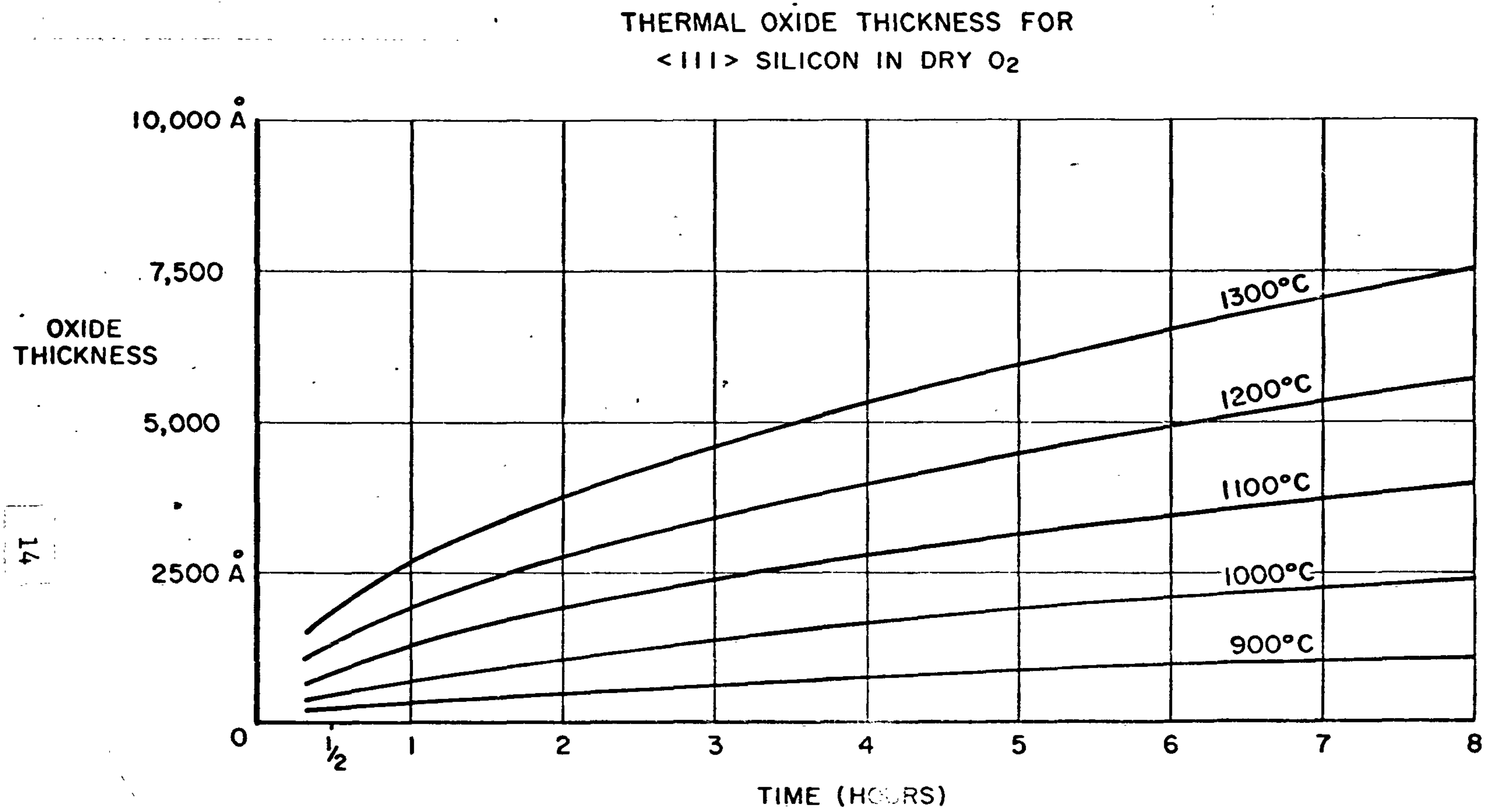
THERMAL OXIDE THICKNESS FOR
<111> SILICON IN DRY O_2
OXIDE THICKNESS
10,000 Å
7,500
5,000
2500 Å
0
½
1
2
3
4
5
6
7
8
TIME (HOURS)
1300°C
1200°C
1100°C
1000°C
900°C

FIGURE 2

THERMAL OXIDE THICKNESS FOR
< 111 > SILICON IN STEAM

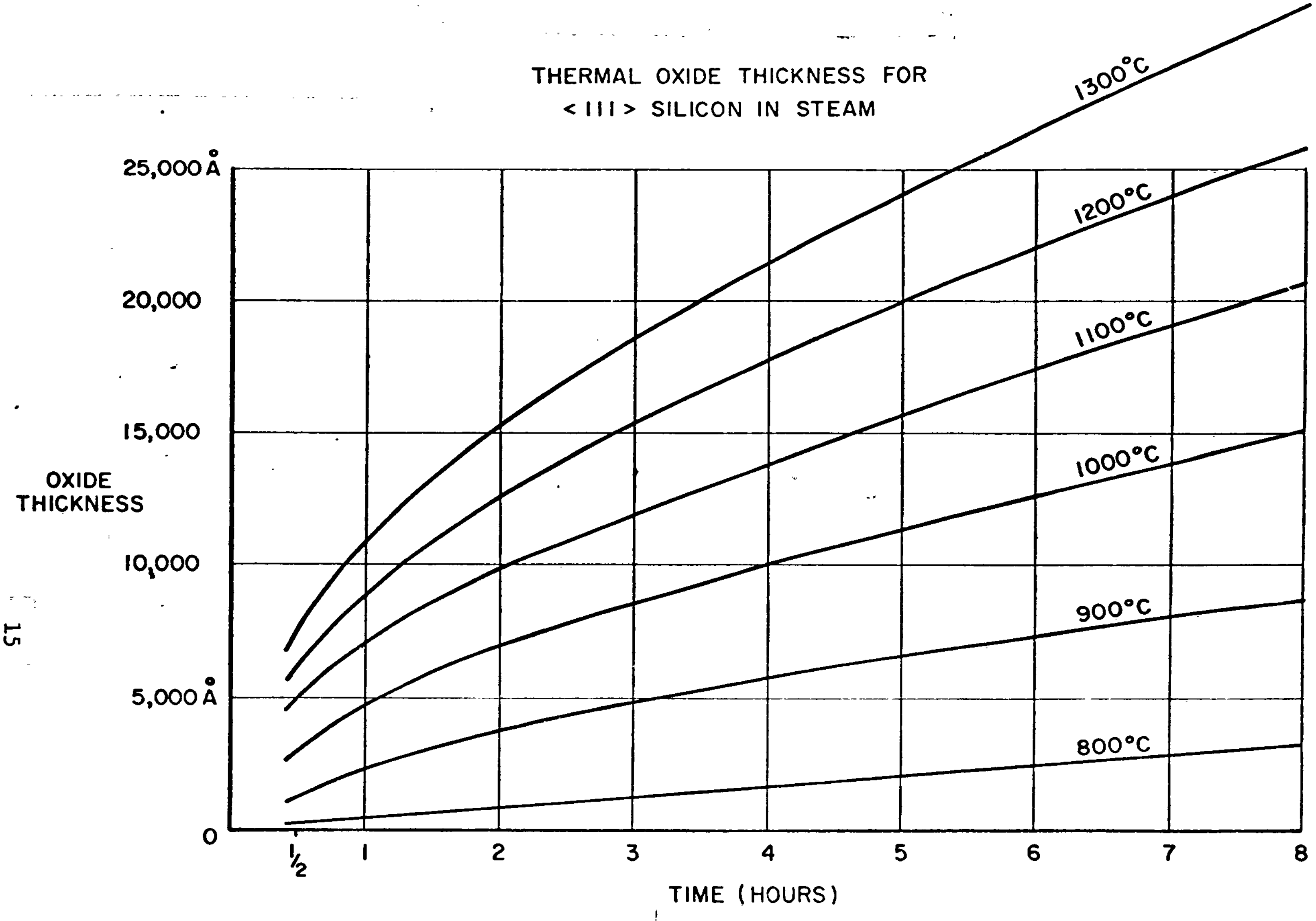

FIGURE 3

We were therefore quite pleased to find that workers in an allied field had noticed the same phenomena. Roberts and Drury of Leeds University in England recently reported on their work on the diffusion of water into silica, and found that the diffusion constant was not "constant" in a transformation range between 800° and 1000°C, but that above that range the results are linear.

Plotting thickness versus temperature, as in the fourth Figure, the relationships are seen to be non-linear at lower temperatures, and therefore a simple equation cannot be constructed, especially since it is expected, by correlation with the results mentioned before from Roberts and Drury, that the curves will change direction again at lower temperatures. Therefore, any kinetic rate equations must have their temperature range specified also, as below:

Thermal Oxidation Growth Rate Relationships

Steam $x^2 = 1.21 \times 10^9\ t \exp(-0.8q/kT)$

Dry Oxygen $x^2 = 3.53 \times 10^9\ t \exp(-1.33\ q/kT)$

Conditions: Closed systems, $T \geq 1100^\circ C$,

<111> surface orientation, 1 atmosphere pressure.

x = film thickness in Angstrom Units

t = time in seconds

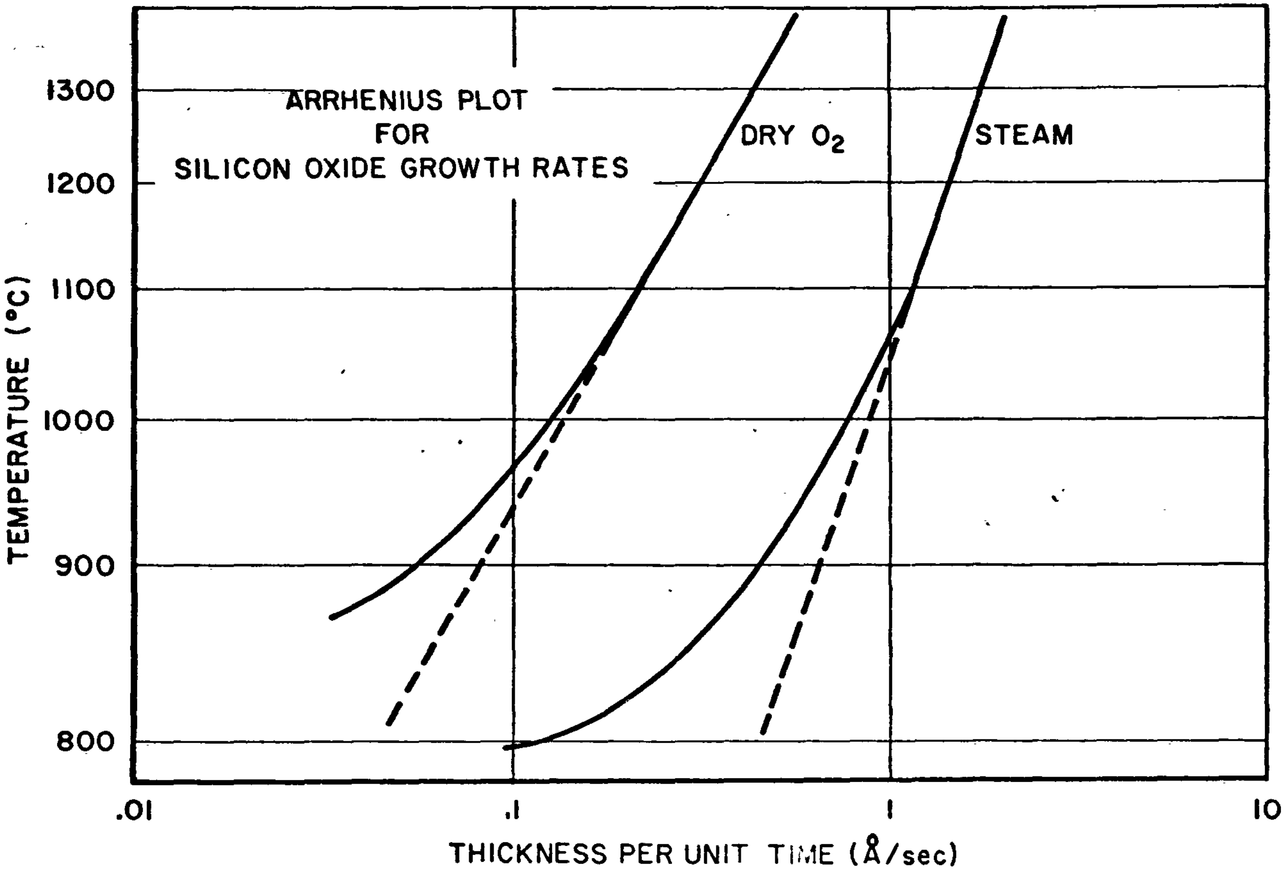
ARRHENIUS PLOT
FOR
SILICON OXIDE GROWTH RATES
DRY O_2
STEAM
TEMPERATURE (°C)
1300
1200
1100
1000
900
800
.01
.1
1
10
THICKNESS PER UNIT TIME (Å/sec)

FIGURE 4

q = electron charge

k = Boltzman constant

T = temperature in degrees Kelvin.

These activation energies that we are postulating here, 0.8 e.v. for the steam system, and 1.33 e.v. for the dry oxygen, are somewhat lower than those previously published by others, as can be expected from the previous graphs. By defining the range of application, however, as well as the accuracy of our measuring methods, we feel that they are quite valid. Comparison with free energy of formation values is also quite good.

As a further convenience for the production workers who need to repeat a certain oxide growth run after run, where the accuracy need not always be within 50 Å, we constructed a color versus thickness chart as shown in Table I.

Now, colors have been observed for oxide thicknesses of well over 1-1/2 to 2 microns; however, the colors begin to fade at around 3/4 of a micron, or at 7500 Å thickness, and a color chart becomes of questionable value past this limit. Since the colors are sufficiently intense up to 7500 Å, one can use this chart for non-critical estimates with accuracy to 100 Å.

TABLE I

SILICON DIOXIDE

THICKNESS VS. COLOR

COLOR	THICKNESS			
GREY	100 Å			
tan	300			
brown	500			
blue	800			
violet	1000	2750 Å	4650 Å	6500 Å
blue	1500	3000	4900	6850
green	1850	3300	5200	7200
yellow	2100	3700	5600	7500
orange	2250	4000	6000	
red	2500	4350	6250	

The conclusions of this work other than the data presented on the graphs and charts were as follows:

1. The rate of oxide growth on silicon is controlled only by time, temperature, pressure, and type of ambient present in the oxidation system.

2. The properties of crystal fabrication, bulk resistivity and type, and any interactions thereof, have no significant bearing on the oxide growth rates.

C. ELECTRICAL EVALUATION OF PASSIVATING COATINGS ON SILICON

Authors: H. W. Cooper
R. W. Rader
S. S. Flaschen

ABSTRACT

Passivating glass coatings of various thicknesses were grown on silicon by: 1) High temperature dry oxygen, 2) High temperature steam, and 3) PbO accelerated low temperature oxidation. The coatings were then evaluated with respect to:

A. Dielectric strength
B. Dielectric Constant
C. Bulk resistivity
D. Temperature coefficient of resistivity

A figure of merit for the dielectric properties of passivating coatings was developed and applied in this study.

The present method of evaluating passivating films entails passivating a diode or transistor and determining parameter stability. Using this approach it cannot be said with certainty whether changes are caused by device or passivation deterioration. Thus, it is desirable to have a technique for evaluating passivating coatings that is independent of a device. Evaluation independent of devices has been accomplished by growing the coating on a polished silicon wafer, evaporating gold spots 1 micron thick and 40 mils in diameter onto the oxide, and measuring the DC resistance of the spot. When the resistance is known, the bulk resistivity and conductance per unit area can be calculated as:

$$\text{resistivity } \rho = \frac{RA}{L}$$

$$\frac{\text{conductance}}{\text{area}} \; G' = \frac{1}{RA}$$

where R = measured resistance in ohms

L = thickness of the oxide in cm

A = area of the gold spot in cm^2.

The conductance per unit area can be used as a figure of merit. The resistance was measured with a General Radio 1230A electrometer, measuring the IR drop in a known series resistor with a known voltage applied. Because of the sensitivity needed to measure currents that were fractions of a picoamp, it was necessary to make the measurements in a shielded enclosure. It has been observed that, after a voltage is applied to a spot, the initial current will be a maximum, and then decreases over a period of hours. The initial rate of decrease was the greatest, and it was at first decided to take readings five minutes after applying the voltage to the spot. This technique gives an estimate of the resistance that is on the low side. The resistance was estimated by plotting V versus I on linear graph paper, and taking the shape of the best straight line through the origin.

Samples of Motorola's accelerated oxide lead glass, steam grown SiO_2 and SiO_2 grown in dry O_2 were prepared. Several spots on each wafer were measured. The following results have been obtained.

	Film	ρ Ω- cm			G'
Type	Thickness	Range	Typical Value	Range	Typ.Value
accelerated oxide	2600 Å	$3\text{-}8 \times 10^{8}$	4×10^{8}	46-130	100 $\mu \frac{\text{mho}}{\text{cm}^2}$
accelerated oxide	2800 Å	1.8×10^{12} 4.3×10^{15}	4×10^{15}	9-20,000	13 $\frac{\text{pico mho}}{\text{cm}^2}$
steam SiO_2	2800 Å	$2\text{-}5\text{x}4.3\text{x}10^{15}$	3.2×10^{15}	9-14	10 "
dry SiO_2	2800 Å	$3.9\text{-}4.4\text{x}10^{15}$	4×10^{15}	8.1-9.2	8.5 "

The Handbook of Chemistry and Physics lists 10^{15} to 10^{16} Ω-cm as a typical resistivity for bulk quartz.

Dielectric constant measurements of the lead glass were made by measuring the capacitance of the glass under the gold spot with a John Fluke 710A impedance bridge, and calculating K from the relation:

$$K = \frac{4\pi dC}{1.11A}$$

K = dielectric constant
A = area in cm^2
C = capacitance in picofarads
d = glass thickness in cm

A number of spots were checked on the high resistivity wafer, and K ranged from 8.61 to 10.2 at 10 Kc with a mean value of 9.55. A published value[1] for a bulk lead silicate glass is K = 16.3 at 100 Kc and K= 16.1 at 30 Mc. The K of SiO_2 is listed as 3.72 at 100 Kc and 3.57 at 30 Mc. Our observed values for K on the thin SiO_2 films were approximately 3.7.

The dielectric breakdown is often not catastrophic; thus an arbitrary breakdown criterion must be defined. This was accomplished in the manner depicted in Figure 5. The 30 minute criterion was decided upon after examination of many specimens.

To determine dielectric strength and bulk resistivity, silicon wafers were prepared with PbO accelerated oxide glasses to thicknesses of 3500 Å and 5000 Å. One millimeter diameter gold spots were then evaporated onto the glass to a thickness of about 1 micron in order to form a number of test areas on

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[1] Properties of Glass, 2nd Edition, G. W. Morey, Reinhold Publishing Company, New York, 1954, p. 505

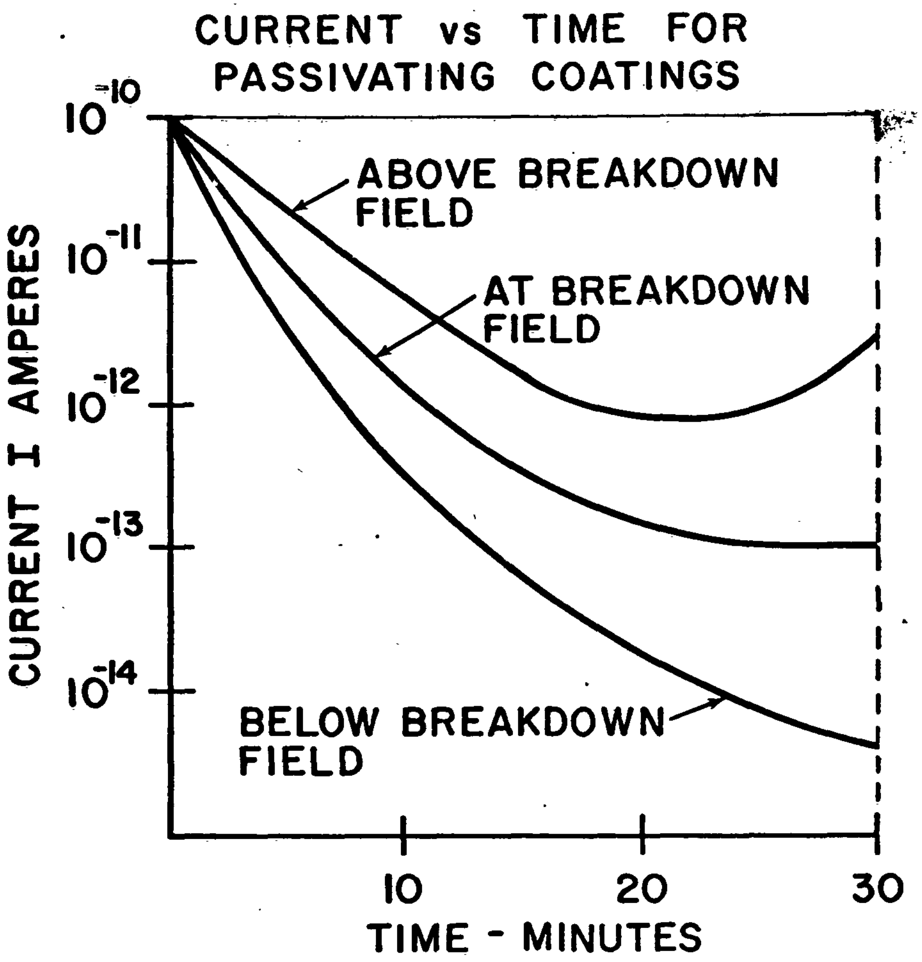

CURRENT vs TIME FOR PASSIVATING COATINGS
ABOVE BREAKDOWN FIELD
AT BREAKDOWN FIELD
BELOW BREAKDOWN FIELD
CURRENT I AMPERES
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10
20
30
TIME - MINUTES

Figure 5

each wafer. Dielectric strength, bulk resistivity and figure of merit data were collected by observing the V-I characteristics of several spots on each wafer.

Due to the previously described behavior of the currents, readings were taken after the voltage had been applied for a period of time. During the time when voltage was being changed, the wafer was shorted out so that for each measurement zero time corresponded to zero voltage. The following is a condensed table of information obtained from these V-I data.

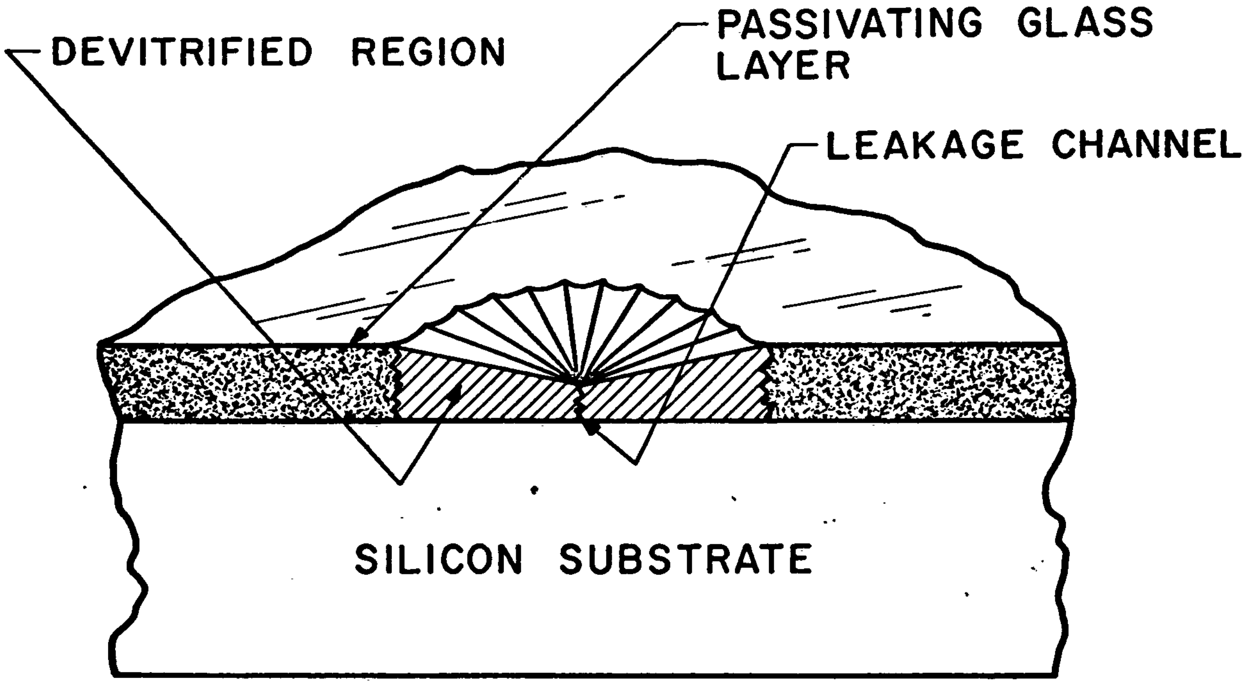
CHARACTERISTIC	5000 Å	3500 Å
Mean R. T. Breakdown	45 V	20 V
Dielectric Strength	9×10^5 V per cm or 9 $\underline{V}$ per 1000 Å	5.7×10^5 V per cm or 5.7 $\underline{V}$ per 1000 Å
Bulk Resistivity	10.3×10^{15} ohm-cm to 17.8×10^{15} "	3.9×10^{15} ohm-cm to 11.5×10^{15} "
Figure of Merit $\left(\frac{1}{RA}\right)$	3.8 pico mho/cm^2	1.4 pico mho/cm^2

The breakdown criterion emerged more simply than was expected in view of the exhibited gradual breakdowns. It was found that at a particular voltage, current began its normal exponential-like decay, but after a period of time, began slowly to increase until the spot became a short circuit unless the voltage was removed. The voltage shown here is that voltage which caused increasing current with lapsed time after an initial decay.

The results of comparing the dielectric strength of the 3500 Å glasses with the 5000 Å glasses showed a lower apparent value for the thinner glass.

Inspection under a microscope indicated approximately three times as many devitrification areas per spot on the 5000 Å glass as were found on the 3500 Å glass. The values of the figure of merit shown in the table tend to bear out the contention that devitrification areas may be thought of as resistors in parallel shunting the good dielectric regions, as shown schematically in Figure 6. The greater the area density of "resistors" (of the same approximate ohmic value for a given glass thickness), the higher is their conduction per unit area. Conduction in the 5000 Å glass was about three times that in the 3500 Å glass.

Considerable time was spent in obtaining reproducible data for the V-I characteristics since current levels were commonly between .01 and 10 picoamperes. Several spots were ruined because of the rather sharp probe point used to contact the gold spot; therefore, a probe was ground into a curved surface of approximately 3/64 inches in diameter.



SCHEMATIC OF A DEVITRIFICATION CENTER

Figure 6

Temperature Coefficient of Resistivity

Preliminary investigation of log resistivity versus temperature showed that the resistivity of the 5000 Å glass decreased over 100 times in an increase of 60°C. Since the applied voltage was near the observed breakdown voltage, it was felt that these results might be erroneous. Applied voltage was lowered and resistivity decreased only about fifty times in the same temperature range. It was noted - but not explained - that at voltages lower than 30 volts, a transition from low coefficient of resistivity to high coefficient of resistivity occurred at approximately 60°C in every sample. One spot of dry oxygen grown SiO_2 dielectric was tested also, and yielded the transition at near 60°C with comparable coefficient of resistivities on either side.

In one experiment, a plot was made of current versus time for one voltage, one test element on 3500 Å lead glass, and four temperatures. Three generalizations were obtained as follows:

1. The time required for current to decay to a value of 1/e of its original value was at least 1/2 hour. Previous experimental data on SiO_2 glass indicated that ten minutes was ample time. One possibility for explaining the difference is the lower mobility of the ions in the molecularly denser lead oxide glasses.

2. Electrical characteristics were found to depend upon past electrical history. The duration of this memory was not determined accurately, but indications were that it was on the order of one hour.

3. We wish to consider two mechanisms of conduction in the glass; one being the normal bulk resistivity of the glass, and the other being the presence of absorbed electrolytic materials. Once the electrolytes had been swept from the glass by application of a voltage for a period of time, current became approximately constant with time. This constant (temperature dependent) is believed to have been due to the bulk resistivity of the glass.

During the time interval when absorption current was the dominating factor, reproducibility had been low in previous measurements. Since the number of absorbed electrolytes present, and their mobilities controlled the amount of conduction, it became clear that in striving for reproducibility, enough time had to be allowed for their asymptotic readsorption before further measurements could be made.

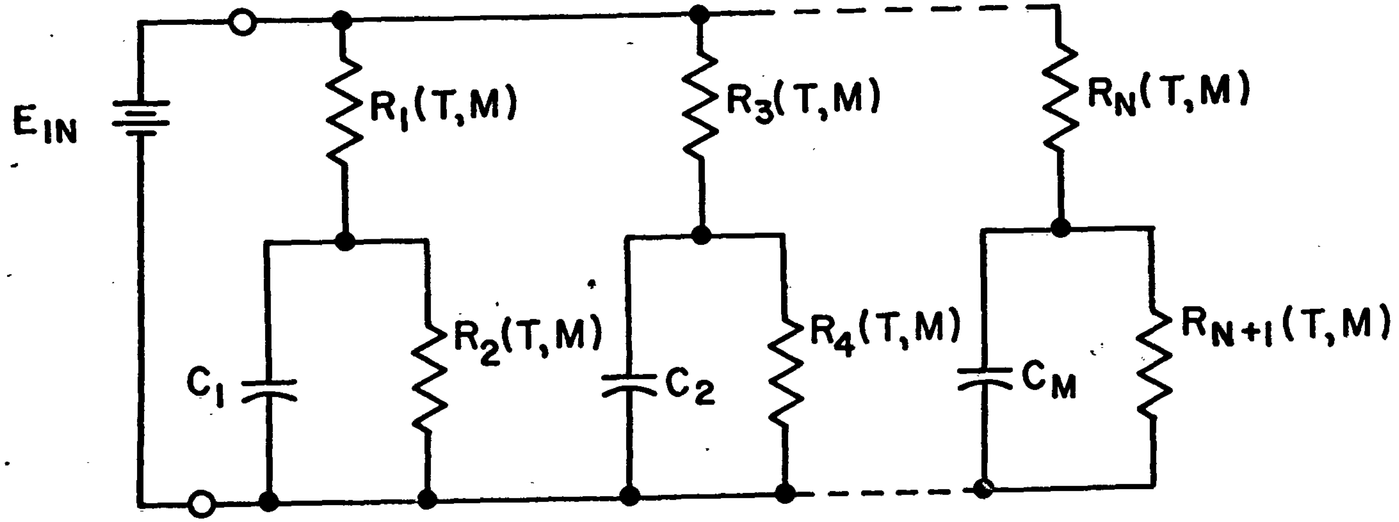
Absorption current was seen to decrease more rapidly as temperature was elevated. This corresponded nicely to the fact that there is less absorbed material present at higher temperatures -

moisture, for example, and that mobilities increase with temperature.

At higher temperatures, discontinuities and changes in the rate of current decay were noted in the period of absorption current domination. This behavior suggests temperature dependencies of the mobilities of the absorbed materials, such that one electrolyte's mobility dominated while its density was sufficiently high, and another's mobility took over upon depletion of the first electrolyte, and so on.

From this interpretation of the results, a physical qualitative model was devised which could represent the system in all of its phases, as is shown in Figure 7.

Consider first the steady state where all capacitors are fully charged. A constant DC resistance is presented to the source terminals which is a function of the temperature and material composition. Prior to the steady state, however, the system has several different time constants, each a function of temperature and material. At higher temperatures, the longest time constants could be short enough to allow their individual effects to be felt, while at low temperatures the longest would dominate the whole period.



EQUIVALENT CIRCUIT PORTRAYAL OF
GLASS LAYER

Figure 7

Further experiments now being planned include investigation of temperature and frequency effects on dielectric loss resistivity and dielectric strength.