PHILCO CORPORATION

LANSDALE DIVISION

Lansdale, Pennsylvania

THIRD QUARTERLY PROGRESS REPORT
DESIGN, DEVELOPMENT, FABRICATION, AND DELIVERY OF IMPROVED MOS TRANSISTORS

November 22, 1965 to February 21, 1966

Contract No. NAS8-11926
National Aeronautics and Space Administration
George C. Marshall Space Flight Center
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FOREWORD

This report was prepared by the Lansdale Division of the Philco Corporation, a subsidiary of the Ford Motor Company, under Contract No. NAS8-11926. It is the third quarterly progress report, covering studies performed during the period from November 22, 1965 to February 21, 1966.

The subject program is administered under the direction of Dr. A. M. Holladay of the Astrionics Laboratory, George C. Marshall Space Flight Center, Huntsville, Alabama. The program bears the Philco Corporation, Lansdale Division, internal number R-505.

SUMMARY

The purpose of this program is to study in detail the causes of instability, high threshold voltage, and sensitivity to gamma radiation of metal-oxide-silicon (MOS) transistors.

Equipment and techniques were set up to study the effects on the properties of oxides of water absorbed from the room air during the processing steps needed to fabricate transistors. It appears that water is not significantly absorbed at room temperatures. The exact procedure used in cooling after thermal oxidation significantly affects the oxide properties. The back flow of room air into the part of the oxidation chamber when the chamber is cooled can supply water which the oxide absorbs before it reaches room temperature. The small amount of water absorbed during cooling lowers the state density. The immobile charge density is not affected.

Two kinds of instability are observed at room temperature. One is due to mobile ions (probably protons) which are activated by a treatment of positive bias at elevated temperatures. The other is due to trapping. These two effects can coexist in the same oxide and oppose each other. The chosen testing procedure activates the mobile ions and cools the sample under bias to avoid recovery before measurements are made.

The exact method of surface preparation has been shown to be very important in determining the relative instability due to mobile ions and to trapping. This is observed on thermal oxides and vapor plated nitrides.

The mobile ion instability has been shown to be very sensitive to the alloying operation.

Metal-insulator-silicon capacitors have been prepared with silicon nitride instead of silicon oxide. These capacitors were exposed to X-ray radiation and found to be very sensitive to such radiation.

Two findings may be expected to make possible the fabrication of transistors with lower threshold voltage. An improvement in immobile charge density has been found in a vapor plated oxide formed with high purity CO_2 on a freshly grown layer of epitaxial silicon. It has been shown that vapor plating, the purity of CO_2, and the silicon surface preparation are each very important. It has also been found that silicon orientations other than the regularly used $\langle 111 \rangle$ yield significantly lower immobile charge densities.

MOS analytical techniques have been put into valuable application in troubleshooting of processes for producing bipolar devices.

Information from the field of glass technology has been reviewed to bring to the program the benefits of relevant fundamental and empirical knowledge.

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1. INTRODUCTION

1.1 Program Objectives

The objectives of this program are to develop the knowledge and understanding necessary for fabricating MOS transistors having

1. More stable electrical characteristics,
2. Lower threshold voltage, and
3. Improved resistance to ionizing radiation.

The results of this program are also applicable toward the improvement of bipolar devices, and are therefore of value in the development of microcircuits containing either bipolar or MOS devices.

1.2 Review of First and Second Quarters

The work during the first six months of this twelve-month program was reported in the First and Second Quarterly Progress Reports which covered the periods May 21, 1965 to August 21, 1965, and August 22, 1965 to November 21, 1965.

The first quarterly report related the program to the broader field of reliable microcircuitry and desirable performance levels. That quarter also included a literature review and correlation of published information. The review covered:

1. The history leading to the development of MOS devices,
2. The advantages they offer,
3. The physical principles on which their characteristics depend,
4. The basic processing steps in their fabrication,
5. The techniques for their evaluation,
6. The detailed model for the oxide structure and for the oxide-dependent behavior of devices,
7. The reported experimental efforts to develop improved oxides,
8. The observed effects of radiation.

The basic equipment, approaches and techniques being used in this program were established in the first quarter.

During the second quarter, the various kinds of charge that influence the performance, stability, and reliability of MOS devices were described in detail. A model was developed for the effects of this charge on device behavior.

Experimental data taken on various kinds of oxides which differ in oxidation and post-oxidation treatments were compared for threshold voltage, stability, and radiation resistance.

On the basis of the comparative data, it appeared likely that more meaningful data could be collected if changes were made in the equipment for forming, storing, and testing oxides so that the water content of the oxide could be better controlled.

The information covered in the first two quarterly reports provided a good basis for the work performed in the third period.

1.3 Order of Presentation of This Report

Succeeding sections of this report record the work done during the third quarter of the program. Section 2 describes some equipment modifications and experimental results that show the effects of water from room air on oxide properties. Instability of both the mobile ion and the trapping type are discussed in Section 3. Section 4 discusses radiation induced degradation. Section 5 discusses promising approaches for reducing the threshold voltage, and gives some experimental results showing the influence of water on this parameter. Section 6 reports on the construction of equipment which is to be used with tritiated water to study the behavior of water in oxides. Section 7 introduces the report given in Appendix B which is a review of pertinent information from the field of glass technology. An analysis of the results of the third quarter comprises Section 8. Section 9 lists the work planned for the fourth quarter.

Appendix A details the calculations of the sensitivity of the radiochemical detection techniques of autoradiography and counting. Appendix B is the report of a consultant in the field of glass technology. Appendix C lists the references that have been added to the bibliography of pertinent literature since the last quarterly report was prepared.

Chart 1 indicates the percentage of accomplishment on each of the scheduled phases of the program. Deliveries of reports and devices are also indicated.

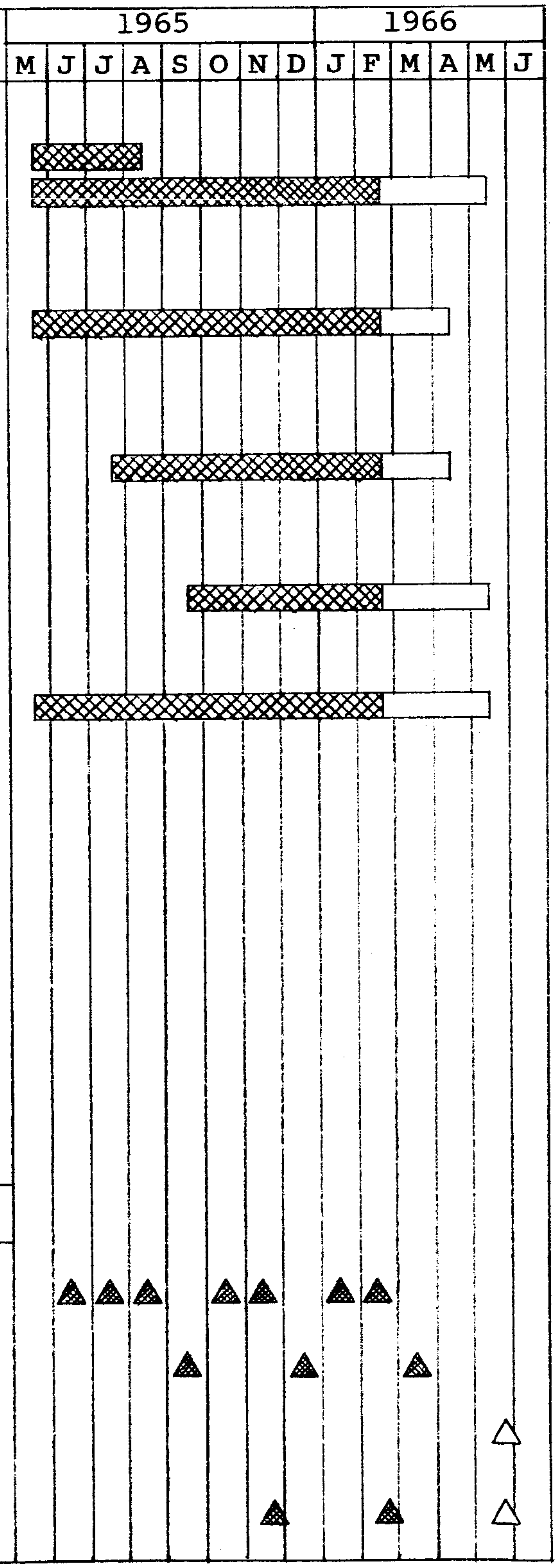
CHART 1. PROJECT PERFORMANCE AND PROGRAM SCHEDULE

Period Covered: May 21, 1965 to February 21, 1966

Phases	% Completion
1. Literature survey	
a. Critical review	100
b. Surveillance	82
2. Determination of the exact causes of instability and of the failure of devices to meet desired performance levels.	70
3. Development of techniques to produce stable MOS devices.	70
4. Development of techniques to produce improved device performance.	70
5. Radiation resistance a. Determination of the effect of gamma radiation on MOS devices fabricated with various structural and processing modifications b. Development of a model for radiation-induced degradation c. Development of techniques for improving tolerance to radiation.	65

Milestones

- Monthly Progress Reports
- Quarterly Progress Reports
- Final Documentary Report
- Delivery of Demonstration Devices (8/delivery)



2. EFFECTS OF WATER FROM ROOM AIR

The second quarterly report called attention to the importance of the water content of oxides. The water content may be expected to affect the instability, threshold voltage, radiation resistance, and fast-state density of MOS devices. Changes in equipment and techniques were therefore made to provide more complete control of the water content of oxides.

The oxidation tube used for preparing thermal oxides was modified to prevent water in the room air from flowing to the oxide while the oxide is being cooled following the oxidation.

To control the water content after oxidation, a gloved dry box has been set up for the storage and testing of oxides in a dry nitrogen ambient. This is shown in Figures 1A and 1B. It takes approximately 1 minute to move a sample from the dry oxidation chamber to the dry box, during which time it comes in contact with room air. The experiment described below shows that such samples are not significantly changed by exposure to room air at room temperature for up to 40 hours.

An experiment was conducted to determine whether the exposure to room air at room temperature for a matter of hours

Figure 1A. Gloved drybox and capacitor testing equipment.

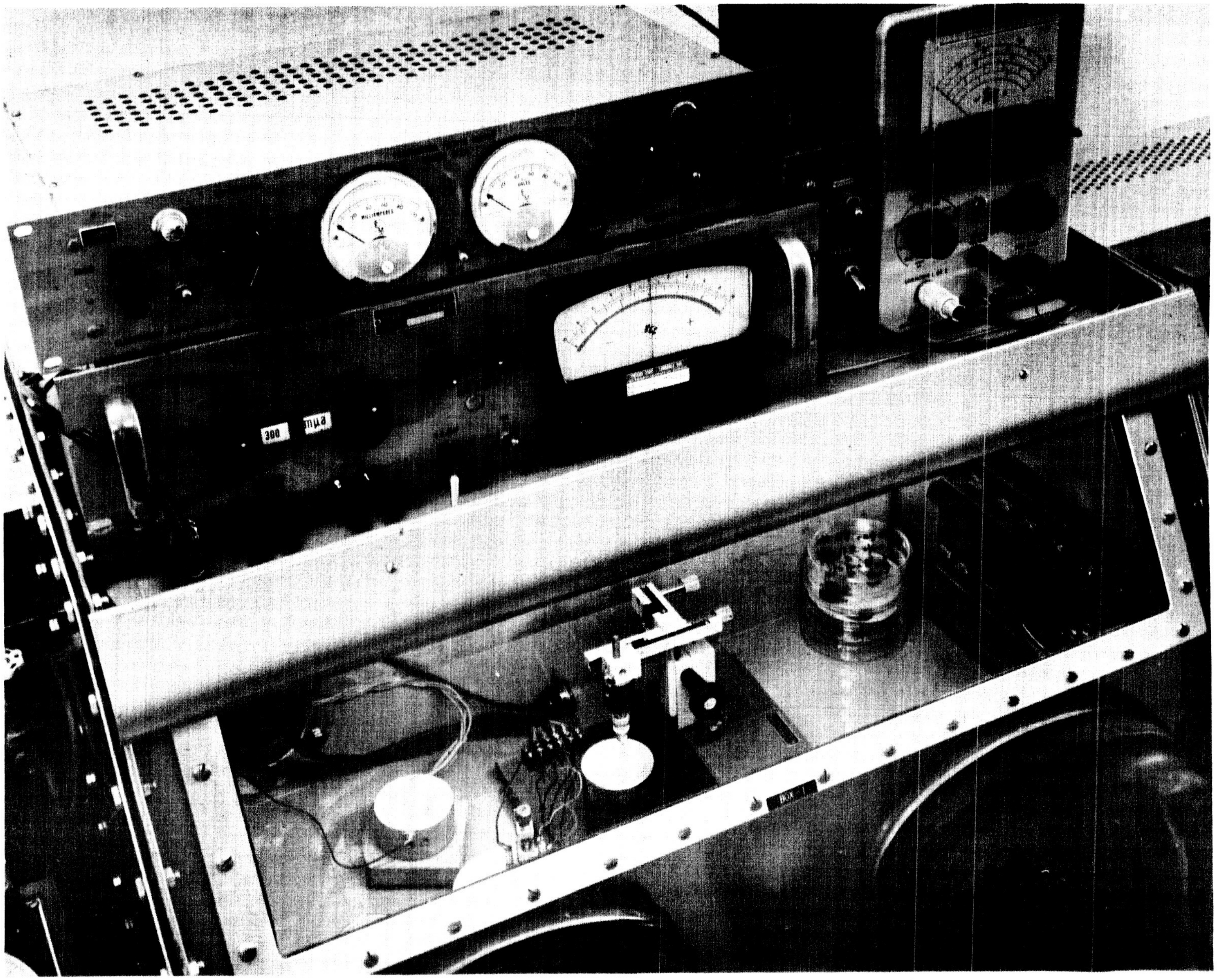
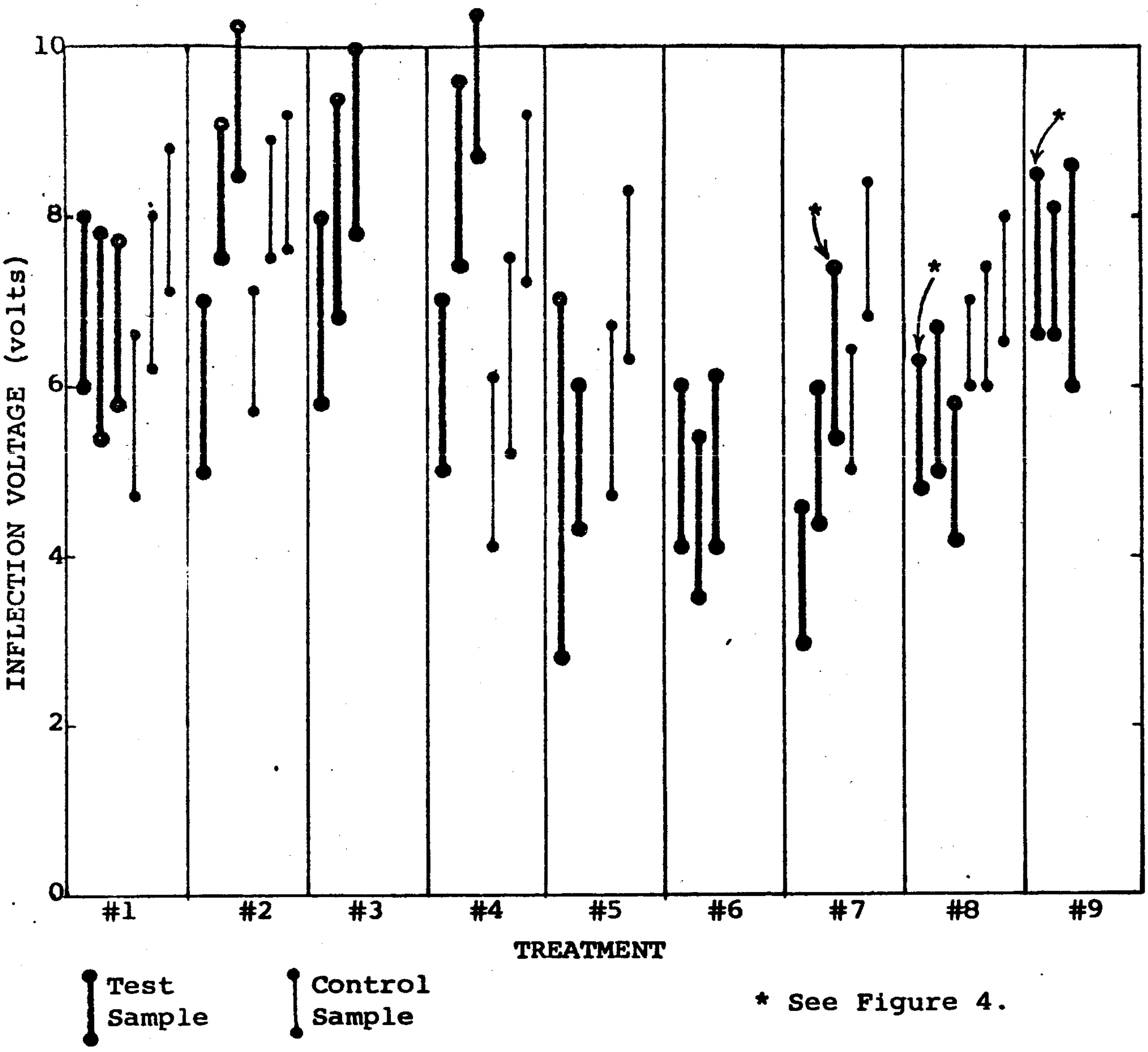


Figure 1B. Close-up view of dry box.

significantly affects the characteristics of oxides containing reduced levels of water. A 2000 Å thick thermal oxide was grown on each of two halves of a 5.0 Ω-cm phosphorus-doped silicon wafer. They were cooled in the dry oxidation tube and placed in the dry box within 90 seconds. One half was used as a test sample and the other served as the control through a sequence of exposures to room air. The measurements were in the form of capacitance-voltage curves measured at a frequency of 140 kHz, with a gold ball probe. Three points were measured over the area of each half wafer after each treatment. The measurements at each point include C-V curves after each of the following drifting steps:

1. -30 V, 1 min., 22°C, and
2. +30 V, 1 min., 22°C.

The drift saturated in time intervals shorter than 1 minute and the observed shifts of the C-V curves were reproducible. Figure 2 summarizes the experimental results. The variation in the inflection voltage (first an increase and later a decrease) of the test sample has not been explained. It may be related to the somewhat similar behavior shown in Figure 10 of the Second Quarterly Report. The oxide properties do not appear to have been significantly degraded by the exposures to room air.



DESCRIPTION OF TREATMENT OF TEST AND CONTROL SAMPLES

Test Sample:

#1 Initial measurements.
#2 After 10 min. in room air.
#3 After 16 hr. in dry box.
#4 After 1 hr. in room air.
#5 After 19 hr. in room air.
#6 After 7 days in dry box.
#7 After 18 hr. in room air and a subsequent bake at 300° C for 1 hr. in the dry box.
#8 After a bake at 400° C for 1 hr. in dry N_2.
#9 After a bake at 400° C for 1 hr. in room air.

Control Sample: The control sample was kept in the dry N_2 at room temperature and tested after most of the treatments in the test sample sequence. The control sample was given the same temperature treatments as the test sample, i.e., 300° C for 1 hr. in treatment #7, and 400° C for 1 hr. in treatment #8.

Figure 2. Summary of C-V data from experiment to determine the effects of exposure to room air.

On the other hand, a change was observed in the state density in the oxide. This state density can be qualitatively evaluated by an examination of the steepness of the slope of the C-V curve in the transition region. The explanation for this is:

> Trapping states are assumed to exist in the oxide or at the oxide-silicon interface. The state of occupancy of each of these traps depends on the electrostatic potential at each of the trap sites. This potential in turn depends on the applied voltage. As the applied voltage is varied, the occupancy of the traps changes. This changes the charge density in the oxide. If the charge density of the oxide changes during the recording of the C-V curve, the C-V curve will have a gradual slope in the transition region.

Figure 3 shows C-V curves taken on two oxides with different levels of water content. These curves were taken on unmetalized oxides with a gold probe. Sample #115 was cooled in the modified oxidation tube designed to minimize the moisture content, whereas #116 was cooled at the end of the tube in the regular way. Sample #115 is therefore a drier oxide. These curves illustrate that drier oxides have higher trapping state densities, in agreement with work reported by Kooi[5]. On this basis, one can

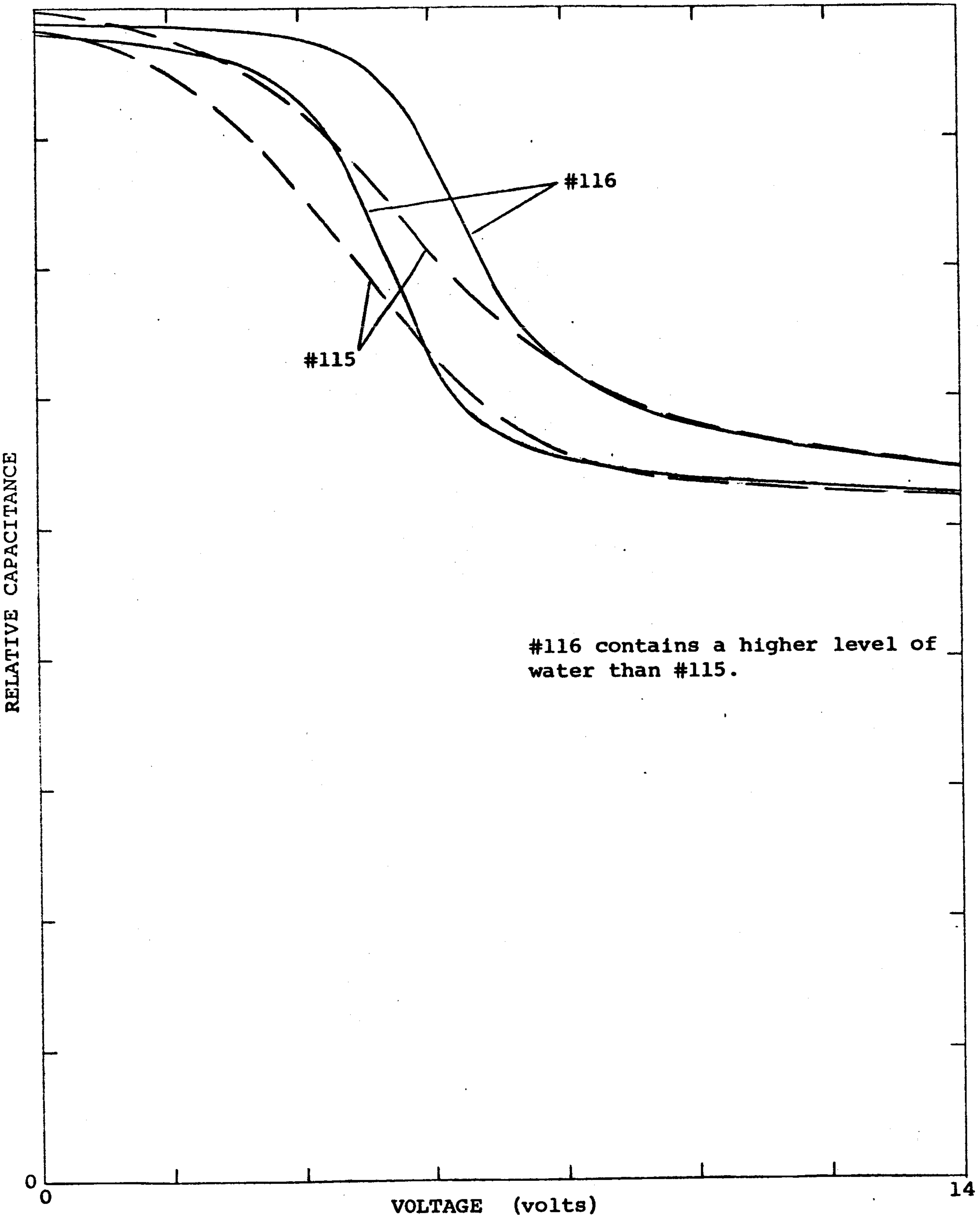


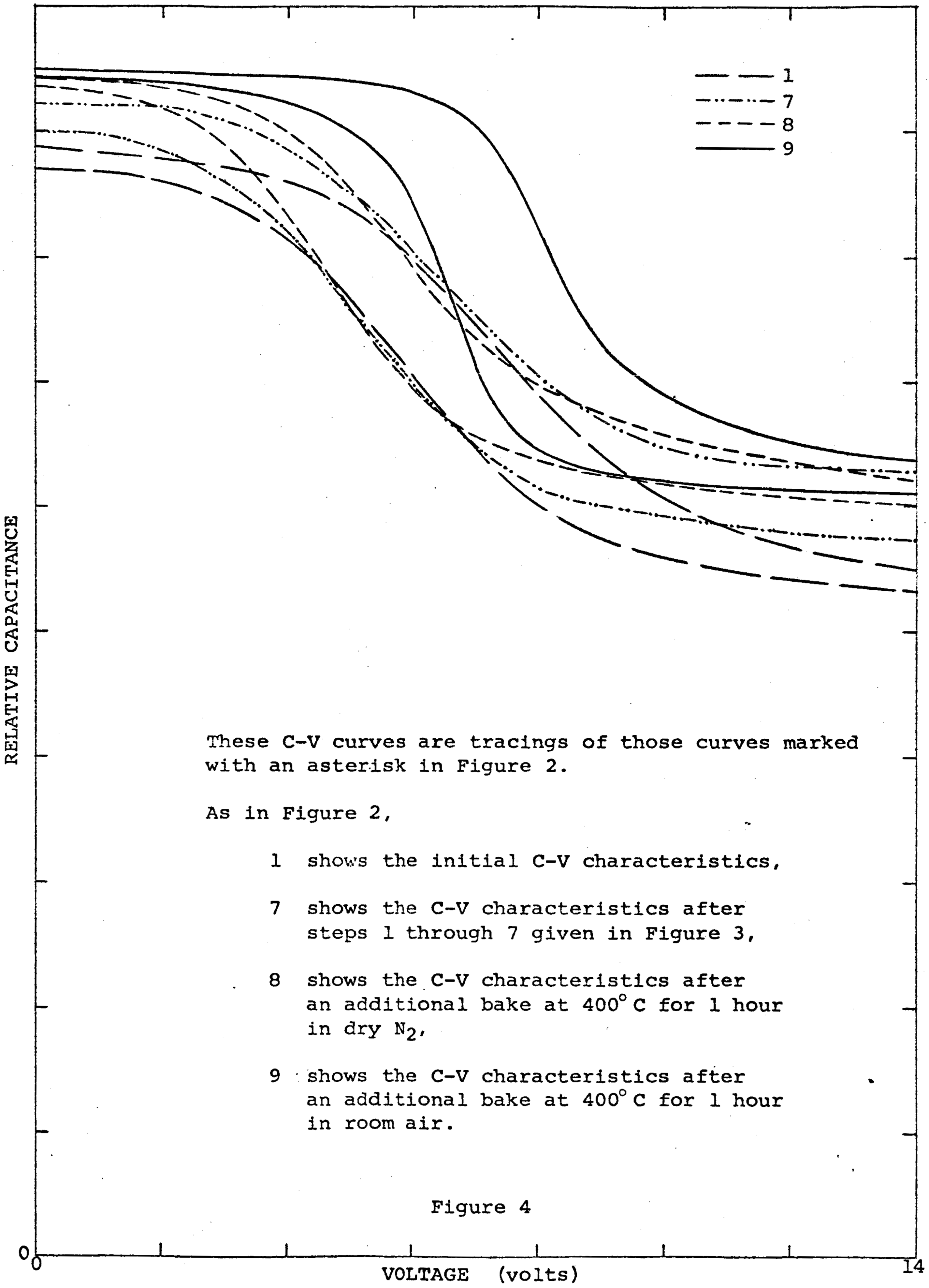
Figure 3. C-V curves taken on two oxides with different levels of water content.

examine the shapes of the C-V curves taken in the experiment conducted to determine the effect of room air on oxides (i.e., the curves from which Figure 2 was prepared). Figure 4 presents tracings of C-V curves taken at the beginning of the experiment, and just before and just after the bakes at 300° C for 1 hour in dry nitrogen and at 400° C for 1 hour in room air. These tracings clearly show that the curve shapes did not change significantly during the sequence of treatments until the bakes at 300° C and 400° C. This indicates that moisture does not diffuse into the oxide at room temperature in room air for a period of time up to 40 hours.

The observations described above agree with the results of several calculations based on data from a paper by Moulson and Roberts[7]. They studied the diffusion coefficient for the entry of infrared absorbing centers in silica glass heated in water vapor between 600 and 1200° C. They found that this diffusion coefficient obeys the equation

$$D = 1.0 \times 10^{-6} \exp(-18300/RT) \text{ cm}^2/\text{sec}.$$

If we assume this equation to hold at lower temperatures and that the diffusing species is the same as that with which



These C-V curves are tracings of those curves marked with an asterisk in Figure 2.

As in Figure 2,

1 shows the initial C-V characteristics,

7 shows the C-V characteristics after steps 1 through 7 given in Figure 3,

8 shows the C-V characteristics after an additional bake at 400° C for 1 hour in dry N_2,

9 shows the C-V characteristics after an additional bake at 400° C for 1 hour in room air.

Figure 4

we are concerned, we can calculate diffusion coefficients to be

$$D_{27°C} = 5.1 \times 10^{-20}\ \mathrm{cm^2/sec.},$$

$$D_{300°C} = 1.2 \times 10^{-13}\ \mathrm{cm^2/sec.},\ \text{and}$$

$$D_{400°C} = 1.1 \times 10^{-12}\ \mathrm{cm^2/sec.}$$

The diffusion lengths calculated from the equation

$$L = \sqrt{Dt}\ ,$$

for a diffusion time of 24 hours are

$$L_{27°C} = 6.6\ \text{Å},$$

$$L_{300°C} = 10100\ \text{Å},\ \text{and}$$

$$L_{400°C} = 30800\ \text{Å}.$$

Clearly, these values are consistent with our experimental observations that although diffusion does not seem to be important at room temperature, it is important at 400°C.

It is further shown in paragraph 3.2.8 that the water content appears to influence the mobile ion instability, and in paragraph 5.2.7 that it affects one kind of immobile charge density.

3. INSTABILITY

3.1 Background Information

The device instability at elevated temperatures was shown in the first and second quarterly reports to be due to the presence of alkali ions in the oxide. This problem has been solved by empirically established techniques that yield oxides with no more than 1×10^{11} alkali ions/cm^2 as tested at 300°C with biases of plus and minus 12 volts. This number of ions yields a stability level that is acceptable for many applications.

3.2 Results of Work During Third Quarter

3.2.1 Testing for Instability

It has become clear that oxides that are free of alkali ions still exhibit a substantial amount of instability. This instability can be readily observed at room temperature after an oxide has been subjected to a positive bias at an elevated temperature. This instability could be a significant problem in MOS transistors which are operated with a positive bias on the gate, e.g., normally-on N-MOST's.

To distinguish between alkali ion instability and the instability at room temperature, each oxide must be tested after drifting bias has been applied at 300°C, then again after drifting at room temperature. A standardized testing prcoedure is used which consists of making C-V curve measurements on packaged MOS capacitors after treatments:

1. -12 V, 300°C, 2 min.
2. +12 V, 300°C, 2 min.
3. -12 V, room temperature, 5 min.
4. +12 V, room temperature, 5 min.

The test devices are heated to 300°C in an oven in the testing laboratory of our Reliability and Quality Control Department. To assure that the devices are cooled to room temperature under bias, a portable apparatus has been built that enables one to maintain a bias on the devices through the bake, during cooling, and up to just before each device is tested. This apparatus is shown in Figure 5.

3.2.2 Mobile Ion (Non-alkali Ion) Instability

When the proper techniques are used to test for instability oxides that are free of alkali ions may exhibit a mobile ion instability. This was first reported by Hofstein[4] who has explained the effect as being due to the trapping of protons at the metal-oxide interface. These protons can be released by

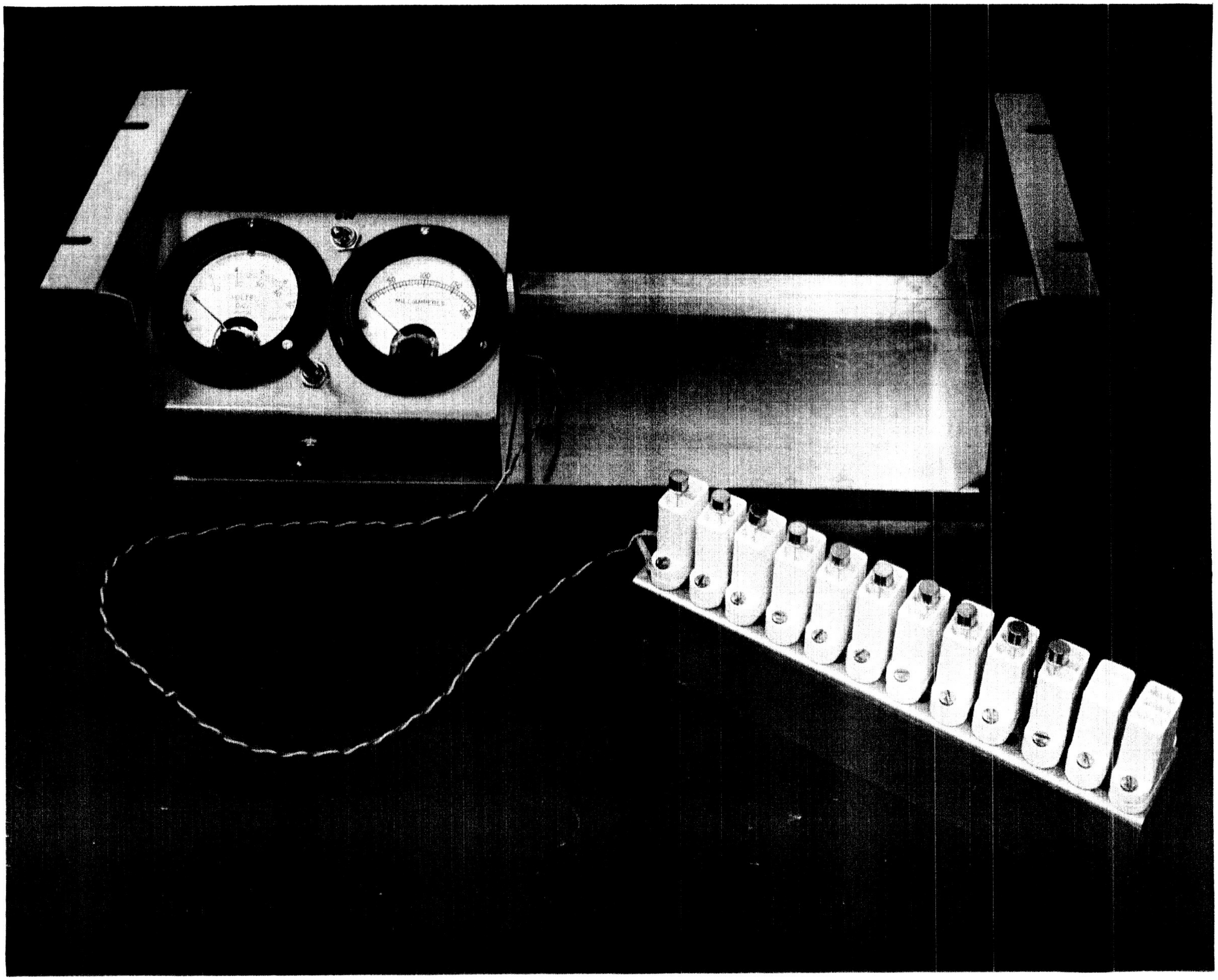


Figure 5. Portable apparatus to maintain voltage on test devices through bake, cooling and up to testing.

baking at elevated temperatures under a positive bias. This trapping phenomenon causes the drift to be assymetrical. The sample must be heated under positive bias to drift the positive ions toward the silicon, but they drift back very easily and quickly under a negative bias at room temperature or at 100°C with zero bias. The direction of shift of the C-V curve due to the motion of protons is the same as it is for the motion of alkali ions -- namely, it shifts toward <u>less</u> negative voltages while a negative voltage is applied to the device.

3.2.3 Trapping Instability

A second type of instability has been found at room temperature, which causes the C-V curve to drift toward <u>more</u> negative voltages when a negative voltage is applied to the device. This effect was first reported by Heiman and Warfield[3]. This effect can be explained in terms of traps either within the oxide or at the oxide silicon interface. The details of the model for this effect are covered in paragraph 3.2.4, below.

3.2.4 Model for Instability Due to Trapped Charge

Assume that there are traps (for electrons or holes) in the oxide or at the oxide-silicon interface. Heiman and Warfield state that these traps lie within approximately 20 Å of the interface. This time constant for the trapping instability is observed to be very similar to the time it takes to develop an inversion layer in silicon near the oxide interface, i.e., on the order of a few seconds. On the other hand, the time constant for traps that are deeper within the oxide is at least six orders of magnitude greater. The time constant for the deeper traps is determined by measuring the recovery time after devices are irradiated with X- or gamma radiation.

The traps may be donor traps, which are neutral when filled or positively charged when empty, or they may be acceptor traps which are negatively charged when filled or neutral when empty. The traps occupy definite energy levels relative to the energy bands of the oxide and of the silicon, which are determined by the exact species of imperfection or impurity that forms the traps. At equilibrium, traps below the Fermi level are filled and those above are empty. This is illustrated in Figure 6.

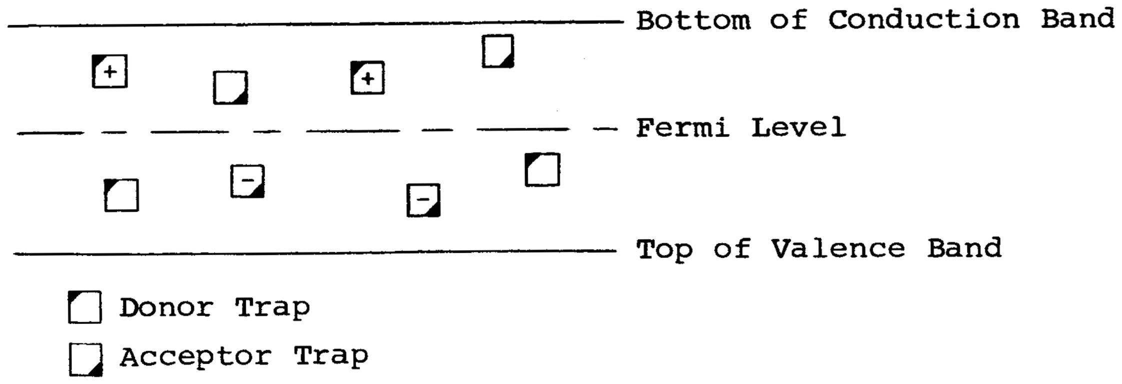


Figure 6.

When a negative bias is applied to the metal, the potential energy of the traps is increased and so some traps are emptied. This creates more positive charge in the donor traps, or reduces the negative charge in the acceptor traps. Similarly, an applied positive bias lowers the potential energy of the traps, filling some of them, thereby decreasing the positive charge in the donor traps or increasing the negative charge in the acceptor traps.

Clearly, when traps are present a negative applied bias increases the net positive charge in the oxide and thereby causes the C-V curve to shift to more negative voltages. This direction of shift is opposite to that due to mobile charge.

3.2.5 Distinguishing Between Instability Caused by Mobile Charge and Trapped Charge

By studying the shift of the C-V curve at different levels of drift bias voltage, one can qualitatively determine the degree to which instability due to mobile charge and that due to trapped charge coexist and partially cancel each other. Assume a sufficient length of time that the drift of mobile charge saturates and a sufficient bias voltage that the amount of mobile charge in the sample is not able to rearrange itself to reduce the field in the oxide to zero. Then, the drift due to mobile charge saturates at a level which is independent of the drift voltage.

On the other hand, the amount of trapped charge depends on the applied voltage, because the occupancy of a trap depends on the electrostatic potential at the trap site. The occupancy of the trap also depends on the temperature because of the influence of the temperature on the Fermi level.

Using the above analytical techniques, our work has shown that both types of instability coexist in given samples. This technique will be further developed in the next quarter.

3.2.6 Effect of Silicon Surface Preparation on Trapped Charge Instability

Work done during the third quarter shows that the amount of trapped charge can be influenced by the manner in which the silicon surface is prepared before the oxidation. Thermal oxides grown on silicon which were etched in HCl vapor at 1200°C or which were grown on a fresh layer of silicon epitaxially grown at 1200°C exhibited mobile charge at room temperature. Thermal oxides grown on silicon etched at room temperature with a liquid etchant containing nitric, hydrofluoric, and acetic acids showed the trapped charge type of instability. The difference in the type of instability observed was shown not to be due to the rinses used after the liquid etch.

The same two types of instability were found for vapor plated silicon nitride layers deposited at 1020°C on silicon wafers prepared by the two etches mentioned above. The relationship between the type of instability and the etchant was the same as that for the thermal oxides.

3.2.7 Effect of Alloying on Mobile Ion Instability

The mobile ion instability has been found to depend on the alloying operation. While it would not be necessary to include alloying in the fabrication of MOS capacitors, alloying is necessary to form good bonds between the metalization and the silicon in MOS transistors. Since the ultimate goal is to make better MOS transistors, we have been alloying all of the capacitors at 550°C for 5 minutes in dry nitrogen.

To determine the effect of the alloying operation on the instability, an oxidized wafer was divided into two parts; one was alloyed, the other was not. Both parts were fabricated into packaged capacitors. The instability in the alloyed capacitors (±12 V, 2 min, 300°C) was of the order of 6 to 10 V on the 2000 Å thick oxide. On the nonalloyed capacitors, the same test showed an instability of less than 1 V.

3.2.8 Effect of Water Content on Mobile Ion Instability

Experiments were conducted to correlate the amount of instability with the water content of oxides. The experimental results indicate that completed MOS capacitors made with drier thermal oxides are more stable than those made with regular oxides. More work is necessary in this area because tests made on these devices after metalization and alloying (550°C, 5 min) but before mounting, baking, and sealing showed the drier oxides to yield less stable characteristics.

4. RADIATION INDUCED DEGRADATION

4.1 Background Information

The previous quarterly reports have described results of experiments designed to evaluate the effects of radiation on MOS devices. These results show that MOS devices are very sensitive to levels of X- and gamma-radiation at levels as low as 10^4 rads. MOS transistors are at least an order of magnitude more sensitive to such radiation than are bipolar transistors.

The model for radiation induced degradation was described in subsection 3.2 of the second quarterly report. Briefly, the oxide is assumed to contain a distribution of donor traps. Radiation ionizes these traps, creating positive charge in the oxide. This charge influences the charge density in the silicon thereby influencing the characteristics of the device.

The effects of X-radiation on MOS devices are basically the same as those of gamma radiation.

4.2 Results of Work During This Period

The work performed during this period concerning radiation has mostly involved the determination of the effects of 100 keV X-radiation on capacitors made of vapor plated layers of silicon nitride.

The intensity of the X-radiation was calibrated by means of film badges and was found to be 1.92×10^3 rads/hour. The source is nearly a point source and therefore the intensity can be increased by an order of magnitude by moving the sample nearer the source of the radiation.

The silicon nitride samples were among the first prepared in our laboratory and they had gross instabilities at room temperature of both the mobile ion and the trapping type. Knowing that traps are contained in these nitride layers, it is not surprising that capacitors made on these layers were very sensitive to X-radiation. Typically, the charge density in 1500 Å thick layers was 2.4×10^{12} cm^{-2} before irradiation. After irradiation with 100 keV X-radiation to 5700 rads the charge density increased to 5 or 6×10^{12} cm^{-2}. Very little recovery was achieved by an annealing treatment at 300°C for 4 hours. We believe this to be the first reported result of irradiation testing of silicon nitride. The result obtained with our initial silicon nitride samples indicate that silicon nitride is as sensitive to irradiation as is silicon oxide. However, silicon nitride layers of better quality might be less sensitive to irradiation.

The effects of radiation on MOS devices may be related to the effects of radiation on the absorption or coloration of glasses. For this reason, a literature search has been started to determine which impurities in vitreous silica are responsible for radiation induced changes in absorption or coloration. If the impurities which are sensitive to radiation insofar as optical properties are concerned are known, it may be possible to make material or process changes to reduce the level of this impurity.

Garino Canina and Priqueler have reported[2] that X-ray irradiation of an aluminum-doped synthetic vitreous silica induces coloration. This effect could be reduced to a very weak coloration if the silica was electrolysed to remove traces of impurity (probably alkali metal). Other samples did not show this coloration.

5. THRESHOLD VOLTAGE

5.1 Background Information

The threshold voltage of available MOS transistors is higher than desirable due to immobile charge in the oxide. This charge density has been found to be 2-3 x 10^{11} charges/cm^2 in oxides prepared by a variety of techniques in many laboratories throughout the world.

The previous quarterly reports provided data showing that the density of immobile charge in thermally grown oxides can be somewhat reduced by heat treatments at 300°C for approximately 1 hour.

It was found that increases in the immobile charge density can be caused by baking thermally-grown oxides in N_2 at 1200°C for 24 hours. Slow cooling has also been shown to substantially increase the immobile charge density.

A model for immobile charge was discussed in the second quarterly report.

The transition and inflection voltages used previously have the advantage that they are easily taken from a C-V curve.

They are quite useful for measuring the instability or the radiation damage and for making rough estimates of the immobile charge density.

In order that the values reported for immobile charge density in this program be comparable with those reported elsewhere, the immobile charge densities in this report have been calculated from the flat band voltage.

5.2 Results of Work During Third Quarter

Promising findings concerning the possibilities for forming transistors with lower threshold voltage were obtained during the third quarter. These possibilities involve the vapor plating of oxides from high purity carbon dioxide and the use of different silicon crystalline orientations.

5.2.1 Vapor Plated Oxide, Matheson Research Grade CO_2, Freshly Grown Silicon

Epitaxial silicon (n-type, resistivity approximately 2 Ω-cm, ⟨111⟩ orientation) was vapor plated on 0.01 Ω-cm antimony-doped wafers at 1200°C. Without removing the wafers from the reaction chamber, the temperature was reduced to 1050°C and the systems were flushed with hydrogen for 5 minutes. A layer of SiO_2 was then vapor plated from a reaction of $SiCl_4$, CO_2, and H_2 at 1050°C. Dry, oxygen-free hydrogen, and electronic grade $SiCl_4$ were used. The CO_2

was Matheson Research Grade, which has a minimum purity level of 99.995%.

Figure 7 shows C-V curves taken on ten MOS capacitors that were measured in the final packaged form, having been subjected to all of the necessary fabrication processes for MOS capacitors. Figure 7 shows the inflection voltage to be less than 0.8 V on these capacitors with oxide layers 850 Å in thickness. This voltage is equivalent to a charge density of 1.4×10^{11} charges/cm^2.

5.2.2 Vapor Plated Oxide, Matheson Coleman Instrument Grade CO_2, Freshly Grown Silicon

An oxide was similarly prepared with Matheson Coleman Instrument Grade CO_2 with a rated purity level of 99.99%. This 1100 Å thick oxide had 2.0×10^{11} charges/cm^2. Comparison of this data with that of paragraph 5.2.1 indicates that the purity of the CO_2 is very important for the preparation of oxides with low immobile charge densities.

5.2.3 Thermal Oxide on Freshly Grown Silicon

To determine the importance of the freshness of the surface layer of the silicon and of vapor plating, an oxide was thermally grown at 1200°C on a freshly prepared epitaxial silicon layer.

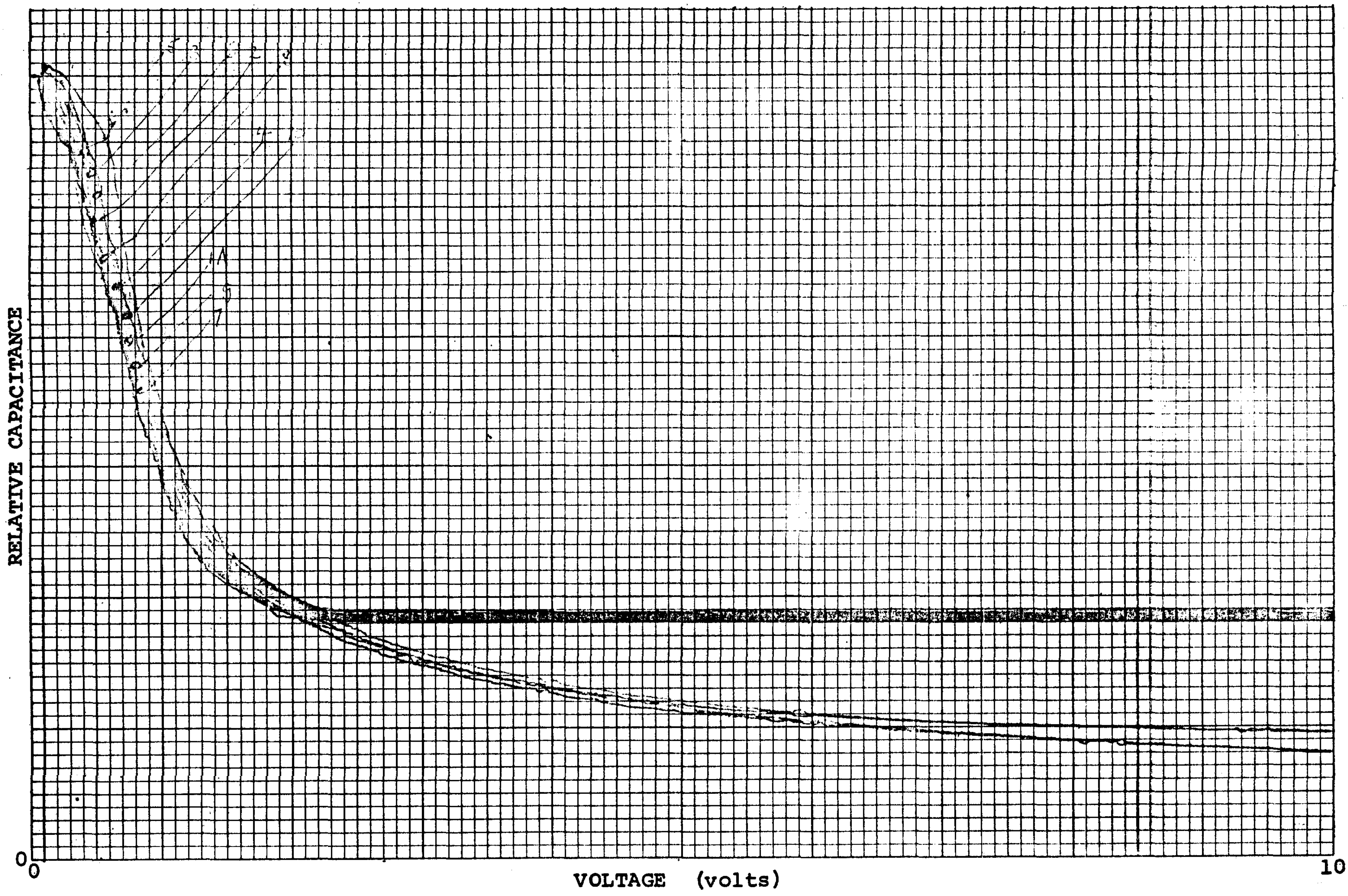


Figure 7. C-V characteristics of 10 capacitors made with vapor plated oxide, with Matheson Research Grade CO_2 on freshly grown silicon.

The time taken to transfer the freshly grown epitaxial silicon from the vapor plating furnace to the thermal oxidation furnace was a few minutes. This oxide contained approximately 3.0 x 10^{11} charges/cm^2, i.e. the 2200 Å thick oxide has an inflection voltage of about 3.0 V.

The relatively low temperature (1050°C) used in preparing vapor plated oxides probably minimizes the density of oxygen vacancies in the oxide near the silicon. These vacancies may be unavoidable in thermally grown oxides because of the part they play in the process by which oxides are thermally grown by reaction with the underlying silicon.

5.2.4 Vapor Plated Oxide, High Purity CO_2, Etched Silicon

A vapor plated oxide was formed with Matheson Research Grade CO_2 on the surface of a p-type wafer which had been prepared by a liquid etch containing nitric, hydrofluoric and acetic acids. This 1000 Å thick oxide contained approximately 3.0 x 10^{11} charges/cm^2.

5.2.5 Crystalline Orientation

All of the devices made on this program were made on silicon oriented on the ⟨111⟩ planes. We believe this same orientation is used in most of the commercially available devices.

Another promising approach to achieving transistors with lower threshold voltage is to form the oxide on silicon surfaces of different crystalline orientations than the ⟨111⟩ orientation now in general use. Balk, et al[1] have found that orientation has a strong effect on the charge density in oxides grown thermally in dry oxygen at 975°C or in oxides grown thermally in dry oxygen at 1100°C in the DWD process (dry oxygen, steam, dry oxygen) and subsequently doped with P_2O_5. Their Table I contains the following data.

SAMPLE PREPARATION	ORIENTATION	OXIDE THICKNESS (Å)	AVERAGE FLAT BAND VOLTAGE AFTER ANNEALING
Dry O_2	⟨111⟩	4600	-9 V
975° C	⟨110⟩	4250	-4 V
	⟨100⟩	3950	-3 V
DWD	⟨111⟩	5300	-8 V
1100° C	⟨110⟩	5300	-3 V
P_2O_5	⟨100⟩	5050	-1.5 V

The charge densities for the DWD process are 5×10^{10}, 1×10^{11}, and 3×10^{11} charge/cm^2 for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ oriented surfaces respectively.

Miura[6] also found that the charge density of oxides thermally grown in dry oxygen at 1140° C is strongly dependent on orientation. Typical data from his paper shows:

ORIENTATION	CHARGE DENSITY
⟨111⟩	1.2×10^{11}
⟨211⟩	4.5×10^{10}
⟨110⟩	2.4×10^{10}
⟨100⟩	-1.2×10^{10}

Note that the ⟨100⟩ oriented surface showed a depletion of electrons in the silicon.

5.2.6 Immobile Charge in Thermal Oxides, Not Dependent on Water Content

The density of immobile charge in thermal oxides made by the techniques for making oxides with a lower water content than that of the regular thermal oxides, has been measured to be quite similar to that of regular thermally grown oxides.

5.2.7 Influence of Water on Heat Treatment Effects on Immobile Charge Density

Experiments have been conducted to establish the degree to which water affected the previously reported experiments* which showed that heat treatments influence the density of immobile charge. The previous experiments showed that heat treatments at 300°C reduce the immobile charge density and that heat treatments at 1200°C for 15 to 24 hours in nitrogen increase the density of immobile charge. Slow cooling from 1200°C over periods of an hour or more was also observed to cause an increase.

Further investigations, utilizing the techniques by which the water content is reduced, show that the reduction of the immobile charge density during a 300°C bake does not depend on the water content. On the other hand, the increase in the

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* See paragraphs 3.4.5 and 3.4.6 in the First Quarterly Report, and paragraphs 4.1.1 and 4.1.2 in the Second Quarterly Report.

immobile charge density due to baking at higher temperatures does not occur in oxides having a reduced water content.

5.2.8 Application of MOS Techniques to Bipolar Device Problem

During the third quarter the gold ball probe and the understanding of oxide properties that were developed in this program were applied to trouble-shoot a problem in the fabrication of bipolar transistors. The transistors had excessive emitter-to-collector leakage current. It would have been very difficult and time consuming to determine the source of the problem in the long sequence of fabrication processes.

This work was performed with funds from another program. The results are included here because they demonstrate the applicability of the equipment and knowledge developed in this MOS program to areas outside the field of MOS devices.

The simple gold ball probe was used to show clearly, quickly and easily that the oxidation furnace tube was forming oxides containing a high density of charge. This charge was inducing a channel between the emitter and collector. After the source of the trouble was pinpointed, the probe also made it possible to quickly establish when the problem was solved. Without this analytical tool it is likely that the problem would appear and disappear before the source of the problem could be located in the lengthy sequence of transistor fabrication processes.

6. RADIOCHEMICAL EXPERIMENTAL EFFORT

6.1 General

Radiochemical analytical techniques have been considered from the beginning of this program as a means for determining the exact species of electrical charge in the oxide responsible for the instability and for high threshold voltage. During the early part of this program, consideration was given to the use of radiochemical techniques to establish whether sodium ions are responsible for the instability at elevated temperatures. However, since the information from a variety of sources reviewed in paragraph 2.1.1 of the second quarterly report establishes the fact that sodium does cause this instability, we sought, therefore, to find other ways in which radiochemical techniques can be used to further the objectives of this program.

As the importance of water became more apparent, as described in the second quarterly report, consideration was given to the possibility of using tritiated water for exploring in detail the effects of water on the properties of oxides.

Dr. S. S. Choi of the Philco Radiochemistry Laboratory made the calculations given in Appendix A of this report which show that tritiated water can be used to detect approximately 1.5×10^{13} water molecules per cm^2, either by counting or by autoradiographic techniques.

6.2 Tritiated Water Apparatus

An apparatus was constructed which permits exposure of dry oxides to controlled pressure levels of tritiated water vapor at various oxide temperatures for long periods of time. For safety, the apparatus is designed to prevent tritium from escaping from the apparatus. Essentially it is a vacuum tight glass apparatus with several arms in which a number of oxide samples approximately 3/8" x 1" in area can be placed. A vacuum pump is connected through a stopcock so that the region surrounding the samples may be evacuated and then isolated from the pump to keep the tritium out of the pump. The samples can be heated to approximately 400°C by means of a radiant heater surrounding the region containing the samples. The reservoir of the tritiated water is connected through a stopcock to the section holding the samples. Following the evacuation of the system, this stopcock is opened to permit the tritiated water to get to the oxide samples. The pressure of the tritiated water vapor will be controlled by controlling the temperatures (below room temperature) of the liquid tritiated water. Dry inert gas can be fed into the system to bring the pressure up to one atmosphere. After exposure of the samples to the tritiated water vapor, the vapor will be returned to the reservoir by cooling the reservoir well below room temperature. After this, the stopcock can be closed to isolate the tritiated water so that the oxide samples can be removed by opening a greased ground glass fitting.

With this apparatus, it will be possible to introduce tritiated water into the oxide. The water so introduced is to be detected by either counting or autoradiographic techniques. An attempt will be made to correlate this information with the electrical behavior of devices. Other possibilities include the study of the movement of water in the oxide under the influence of electrochemical action in the MOS structure at elevated temperatures or in the drift field of an applied bias.

7. RELEVANT INFORMATION FROM THE FIELD OF GLASS TECHNOLOGY

To bring to the program the benefits of the fundamental and empirical knowledge available in the field of glass technology, Professor A. E. Owen of the Department of Glass Technology, University of Sheffield, Sheffield, England, was retained as a consultant. Professor Owen's extensive knowledge in the field of the electrical properties of glass and vitreous silica is evident in two of his papers: "Electrical Conduction and Dielectric Relaxation in Glass", Progress in Ceramic Science 3, 77-196 (1963); and "The Electrical Properties of Vitreous Silica", co-authored with R. W. Douglas, J. Soc. Glass Technology 43, 159T-178T (1959).

Professor Owen was informed of the objectives of this program before he attended the Silicon Interface Specialists Conference in Las Vegas, Nevada, November 15-16, 1965. Philco personnel were active in organizing and participating in this conference which was sponsored by the Electron Devices Group of IEEE. It brought together approximately 85 specialists active in the field of MOS physics and technology. The objective was to bring about a free interchange of ideas to increase the knowledge and understanding of silicon interface phenomena. An effort was made to include representatives of all known research laboratories and manufacturers active in the field of MOS devices in the United States.

At this conference, Professor Owen became conversant with the state-of-the-art in MOS technology and the chief problem areas. After the conference, he visited the Advanced Development Laboratory of Philco's Lansdale Division for consultation. On December 17, 1965, having had time to consider the problems, he prepared the report that is included as Appendix B.

The significance of Professor Owen's comments were considered in planning the work for the remainder of the program.

8. ANALYSIS OF RESULTS

Analysis of the results of the work described in the previous sections of this report leads to the following conclusions:

1. Both empirical data and theoretical calculations indicate that exposure of oxides to the water in room air at room temperature for several days does not affect the oxide properties.
2. A bake in room air at 400°C for 1 hour introduces an amount of water that affects the oxide properties.
3. The choice of a testing procedure for instability should involve the following considerations:
    a. There is a mobile ion instability that is observed at room temperature only after the sample has first been subjected to a positive bias at an elevated temperature.
    b. The presence of mobile ions may not be detected unless a positive bias is maintained on the sample while it is being cooled to room temperature.
    c. An instability due to trapping is also observed at room temperature. This instability can coexist with mobile ion instability and the two counteract each other.

4. One can measure the degree to which mobile ion and trapping instabilities coexist in a given sample by conducting drift tests at several drift bias voltages.
5. The relative magnitude of mobile ion and trapping instabilities is dependent on the surface preparation of the silicon.
6. The observation that alloying increases the mobile ion instability indicates that a reaction between the aluminum and water takes place to form mobile protons, or that the heat treatment frees protons trapped at the metal-oxide interface.
7. Silicon nitride has been shown to be very sensitive to radiation. The degree to which the sensitivity can be reduced is not yet known.
8. It is possible to form oxides on $\langle 111 \rangle$ oriented silicon that have only 1.4×10^{11} immobile charges/cm^2. This has been shown for a vapor plated oxide formed with very pure CO_2 on a freshly grown layer of epitaxial silicon. Related experiments show that the purity of the CO_2, the vapor plating, and the silicon surface preparation each have a large effect on the resulting density of immobile charge.

9. The silicon crystalline orientation has a large effect on the immobile charge density. The highest density is found on <111> and the lowest on <100> orientation.

10. Drier oxides do not have a lower minimum immobile charge density. The <u>reduction</u> in mobile charge density by baking at 300°C <u>is not</u> dependent on the water content. The <u>increase</u> in immobile charge density induced by baking at 1200°C <u>is</u> dependent on the water content.

11. MOS analytical techniques can be used to determine the cause of channelling in bipolar transistors and to determine efficiently when the problem is corrected.

9. FUTURE WORK

Work planned for the fourth quarter includes:

1. Development of oxides with a very low density of immobile charge, involving:
    a. Vapor plating of the oxide,
    b. Various kinds of silicon surface preparation,
    c. Purity of chemicals, especially CO_2 and H_2,
    d. Different crystalline orientation, especially <100>,
    e. Different oxide formation temperatures.
2. Study of causes of instability involving:
    a. Alloying schedule,
    b. Radiochemical experiments with tritiated water,
    c. Various kinds of silicon surface preparation.
3. Development of analytical techniques to establish the degree to which two partially compensating types of instability coexist in oxides.
4. Determination of the effects of X- and gamma-radiation on various capacitors and transistors which are:
    a. Made with vapor plated oxides made with ultra-pure CO_2 and H_2 on silicon having the best surface preparation,
    b. Made with good quality silicon nitride,

  c. Made on silicon of various orientations,
  d. Made on both n- and p-type silicon,
  e. Made with very dry oxides.

5. Conducting of exploratory experiments such as the evaluation of a thermal oxide formed very slowly in oxygen diluted with helium or nitrogen.
6. Fabrication of transistors with the most promising processes to demonstrate the achievements of the program and the feasibility of the over-all processing schedule.
7. Measurement of the surface recombination velocity of the most promising oxides in transistor structures.

10. REFERENCES

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APPENDIX A-1

EVALUATION OF DETECTION SENSITIVITY OF TRITIUM BY AUTORADIOGRAPHY

Various types of photographic emulsion or plate covering a wide range of sensitivity can be used for autoradiographic study. The particular emulsion selected is determined by the type of radiation to be recorded, the level of radiation, and the degree of resolution required. For instance, X-ray films are more sensitive than nuclear emulsion by a factor of 10 to 100, but yield poor resolution[1,2].

Kodak Fine Grain Autoradiographic Stripping Plate AR-10 (emulsion characteristics similar to those of Kodak Nuclear Track Emulsion type NTB) has been chosen for the evaluation of sensitivity for tritium detection, although it has lower sensitivity than some of the other nuclear emulsions such as NTB3[3] because it has a lower inherent background fog level. The choice is rather arbitrary.

The sensitivity of the emulsion to the particular radiation is dependent upon various factors, such as exposure duration, temperature and humidity of the environment during the exposure, cleanliness of the preparation, conditions of photographic processing, and the inherent background fog level.

With proper care, the background fog level, using the emulsion chosen above, averages three to five grains per 10 μ square when the emulsion-coated specimen is stored at room temperature during exposure[2]. However, there is evidence that the background fog level can be reduced greatly if the specimen is stored at 4 to 5°C during exposure[4]. Thus it may be safe to consider 3 grains/$(10\mu)^2$ as a typical background fog level in this sensitivity evaluation. Therefore it is reasonable to regard 6 exposed grains/$(10\mu)^2$ above background as sufficient for relative measurement in autoradiography.

It has been reported that an over-all efficiency of tritium in smear autoradiography is about 5 percent of the total disintegration[5], and can be considered the same in our case. The amount of tritium required for this can be calculated as follows: 6 grains = 5 percent of the total disintegration, and therefore the total disintegration is equal to 120 disintegrations/$(10\mu)^2$ during the exposure time.

If N_o and N represent the total number of tritium atoms before and after the exposure duration, respectively, over a hundred square micron ($100\ \mu^2$) area, then

$$N = N_o e^{-\lambda t} , \qquad \text{(Eq. 1)}$$

where λ = decay constant of tritium, 1.79×10^{-9} sec^{-1}, and

t = decay time (equal to the exposure time).

$$N_o(1-e^{-\lambda t}) = 120. \qquad \text{(Eq. 2)}$$

If the exposure time is 10 days, then

$$1-e^{-\lambda t} = 0.0015.$$

That is, 0.15% of the initial tritium atoms is 120 atoms.

Therefore,

$$N_o = 8 \times 10^4/(10\mu)^2 = 8 \times 10^{10} \text{ tritium atoms/cm}^2.$$

The H_2O (molecule)/tritium (atom) ratio in 10 curies/ml tritiated water is calculated as follows:

$$A = \lambda N,$$

where A = activity in disintegrations per second (dps),

λ = decay constant of tritium, and

N = number of tritium atoms.

$$10 \text{ curies} = 3.7 \times 10^{11} \text{ (dps)} = 1.79 \times 10^{-9} N,$$

$$N = 2.06 \times 10^{20}.$$

The number of H_2O molecules in 1 ml $\simeq \frac{6.023 \times 10^{23}}{18}$,

$$N_{H_2O} = 3.35 \times 10^{22} ,$$

$$N_{H_2O}/N = \frac{3.35 \times 10^{22}}{2.06 \times 10^{20}} \simeq 162.$$

Since, as shown by the above calculations, the ratio of H_2O molecules to tritium atoms in the tritiated water (10 curies/ml) is about 162, the corresponding surface density of water is $\simeq 8 \times 10^{10} \times 162 = 1.3 \times 10^{13}$ (H_2O) molecules/cm^2.

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3. Boyd, Op. Cit., p. 53.
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5. Ibid, p. 76.

APPENDIX A-2

EVALUATION OF THE COUNTING SENSITIVITY OF TRITIUM

Tritium emits beta particles of 18 keV[1] maximum energy, the lowest of any known isotope, and the activity may be counted by using one of the following[2-8]:

1. Gas counting with a proportional or Geiger counter,
2. Liquid scintillation counting using internal phosphor,
3. A solid, flow type proportional or Geiger counter.

Although the first and second methods give a higher counting efficiency[3-8], the nature of the problem makes one choose the third method.

The counting set-up to be used here is the Nuclear Chicago gas flow counter which has 2π geometry and can be operated with or without a window. The experimental test result indicates the background counting of the set-up to be about 25 counts per minute.

If we consider that the limit of the precise relative measurement of radioactivity is about twice the background counting, then the minimum activity required should be about 50 counts per minute above the background. The counting efficiency of the set-up chosen for tritium is about 1%[4,7,8]. Since it has 2π

geometry, half of the radiation emitted will be in the wrong direction. Thus the actual minimum activity (A_m) required will be

$$A_m = 50 \times 2 \times 100 = 10^4 \text{ disintegrations per minute (dpm).}$$

The number of tritium atoms, N, which gives the above disintegration rate can be calculated as follows:

$$A = \lambda N , \qquad \text{(Eq. 1)}$$

where A = activity in disintegrations per second (dps),

λ = decay constant of tritium,

and

$$\lambda = 0.693/T_H , \qquad \text{(Eq. 2)}$$

where T_H = half-life of tritium.

Since the half-life of tritium is 12.26 years[9],

$$\lambda = 1.79 \times 10^{-9} \text{ sec}^{-1} \qquad \text{(Eq. 3)}$$

and

$$A_m = 10^4 \text{ dpm} = \frac{1}{6} \times 10^3 \text{ dps} . \qquad \text{(Eq. 4)}$$

From Eq. 1,

$$N = A/\lambda , \qquad \text{(Eq. 5)}$$

and from Eq. 3, 4, and 5,

$$N = 9.39 \times 10^{10} . \qquad \text{(Eq. 6)}$$

The maximum specific activity of commercially available tritiated wafer is 10 curies per ml[10]. This corresponds to a H_2O (molecule)/tritium (atom) ratio of about 162. The calculation of this ratio is given in Appendix A-1).

Thus the minimum abount of water on the surface of the individual sample which is associated with the minimum activity of tritium for the precise relative counting will be

$$9.39 \times 10^{10} \times 162 = 1.52 \times 10^{13} \ (H_2O)/\text{sample},$$

and the surface area per sample can be as large as 5 cm^2.

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APPENDIX B

CONTRIBUTIONS OF A GLASS TECHNOLOGIST

What contribution can glass science and technology make to the problems of instability in MOS devices which are caused by the motion of charges in the SiO_2 layer? The first reaction of a glass specialist to this question must be to ask, "Are SiO_2 films grown thermally on silicon at relatively low temperatures really 'glasslike'?"

Glasses are essentially supercooled liquids with a <u>continuous</u> (continuous in the normal silicate glasses; glasses with discontinuous networks are known) frozen-in network having a non-equilibrium liquid-like configuration. The exact configuration depends very much on the rate of cooling from the liquid; as a consequence the two features characteristic of the glassy state are(1):

1) The existence of a transformation range; i.e., a temperature interval in which the frozen-in glassy configuration can, within experimental times, relax to take up the <u>equilibrium</u> configuration and hence give rise to time-dependent properties in this temperature range.
2) The physical (and chemical) properties are sensitive to thermal history. The position of the transformation

range itself depends upon the cooling rate, becoming lower in temperature the slower the rate. This sensitivity to thermal history is, however, no more than a consequence of the existence of the transformation range phenomenon (1).

There are cases where the films grown on silicon are, at least in part, glassy -- e.g., after treatment in P_2O_5 vapor at high temperature during which a liquid layer is probably formed. In general, however, to correctly describe SiO_2 films grown on silicon as glasses -- and hence to draw on what is known about the glassy state -- it would strictly be necessary to demonstrate the existence of a transformation range in the SiO_2 films. To carry out an experiment to elucidate this point would probably be very difficult. It is true that MOS device characteristics are sensitive to heat treatment processes, but to what extent this is due to "relaxational changes in the bulk" of the oxide film rather than effects at the interfaces or even in the silicon itself, is not clear, and to separate the various sources of change in such a complex system would also be a difficult task.

In raising this question one is not being merely pedantic, for the effects of transformation range phenomena on the physical properties of glasses at room temperature are not trivial. Take, as an example, the electrical resistivity -- probably the most relevant property in the present context. The room temperature resistivity of a typical soda-lime-silicate glass can vary by an order of magnitude between a rapidly chilled and a well-annealed specimen; compositionally, this change in resistivity is equivalent to a very considerable difference in the sodium concentration. Obviously such effects cannot be overlooked in interpreting the physical properties of glasses.

What, therefore, is the nature of SiO_2 films grown on silicon? No doubt they are amorphous, but could they be very finely divided polycrystalline layers? If this were the case, grain boundaries would of course be very important in diffusion mechanisms, and comparisons with glass or bulk crystalline forms of silica would be quite invalid. The good strength, hardness and scratch resistance of the films perhaps argues against this but is not conclusive. The most direct test would be low-angle X-ray diffraction, for a glass should not show low-angle scatter (cf. with silica gel). Alternatively, one should ask whether there is any anisotropy in the SiO_2 films. Is there, for instance, a preferred orientation perpendicular to the silicon surface; e.g., a configuration corresponding to the c-axis of quartz?

To reiterate: The essence of glass formation is a continuous change in energy, entropy and volume on going from the liquid to the glassy state, but with discontinuities in derivative properties (1). It is difficult to conceive that there can be a similar continuity between the phases involved in the formation of thermally grown SiO_2 films on silicon, and in this sense these films cannot be "glassy". To what extent this difference in "thermodynamics" affects the properties is problematical, and subsequently the assumption is made that meaningful comparisons between glasses and the SiO_2 films in MOS devices can be made. One is encouraged in this assumption by the fact that the SiO_2 films have dielectric properties, an index of refraction and a density comparable to those of fused silica; there are twenty-two phases of silica, and at least some of these are likely to have properties not very different from fused silica.

Before proceeding, one more note of caution should be sounded. The great majority of electrical measurements on glasses have been made in the low-field condition, i.e., less than 10^3 V/cm, where Ohm's law applies. This contrasts with the much higher field strengths normally involved in MOS device studies. Generally, however, glass continues to be an electrolytic (cationic) conductor at high field strengths and the same type of ionic model may be applied to the high field conductivity (2). This is probably true even at breakdown which normally occurs by Joule heating and thermal catastrophe, rather than by electron avalanche.

The critical property of the SiO_2 in MOS structures is its ability to store and transfer charge, and it has been proposed by several authors that the charged species responsible for the electrical properties of the oxide is an oxygen vacancy (V^{++}) (3). If, however, there is any similarity to the conduction mechanism in bulk glass, this would seem unlikely. This is not to say that oxygen vacancies do not exist in glass; a model based on oxygen deficiency has been proposed for certain paramagnetic centres in glass observed by electron-spin-resonance experiments after neutron irradiation (4). It is a fact, however, that oxygen <u>ion</u> diffusion in glasses is very small indeed, and many orders of magnitude less than for common cations such as the alkali ions. Because of this large difference it is not easy to compare oxygen and sodium ion diffusion coefficients at the same temperature, but where this is possible (e.g. at 450°C) experimental results indicate that the diffusion coefficient for oxygen is at least a factor of 10^7 lower than that for sodium ions (5); at room temperature the difference is likely to be even greater. The diffusion coefficients and (electrical) mobility are directly related to each other through the Nernst-Einstein equation (2) so that if oxygen ion vacancies are to make an equal contribution to the conductivity, and hence charge transfer, they would have to be in a concentration at least 10^7 times greater than the sodium ions. Sodium is one of the most troublesome of impurities and it certainly seems likely that in fused silica the conductivity can be attributed to contamination by sodium or other alkali ions (6). This is apparently so even in the purest grade of fused silica -- the synthetic varieties produced from semiconductor quality silicon via a volatile halide -- which contains only a few parts of alkali per hundred million, i.e. approximately 10^{14} per cc. In the normal commercial grade of fused silica - produced from natural quartz - the alkali impurity level is measured in parts per million.

The opportunities for contamination of the oxide in MOS structures are such (e.g. during oxidation by transport from the reaction tube or from the gases themselves, during etching or photoresist treatments, etc.) that it would be surprising if sufficient sodium or other alkali were not present in sufficient quantities to have a dominating effect on the electrical properties of the oxide film. At the IEEE Silicon Interface Specialists Conference in Las Vegas, November 15-16, 1965, levels of 10^{15} Na atoms/cc seemed to be regarded as the best obtainable purity under present conditions, and most oxide films probably have more. By comparison with the situation in fused silica this would, in the writer's opinion, be enough for the sodium impurity to effectively control the conduction mechanism in the oxide. If, in these circumstances, oxygen ion vacancies were sufficiently mobile to carry an appreciable part of the current this would in itself suggest a significant difference between the oxide film in MOS structures and fused silica and glasses. It should be pointed out, however, that if there was a relatively large concentration of oxygen ion vacancies capable of limited movement, these could contribute to charge motion by dielectric polarization. The sodium ions will also contribute to polarization, of course, by dielectric relaxation (2). In addition, it must be remembered that in "wet" grown oxides there will probably be relatively large amounts of protons which might be expected to be even more mobile than alkali ions. This situation is slightly more complicated, however, because the protons are associated with hydroxyl groups and the work of Hetherington, et al have shown that in glasses there are mobile and immobile forms of the hydroxyl group (7-9).

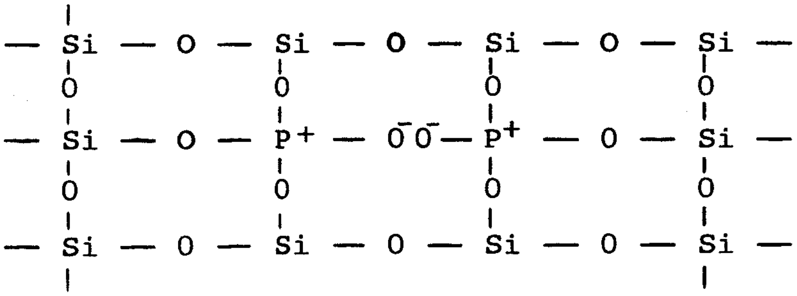
If, therefore, comparisons with glasses are valid one can conclude that the predominant mechanism of charge transfer in the oxide of the MOS structure is by sodium and/or hydrogen ion migration. Moreoever, it is unlikely, because of the various treatments used, that the sodium contamination could be reduced to a level where it is insignificant in this respect. Electrolysis would perhaps remove all or part of the sodium ions or protons, but for the electrolysis to proceed to any extent the ions removed would have to be replaced by some other species of comparable mobility. The electrochemistry could be quite complex, but in the simplest terms, if the silicon was made positive and the metal negative, sodium would only be removed if:

1) Positive "holes" (presumably oxygen ion vacancies) entered at the silicon-oxide interface, and
2) The sodium ions could be discharged at the metal.

If the positive "holes" were not reasonably mobile, charge separation would occur, setting up an opposing space-charge, and the electrolysis current might drop to negligible proportions.

A similar effect would occur if the metal electrode did not discharge the sodium ions.

Supposing, however, electrolysis could be achieved in the manner postulated, the sodium ions would have been replaced by an equivalent amount of positive oxygen ion vacancies. It might be possible to remove these by a subsequent oxidation or high temperature treatment, but even this presents difficulties (see later paragraph). Failing in the effort to eliminate or remove the alkali impurity, the only other alternative is to reduce its mobility by some means. This would seem to be the function of treatments in P_2O_5 vapor which are reported to improve the stability of MOS structures (10). Phosphorus can replace the silicon in SiO_2 isomorphously and when introduced in the form of P_2O_5 may cause the formation of non-bridging oxygen ions and $P^+ - O^-$ dipoles:



The effect of P_2O_5 in SiO_2 may be twofold:

1) The dipoles may act as "traps" for the alkali ions, hence reducing their mobility (N.B., the ion-dipole interaction is relatively strong).
2) By forming non-bridging oxygens the P_2O_5 may break down the continuous glassy network. This effect might increase the mobility of modifying ions.

Insofar as theory has progressed, it appears that the barrier to ionic motion in glasses is predominantly electrostatic rather than spatial or configurational (see Ref. 2 pp 121-122 and pp 180-184); the first effect would probably be the most important, therefore, leading to an over-all decrease in mobility of the alkali ions. In circumstances where the alkali is in trace amounts with relatively large concentrations of P_2O_5, this conclusion seems even more likely.

Alternatively, an even simpler explanation could be postulated in purely "chemical" terms; namely, the phosphate glass may be expected to have a greater affinity for the alkali (because P_2O_5 is a more electronegative oxide than SiO_2), so that an outer layer of phosphate glass would act as a "getter" for alkalis. This chemical approach may be given added weight by the observation that treatment with B_2O_3, unlike treatment with P_2O_5, tends to degrade the stability of MOS structures. On the "physical" arguments used above this is surprising, for B_2O_3 is known (a) to decrease the conductivity of sodium silicate glasses (2), and (b) to make the glass more compact (provided not too much B_2O_3 is added), i.e., to increase the density. On the other hand this would be consistent with the chemical argument for B_2O_3 is less electronegative than SiO_2 and alkalis would therefore tend to favor the latter. This is not a very conclusive observation, however, because it is extremely difficult to obtain B_2O_3 completely free of water, and it is possible that in the B_2O_3 treatment appreciable amounts of water (protons) will enter the oxide layer.

Phosphorus and boron are network-forming oxides. The other method of reducing the mobility of alkali ions in silica would be to introduce larger and relatively immobile network modifying oxides. For example, barium oxide is known to increase the resistivity of a sodium silicate glass by three orders of magnitude when the BaO is substituted for SiO_2 in an equivalent amount to that of the Na_2O (2). If the barium was present in excess, a larger effect might be expected. The oxides of calcium, strontium and lead also increase the resistivity appreciably, but to a smaller extent than barium.

The resistivity of glasses is also increased considerably by the "mixed alkali effect" (2). Glasses containing either Na_2O <u>or</u> Li_2O, say, in equivalent amounts, have roughly the same resistivity, but if Na_2O is substituted for some of the Li_2O in the glass the resistivity does not change linearly but goes through a very pronounced <u>maximum</u> when the Na_2O and Li_2O are present in roughly equimolecular amounts. The resistivity of the mixed alkali glass may be four decades higher than either of the single alkali glasses. The effect is found for any pair of alkalis and may be more pronounced the greater the size difference between the two alkali metals. At the present time there is no satisfactory explanation for this phenomenon but the most plausible one is based upon the idea that during glass formation each alkali ion tends to influence its own environment and to create "holes" which are energetically favorable to itself (2). During subsequent migration, therefore, the larger ion sooner or later finds itself confronted by a "hole" vacated by a smaller ion, its motion is blocked, and hence all ionic migration stops. In its simplest terms this explanation does, in fact, lead to a zero conductivity (see Ref. 2 pp 136-139).

It is conceivable that one might make use of either the "heavy ion" or the "mixed alkali" effects to reduce the alkali ion mobility in the MOS structure. But the nature of glass and the glass-forming process should again be borne in mind and contrasted with the processes involved in forming MOS devices. Glasses are formed from a melt and network-modifying ions (alkalis or alkaline earths) in the melt have the opportunity, during the cooling process, of influencing their own environment to a considerable extent, i.e., to "dig" holes which are energetically favorable. There is no reason to suppose that an ion introduced into a solid glass by diffusion, say, after cooling, would have exactly similar properties to the same type of ion melted into the glass. Since most of the alkali impurity in the MOS structure is probably introduced after the oxide formation, this is an important distinction. If, for instance, it was suspected that the impurity was mainly sodium and that this was introduced by contamination and diffusion from etching solutions, it would not be advisable to attempt at the same time to diffuse in a roughly equivalent amount of potassium, hoping to make use of the mixed alkali effect in reducing the sodium ion mobility. The net result would almost certainly be equivalent to having twice as much sodium present! Similarly, it would not even be advisable to deliberately introduce a larger alkali atom during growth, hoping that this would counteract the effect of sodium introduced at a later stage by diffusion. The larger alkali ion, present on its own, would have a mobility not very different from sodium, and the sodium diffused in subsequently by contamination would not -- accepting the explanation mentioned above -- have the opportunity of inducing the mixed alkali effect. It would seem more profitable to try the inclusion of a large multivalent network-modifying ion which is known to have a low diffusion coefficient (e.g., BaO or PbO) but, again, this should be incorporated during the growth of the oxide.

All of the foregoing discussion has been concerned with reducing the mobility of the relatively mobile ions responsible for charge transfer. It is more difficult to make suggestions for the removal of "fixed" charges, i.e., those charges which exist independent of time or of treatment. It is accepted that the oxide layer grows by oxygen diffusion and the general concensus of opinion is, apparently, that this growth occurs by an ionic mechanism involving oxygen vacancies rather than by molecular or atomic diffusion of oxygen (although there seems to be some doubt about this in "wet" grown oxides). If this is the case, then there must always be a finite concentration gradient of positively-charged oxygen ion vacancies. In a free SiO_2 film these could probably be virtually completely removed by an annealing treatment in an oxidizing atmosphere. But with an oxygen sink always present in the MOS structure (i.e., the silicon) an oxidizing treatment would presumably result simply in an increase in the thickness of the oxide, with perhaps a dilution of the non-stoichiometry, at best. By immobilizing the alkali ions, a considerable reduction in the dielectric polarization is likely to result. In glasses containing more than a few percent of alkali, for instance, the alkali ions not only cause the conductivity but also dominate the dielectric relaxation up to frequencies of at least 1 MHz and probably beyond (2). In fused silica, however, water present in small amounts may control the dielectric properties (6).

An alternative may be to lay down films, instead of SiO_2, of a glass known to have good dielectric properties. Materials which come to mind are the boroaluminates, particularly those of calcium, strontium, barium, lead and bismuth, most of which have been studied in some detail. Attempts have been made to deposit rather complex glasses, e.g., lead or zinc aluminoborosilicates, and encouraging results have been obtained (see Ref. 3 pp 385-393). Generally, however, these glass films have been deposited by inconvenient sedimentation techniques. A more convenient method, suited to continuous processing, might be to first evaporate a comparatively thick aluminum film onto the silicon and then to oxidize this in B_2O_3 vapor; the other metal (e.g., lead or zinc) could be introduced either by depositing it with the aluminum or by carrying it in the vapor phase with the B_2O_3. The oxidation should be continued until all of the aluminum, and probably some of the underlying silicon, has been oxidized.

Most of the boroaluminate glasses are known to have good electrical properties. The resistivity can be appreciably greater than that of the best quality of fused silica. The dielectric loss is small, changes only slowly with temperature up to 200 or $300^{o}C$ and is only slightly dependent on frequency in this same temperature range. The dielectric constant is practically constant, indicating little dielectric polarization, for frequencies between 10^2 and 10^5 Hz in this temperature range. At room temperature the dielectric loss does not begin to increase sharply until frequencies higher than 10 MHz are reached. Variations on this method can be imagined for specific circumstances. The boroaluminates may, for instance, be sensitive to atmosphere moisture. This depends on composition, but their inertness can be greatly improved, without detracting from the good electrical properties, by incorporating some silica. In the film formation technique this could be achieved by depositing silicon monoxide, say, along with the aluminum, or by oxidizing also some of the underlying silicon and raising the temperature to the point where the boraluminate glass is molten, thus eventually forming a boroaluminosilicate.

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APPENDIX C

The following list of papers and articles is in addition to the literature review that was included in the first and second quarterly reports. Many of these items have appeared since the two quarterly reports were prepared.

1. Balk, P., P.J.Burkhardt, and L.V. Gregor, "Orientation Dependence of Built-in Surface Charge on Thermally Oxidized Silicon," Proc. IEEE, 53, 2133-2134 (December 1965).

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