

PHILCO CORPORATION  
LANSDALE DIVISION  
Lansdale, Pennsylvania

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

August 22, 1965 to November 21, 1965

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

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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 second quarterly progress report, covering studies performed during the period from August 22, 1965 to November 21, 1965.

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.

Detailed models relevant to the chief problem areas have been developed that provide a useful basis for setting up experiments to test the models and add to their known details.

Gross instability due to alkali ion contamination has been studied by various investigators. The behavior of alkali ions in MOS oxides has been fairly well established and techniques have been developed for preparing good oxides that are free of alkali ions.

The effects of radiation on MOS devices have been evaluated. A useful model has been developed that provides the basis for explaining most of the observed effects of radiation. A variety of oxide types were tested to determine their sensitivity to radiation. There was not much difference among oxides of various types insofar as radiation resistance is concerned.

Based on the information developed to date, it is believed that the effects of water on the mobile charge density, fixed



charge density and radiation sensitivity are of sufficient magnitude that a major effort is being made to introduce equipment and techniques to the program that will control the water content.

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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 with:

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

The results of this program should also be applicable to improving bipolar devices, and therefore will be of value for the improvement of microcircuits containing either bipolar or MOS devices.

### 1.2 Model of Charge Distribution

The electrical characteristics of an MOS device are very dependent on the distribution of electrical charges throughout its structure.

The basic MOS structure is shown in Figure 1 with a representation of the distribution of the various charges on which the device characteristics depend.

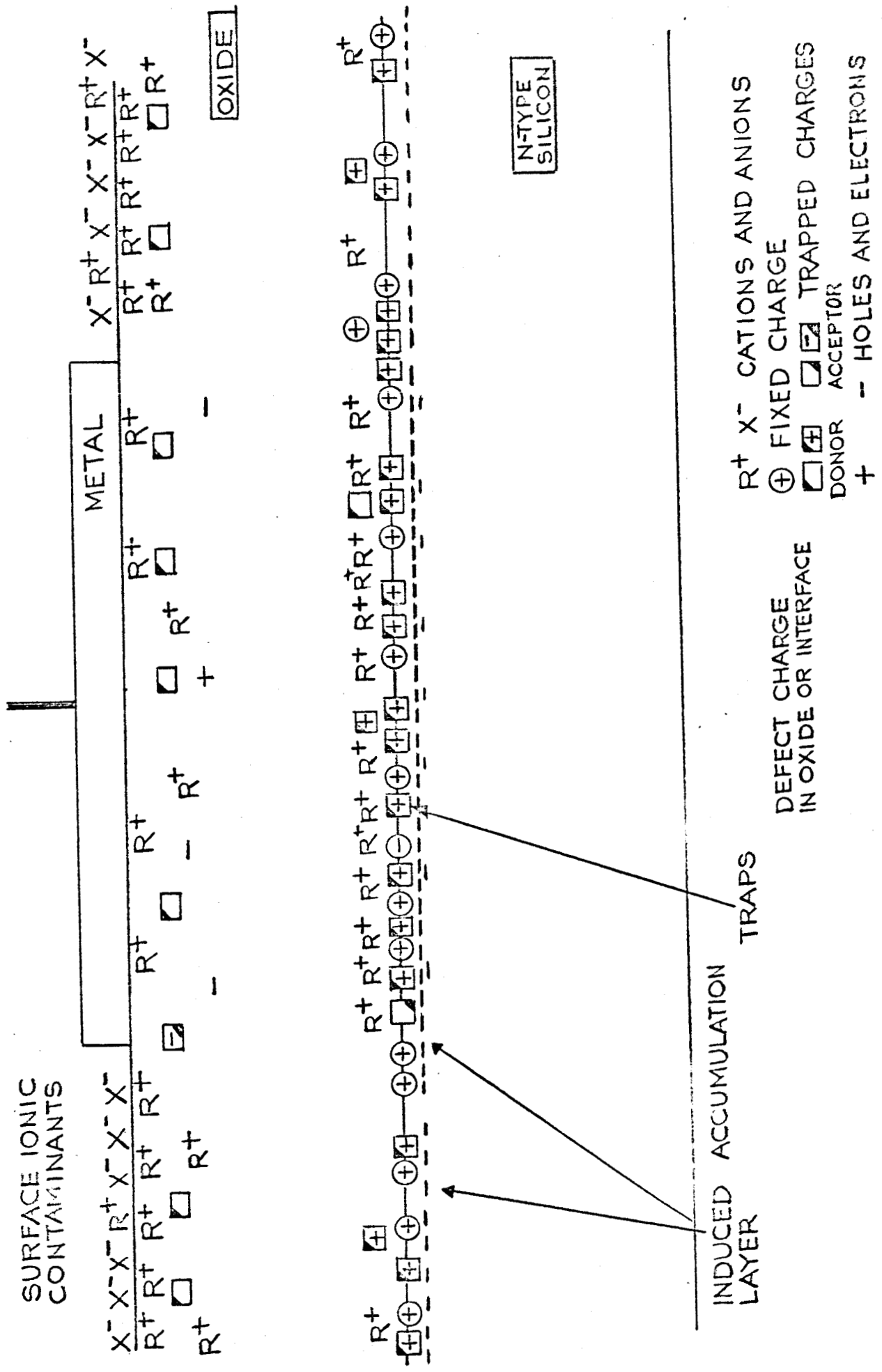


Figure 1. Distribution of charges in a MOS structure.

The behavior of charges in the silicon of MOS devices is similar to that in bipolar transistors. The charges responsible for the MOS device problems with which this program is concerned are located in the bulk of the oxide, at its interfaces with the metal or silicon, or on the top surface not covered by the metal.

These charges can be divided into three types: fixed, trapped, or mobile. Fixed charge can be due to immobile impurity ions or to charged lattice defects. It is widely believed that much of this charge may be due to the oxygen vacancies that exist in thermally grown oxides.

Stevens and Katz<sup>14</sup> have discussed the wide variety of possible imperfections that might exist in the SiO<sub>2</sub> network. The following is a list of the imperfections they described, along with their opinions concerning the abundance of each type.

- |                 |  |
|-----------------|--|
| Silicon Vacancy | - Silicon vacancies are not likely because of the very high bonding energy with oxygen.  |
| Oxygen Vacancy  | - Oxygen can exist either in bridging or in non-bridging positions in the lattice. Non-bridging oxygen atoms can break away from |

the lattice, leaving oxygen vacancies.

Interstitial Silicon - Interstitial silicon is unlikely because of the strong tendency to bond with oxygen.

Interstitial Oxygen - This exists as a non-bridging oxygen atom which exists as a part of the Si-O network. Under certain special circumstances interstitial oxygen exists which is not a part of the network.

Replacement of Silicon By Another Cation - The replacement of silicon by cations ( $Al^{3+}$ ,  $B^{3+}$ ,  $P^{5+}$ ) is very common.

Replacement of Oxygen By Another Anion - This possibility should not be overlooked, but does not seem to occur to any important extent.

Interstitial Cations Other Than Silicon - Interstitial cations in glasses and quartz crystals are very common.

Interstitial Anions Other Than Oxygen - This occurrence is unlikely, but may be possible in special circumstances.



Trapped charge is that charge which is temporarily bound to sites in the structure which have a lower potential energy for the charge than the surrounding regions because of some localized defect. Such traps are due to irregularities in the oxide such as impurity atoms or lattice imperfections. There is very probably an abundance of such lattice imperfections in the amorphous oxide. Such an interface as that between the oxide and the silicon should be expected to have a relatively high density of lattice and bonding irregularities, and therefore a high density of traps.

The properties of these traps depend on the energy level associated with the trap and the location of the trap within the structure of the device. The exact species of the imperfection that functions as a trap determines whether the trap is a donor or acceptor trap — i.e., whether it is neutral when it holds an electron and positively charged when it releases it, or is negatively charged when it holds an electron and neutral when it releases it. The exact species also determines its position in the energy gap relative to the valance and conduction bands of the oxide.

Whether or not a trap is occupied by an electron at equilibrium depends on the electrical potential at the position

of the trap. This potential depends on the materials involved, the geometry of these materials, and the electrical potentials imposed either by the electrochemical potentials created by the structure itself or due to applied voltages. The rate at which such traps can change their state of charge depends on the number of separate charged particles available to communicate with the traps when the electrical potential is varied. The number of such charges depends on the material and the electrical potential in the region. To illustrate this point, let us suppose that the traps are hole traps at the oxide-silicon interface. The rate at which such traps can be filled following an abrupt change in potential is proportional to the density of holes in the inversion layer in the silicon.

There are several main kinds of mobile charge with which this work must be concerned. There are holes and electrons in the oxide similar to those in the silicon, and indeed it is these holes and electrons, along with any that can tunnel from the metal or the silicon, that fill or empty the traps in the oxide.

Various contaminating substances, the most important of which are the alkali ions and hydrogen- and water-related species, are responsible for the instabilities in MOS devices.

These mobile ions diffuse and drift through the oxide between the metal and the silicon and along the surface of the oxide to make very significant changes in the surface potential distribution in the silicon.

### 1.3 Work to Date

During this first six-month period, the work on this program has:

1. Set up the necessary fabrication and test equipment to make a preliminary evaluation of the problems,
2. Made a comparative evaluation of various kinds of oxides, differing in oxidation processing and post-oxidation treatments, for threshold voltage, stability under bias and at elevated temperatures, and for radiation resistance,
3. Correlated and evaluated the theoretical and experimental work of this and other laboratories to develop a coherent understanding of MOS structures and to evolve a model which agrees with experimental observations to date,
4. Established a good level of awareness and understanding of the related work reported by others in the journals and at recent conferences (see Section 7),

5. Revealed the fact that the water content of oxides plays an important part in the determination of oxide stability and sensitivity to radiation, and that it is very important to control the water content of oxides in these studies,
6. Enabled us to choose the equipment and techniques for the further experimental phases of the program.

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

#### 1.4 Areas of Discussion

Succeeding sections of this report deal with each of the main problem areas with which this program is concerned. These are:

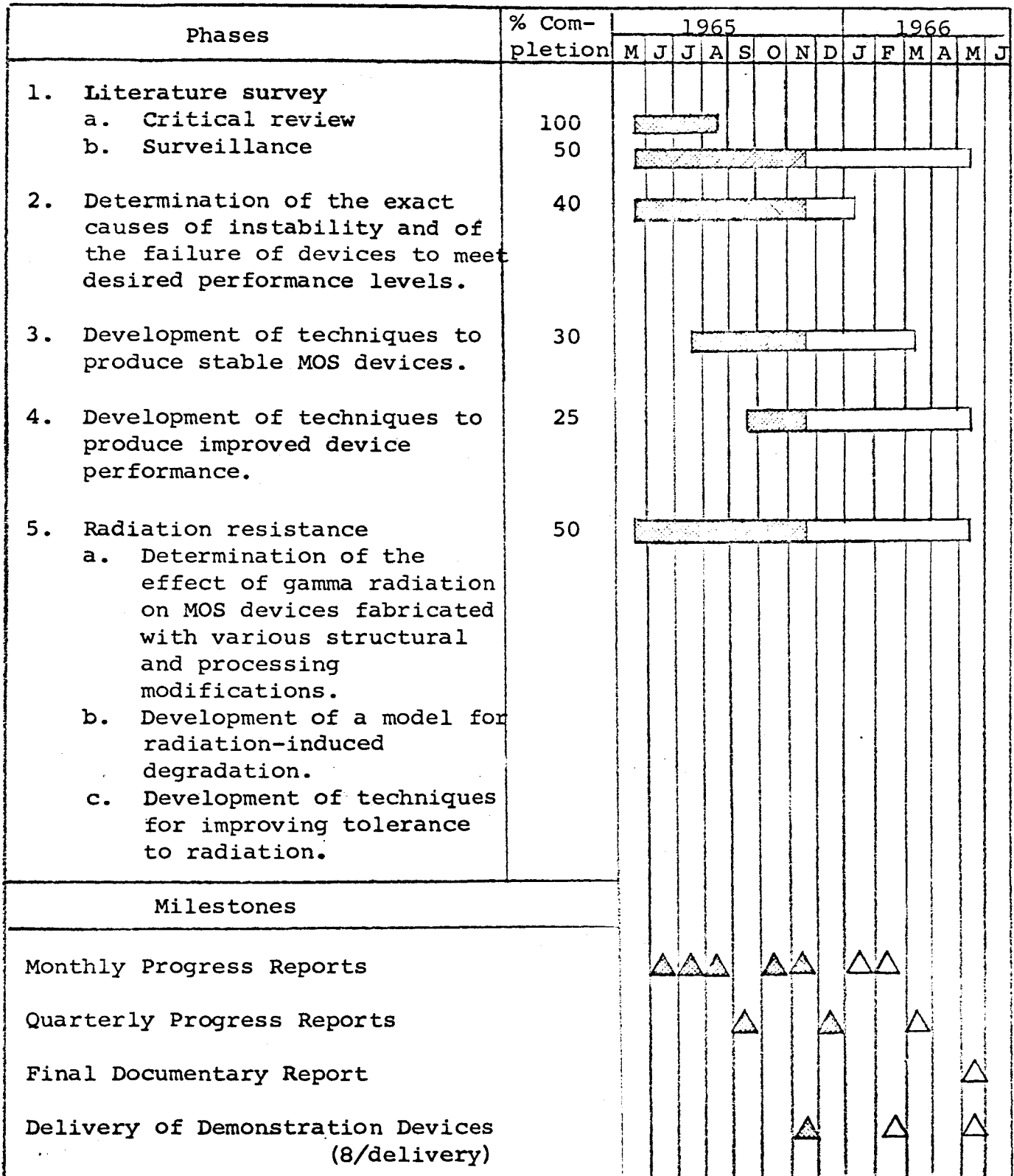
2. Instability at elevated temperatures under an applied bias,
3. Radiation-induced degradation,
4. High threshold voltage.

Each of these sections includes:

1. Background information,
2. Model,
3. Possibilities for improvement.

CHART 1. PROJECT PERFORMANCE AND PROGRAM SCHEDULE

Period Covered: May 21, 1965 to November 21, 1965



Section 5 reviews the present state of the program. It includes a summary of our interpretation of the significant results obtained to date, and our ideas for possible approaches to improving MOS devices. Section 6 contains a statement about our plans for future experimentation. Section 7 lists conferences attended by program personnel, and Section 8 lists the references alluded to in the text.

## 2. INSTABILITY AT ELEVATED TEMPERATURES

### UNDER AN APPLIED BIAS

Probably the most important problem area concerning MOS devices is the observed instability at elevated temperatures under an applied bias. The literature contains many references describing the causes of this instability as being due to alkali ions, hydrogen, and water. The densities and distributions of these contaminants are very dependent on the control of materials and ambients throughout the MOS device fabrication processes.

#### 2.1 Background Information

In addition to the references mentioned in subsections 2.5 and 2.6 of the literature review part of the First Quarterly Report, the supplementary list of references in Appendix A of this report includes a number of excellent papers that provide background information from which a model can be developed.

##### 2.1.1 Alkali Ion Contamination

The gross instability of MOS devices under bias has been shown to be due to alkali ions in concentrations ranging from about  $10^{11}$  cm<sup>-2</sup> up to much higher densities. Supporting

evidence for the motions of alkali ions in SiO<sub>2</sub> can be found in the work of such glass technologists as Proctor and Sutton<sup>11</sup> and Owen and Douglas<sup>9</sup>. Snow, Grove, Deal and Sah<sup>13</sup> have studied MOS devices in which they intentionally introduced alkali ions into the oxides. On this basis they have constructed a very useful model for the instability due to such ions. Similar work by Logan and Kerr<sup>7</sup> substantiated and extended the theory that alkali ions are a principal cause of the gross MOS device instability problem.

More recently, Yon, Kuper and Ko<sup>17,18</sup> have used the techniques of radiochemical analysis to carefully study the behavior of sodium in oxide layers. They used neutrons to activate the sodium and then measured the activity as successive etches removed thin layers of the oxide. They were able to find good correlation between the sodium content in the first 1000 Å of oxide adjacent to the silicon and the position of the inflection voltage of the C-V characteristic curve. They correlated the drift in sodium atom distribution with the observed change in this inflection voltage. They detected small differences between the cases in which sodium was introduced as NaOH, NaCl and NaBr. In one case, with NaBr, they found that the sodium concentration increased near the silicon interface while the



C-V curve shift indicated a decrease in ion concentration.

This they attributed to a compensating effect due to the bromine ion. This is not understood, since one does not expect bromine to be more mobile than chlorine or the hydroxyl.

They studied how the impurities were redistributed by different conditions of bias voltage and temperature. They find, in support of earlier work by Snow et al.<sup>13</sup>, that the sodium segregates toward the oxide interfaces with the metal and the silicon. They show that when sodium is deliberately introduced into the oxide by diffusion, not all of the sodium is ionized. They further show that a phosphosilicate layer on the oxide getters the sodium; i.e., sodium segregates to it and is held in it.

Similar work involving radiochemical techniques done by Carlson et al.<sup>1</sup> and by T. M. Buck\* substantiates these findings.

On the basis of the evidence summarized above as well as observations on purposely contaminated wafers in our laboratory, we believe it to be well established that alkali ions are responsible for high temperature gross instabilities found in

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\* T.M. Buck, oral report at the Silicon Interface Specialists Conference, Las Vegas, Nevada, November 15-16, 1965.

MOS devices. The best solution to this problem is to prevent such ions from getting into the oxide. This is accomplished with a good degree of success by careful processing to prevent sodium contamination.

### 2.1.2 Effect of Phosphosilicate Glass

An alternate technique which has been used to immobilize such ions in oxides involves the deposition of a phosphosilicate layer on the oxide. As described above, radiochemical techniques show that phosphorus does getter and immobilize sodium atoms. However, this technique has various disadvantages. It has been reported<sup>5,16</sup> by various investigators that a high density of surface states is introduced into the energy gap of the silicon near both the conduction and the valence bands when such a phosphorus deposition is made.

Other explanations have been proposed for the effectiveness of phosphosilicate glass. Pliskin<sup>10</sup> has studied the effect of phosphorus on SiO<sub>2</sub> by infrared spectroscopy and suggests that the phosphosilicate establishes a higher degree of polymerization of the SiO<sub>2</sub> tetrahedra to form a tighter or more dense structure which impedes the diffusion of impurity ions through the film.

Another possibility is that due to the higher conductivity of the phosphosilicate layer, the electric fields are reduced in this region, and this region of lower field reduces the drift rate of impurity ions.

Having developed empirical techniques for fabricating oxides free of alkali ions, the important remaining problems insofar as instability is concerned are related to the presence of hydrogen and water.

### 2.1.3 Effectsof Hydrogen and Water

The effects of hydrogen and water on oxide properties are apparently more subtle and complex. Many investigators have shown that hydrogen and water diffuse through fused silica. Many papers report on the observed severe alterations of device characteristics during heat treatments in hydrogen- or water-containing ambients. Hydrogen ion diffusion is also suspected as the cause of bias-induced instability which occurs in some samples at room temperature.

A recent paper by Hetherington et al.<sup>4</sup> on the high temperature electrolysis of vitreous silica gives a number of examples of the subtleties involved with hydrogen and water in  $\text{SiO}_2$ . When hydrogen is introduced into glass by electrolysis,

it exists as hydroxyls which are not replaceable by sodium in subsequent hydrolysis. Optical density measurements show that sodium can be replaced by hydrogen present as Si-OH groups. Efforts to electrolyze hydroxyl-containing vitreous silica have shown that "water" diffused from the anode to the cathode when the silica contained aluminum, but not when aluminum was absent. Hetherington et al. state that in a reaction of water vapor with silica, the diffusing species are believed to be either water molecules or hydroxyl pairs and that in a reaction with hydrogen they are believed to be hydrogen molecules. Hetherington et al. suggest that protons are involved in electrolysis. Further, they found that the hydroxyl produced by reaction of vitreous silica with either water vapor or hydrogen can be removed by treatment in vacuum at high temperatures. They find that this cannot be done for hydroxyl introduced by electrolysis. Their work further suggests that each unusually stable hydroxyl is associated with an aluminum atom replacing silicon in the vitreous network. Another finding is that electrolytically introduced hydroxyl blocks the migration of lithium, sodium, and potassium atoms when attempts are made to introduce these by a subsequent electrolysis from an anode source.

On the basis of the many references in the literature to the effects of water and hydrogen on the properties of silicon,

The silicon used for experimental purposes had about 5 ohm-cm resistivity, was oriented on the  $\langle 111 \rangle$  planes, and, with one exception, was phosphorus-doped n-type. The following types of oxide were tested:

1. These oxides were thermally oxidized in dry oxygen at  $1200^{\circ}\text{C}$ . The processes are those designed to yield good oxides free of alkali ions. The thickness was  $2950 \text{ \AA}$ .
2. This oxide was prepared in the same way as No. 1, above, but was subsequently given a  $200 \text{ \AA}$  deposition of phosphosilicate glass using a  $\text{POCl}_3$  source. The thickness was  $2700 \text{ \AA}$ .
3. This oxide was also prepared in the same way as No. 1, above. It was subsequently baked in dry nitrogen at  $1200^{\circ}\text{C}$  for 15 hours. The thickness was  $3000 \text{ \AA}$ .
4. Two oxides were formed by vapor plating at  $1200^{\circ}\text{C}$ . One was on p-type silicon and the other on n-type silicon. The respective oxide thicknesses were 2600 and  $2850 \text{ \AA}$ .
5. A vapor plated oxide was formed at  $380^{\circ}\text{C}$ . Its thickness was  $3700 \text{ \AA}$ .

6. This oxide was thermally grown in wet oxygen. Its thickness was 3000 Å.
7. This oxide was anodically formed. Its thickness was 900 Å.
8. This was a vapor plated mixed oxide ( $\text{Al}_2\text{O}_3\text{-SiO}_2$ ). Its thickness was 3600 Å.

Each of these oxides was subjected to a standardized testing procedure. The capacitance-voltage curve was measured after each of the following processing or treatment steps:

1. Initial
2. 300°C, dry  $\text{N}_2$ , 1 hour
3. 400°C, -20 volts, 10 minutes
4. 400°C, +20 volts, 10 minutes
5. Metalize and etch back
6. 300°C, dry  $\text{N}_2$ , 1 hour
7. 400°C, -20 volts, 10 minutes
8. 400°C, +20 volts, 10 minutes
9. Alloy and mount
10. 300°C, 1/2 hour
11. 200°C, -20 volts, 1 hour
12. 200°C, +20 volts, 1 hour
13. Irradiate in  $\text{Co}^{60}$  source

14. 300°C, 1 hour
15. 200°C, -20 volts, 1 hour
16. 200°C, +20 volts, 1 hour.

This testing sequence was designed to show the extent to which each oxide changed its fixed charge density during a simple one hour bake and the mobile charge density following each of the main steps in the fabrication process. The 400°C temperature was chosen for the drifting steps to be certain that the gold ball probe would detect mobile ions in unmetallized oxides. It now appears that this step, carried out in room air, may have added significantly to the water content of the oxide. After the devices were mounted, the baking temperature was reduced somewhat to minimize the chemical reaction at the gold-to-aluminum bond. It may be that this problem is merely one of long-term reliability of the bond and that future tests of the stability of packaged MOS devices can be conducted at 300°C. The alloying was done at 550°C for 5 minutes in dry nitrogen.

Table 1 is a tabulation of the charge densities, as calculated from the inflection points in the C-V curves, for the fixed and mobile charge densities after each step in the fabrication process for each of these oxides.

Table 1

Charge Densities (Charges/cm<sup>2</sup>)

Oxide Type	Oxidation			Metalization		Alloy and Mounting	
	Fixed Initial	Fixed After Bake	Mobile	Fixed	Mobile	Fixed	Mobile
1. Ion free thermal	5-6 x 10 <sup>11</sup>	3-4 x 10 <sup>11</sup>	None	1-3 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	7 x 10 <sup>11</sup>
2. Phospho-silicate	1 x 10 <sup>12</sup>	9 x 10 <sup>11</sup>	None	8 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	7 x 10 <sup>11</sup>	3.5 x 10 <sup>11</sup>
3. 1200°C N <sub>2</sub> bake	2.3 x 10 <sup>12</sup>	1.7 x 10 <sup>12</sup>	None	2.3 x 10 <sup>12</sup>	1 x 10 <sup>11</sup>	1.7 x 10 <sup>12</sup>	4 x 10 <sup>11</sup>
4. Vapor plated 1200°C							
p-type Si	4 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	None	4 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	1.5 x 10 <sup>11</sup>
n-type Si	4 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	None	4 x 10 <sup>11</sup>	2 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	10 <sup>12</sup>
5. Vapor plated 380°C	3.2 x 10 <sup>12</sup>	7 x 10 <sup>11</sup>	None	7 x 10 <sup>11</sup>	7 x 10 <sup>11</sup>	4.5 x 10 <sup>11</sup>	2 x 10 <sup>12</sup>
6. Wet thermal	6 x 10 <sup>11</sup>	4 x 10 <sup>11</sup>	None	6 x 10 <sup>11</sup>	1.5 x 10 <sup>11</sup>	4.5 x 10 <sup>11</sup>	3-4 x 10 <sup>11</sup>
7. Anodic	(Note 1)	2 x 10 <sup>11</sup>	None	(Note 2)	(Note 2)	3 x 10 <sup>11</sup>	2.8 x 10 <sup>12</sup>
8. Mixed Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> (Note 3)	2 x 10 <sup>11</sup>	2 x 10 <sup>11</sup>	None	(Note 2)	(Note 2)	Cannot be measured	5 x 10 <sup>12</sup>

## Notes:

1. The inflection region of the C-V curve was too broad to make a reasonable measurement. Such a curve is interpreted as resulting from a high trap density.
2. Oxides 7 and 8 were not tested after metalization. After alloying and mounting they were tested at 300°C, ±20 V for 2 minutes.
3. As described in the text, these data are not of high accuracy because the C-V curves are poorly shaped. However, the qualitative results are believed to be valuable.



On the basis of the information given in Table 1, there seems to be no clearcut advantage involved with choosing any one of the oxidation processes or post-oxidation techniques thus far evaluated other than thermal oxidation.

In view of this information and the often-reported effects of water, we now believe that the effects of water may have had a major influence on the results shown in Table 1.

#### 2.1.5 Mixed Oxides

In addition to the work summarized in Table 1, several other significant empirical observations have been made. A silicon wafer was given a vapor plated deposition of  $\text{Al}_2\text{O}_3$  at  $380^\circ\text{C}$ . The C-V curve on this oxide indicated that the oxide contains a relatively large density of negative charge. This is important because of the fact that the charge in all of the other oxides tested was positive. This charge appears to be immobile at  $400^\circ\text{C}$ ,  $\pm 30$  volts for one hour. Unfortunately, it is difficult to make measurements on this oxide because it has a high density of leakage current paths.

The observation that  $\text{Al}_2\text{O}_3$  contained negative charge led us to make a mixed oxide of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in the hope that the process could be developed to the point where the positive and

negative charges are in equal concentration, and therefore there is no net charge. Such mixed oxides ( $\text{Al}_2\text{O}_3\text{-SiO}_2$ ) were vapor plated at  $380^\circ\text{C}$ . As formed, these oxides have about  $4 \times 10^{12}$  charges/ $\text{cm}^2$  that are very mobile at room temperature. These charges drift to cause shifts in the C-V curve between +30 volts and -30 volts in several seconds at room temperature. Such an oxide was then subjected to  $1200^\circ\text{C}$  in dry nitrogen for 15 minutes, and the result is that described as Oxide No. 8 in Table 1. In the case of the mixed oxide, it was also noted that the inflection region in the C-V curves was gradual. This is interpreted to be due to a high trapping state density. During this bake, some of the aluminum diffused into the silicon, making a fairly high density p-type surface (as determined by comparative sheet resistivity and thermal probe tests on both sides of the wafer after the oxide was etched away).

## 2.2 Model

The oxide is assumed to contain sodium and hydrogen ions. The hydrogen ions are probably introduced as water, which reacts with the aluminum to form hydrogen. Depending on the temperature, these ions drift under the force of applied electric fields to change the distributions of charge in the oxide. Such drifting takes place at room temperature for hydrogen, and at temperatures above about  $100^\circ\text{C}$  for sodium.

According to Gauss' law, any charge in the oxide must induce layers of charge in the metal and in the silicon at the oxide interfaces, so that the sum of the induced area charge densities is equal in magnitude and opposite in polarity to that in the oxide.

The amount of charge that appears in the silicon depends on the voltage applied between the metal and the silicon. This is because these charge layers establish the field distribution in the oxide, and the integration of the field over the distance across the oxide must be equal to the voltage across the oxide.

For silicon with a given dopant density (and a given distribution of traps), there is a unique relationship among the area density of charge in the silicon, the depletion layer thickness, and the density of charge in the inversion layer.

### 2.2.1 Effects of Ion Drift

When the sodium or hydrogen ions drift to rearrange their distribution under the influence of an applied field, they thereby induce a change in the area density of charge in the silicon. This change in total area charge density in the silicon in turn causes a change in the depletion layer thickness

and in the charge density of the inversion layer for a given applied voltage (assuming the voltage is such that the depletion layer and inversion layer exist).

The effect of a movement of charge in the oxide to change the depletion layer thickness or the inversion layer charge density is the cause of instability in the characteristics of MOS devices.

Stability can be achieved in either of two ways. One way is to form MOS devices which are free of mobile ions in the oxide, and the other is to immobilize such ions if they are present.

The absence of such impurities requires no further explanation in a discussion of the model.

### 2.2.2 Immobilizing Impurity Ions

There are several possible ways of immobilizing impurity ions or atoms. The presence of phosphorus in the oxide may establish a higher degree of polymerization of the  $\text{SiO}_2$  tetrahedron to form a more dense structure which will impede the drift of impurity ions through the oxide film. Alternatively, the presence of a substance such as phosphorus may provide sites to which sodium ions can be attracted and held.

It may be possible to introduce levels in the energy gap of the oxide by adding some other material, possibly phosphorus, so that the position of the Fermi level is raised to the point where sodium atoms are neutral rather than ionized. In this case, the sodium would not be ionized in the phosphorus layer and therefore would not drift through it under the influence of a field. The added phosphorus levels would be expected to be ionized, but if they are not mobile and are near the metal rather than the silicon, such added impurities could improve the stability of the device characteristics without adding to the immobile charge density near the silicon.

### 2.2.3 Chemical and Electrochemical Conditions

It is possible that some substances may have a catalytic effect that influences a chemical reaction, and therefore affects the bonding structure in the oxide. This might change the distribution of allowed states in the energy gap and thereby alter the number of ions in the oxide. Similar effects may be involved with hydrogen and aluminum, except that the aluminum seems to increase the number and/or mobility of the hydrogen ions.

The MOS structure is an electrolytic cell in which the aluminum is the anode and the silicon is the cathode. The electrochemical potential developed by this cell is capable of creating mobile charge, drifting it, and establishing the potential distribution that can affect the state of ionization of individual impurity or defect sites.

### 2.3 Possibilities for Improvement

The empirical techniques that have been developed to form MOS structures with a minimum of alkali ion contamination produce MOS devices that are quite stable. There are possibilities for improving these techniques by more precisely determining where the small percentage of MOS devices are contaminated when these empirical techniques yield unstable devices.

Occasionally, MOS devices are found to have an instability at room temperature. This is believed to be related to the water content of oxides. This is not well understood because most oxides do not show this instability even when they have been exposed to water during the fabrication processes.

The effort yet to be made on this part of the program will be directed at determining the causes of these occasional contaminations which cause some batches of devices to be unstable.

### 3. RADIATION INDUCED DEGRADATION

#### 3.1 Background Information

We have exposed both capacitors and transistors formed of most of the oxides described in the previous section to radiation from a cobalt<sup>60</sup> source and to a low-energy X-ray machine.

The X radiation was 45 keV in energy and of uncalibrated intensity. This radiation produced significant changes within 15 minutes. One of the chief values of working with X-rays is that the X-ray machine is conveniently located near the laboratory and thus can be used to make quick rough checks on the effect of ionizing radiation on devices. The degradation from X-rays is similar to that produced by gamma radiation except for differences in the amount of absorption in the packaging ambient material. Our experiments indicate that the effect of packaging ambient materials is greater in the case of X-rays than in the case of gamma radiation.

The data presented here is limited to those for gamma radiation. The dose rate was  $8 \times 10^4$  rads/hour.

##### 3.1.1 Effects of Gamma Radiation on Transistors

A group of p-channel MOS transistors was fabricated with the regular thermal oxides. The effects of both bias polarity

and temperature on the rate of degradation under gamma radiation were sought. The data were collected in the form of photographs of the transfer characteristics taken from a curve tracer. A photograph of the equipment used is shown in Figure 2. These transistors were formed as part of a microcircuit configuration. There was a diode in parallel with the gate and source connection which prevented application of positive voltage to the gate. The test was then conducted at two temperatures,  $-78^{\circ}\text{C}$  and  $+95^{\circ}\text{C}$ , and at 0 and -20 volts bias. These voltages represent reasonable limits on the normal operating voltage range for such devices. The results are shown in Figures 3 through 6. The same devices were tested first at the higher temperature and then at the lower temperature. Very simply, the data show that in this range of temperature and voltage, the rate of degradation is much the same for any of the indicated conditions.

### 3.1.2 Effects of Gamma Radiation on Capacitors

The measurements with capacitors yielded more useful information. Figures 7a and 7b show the results for two typical capacitors which display the important qualitative observations. (The number associated with each curve shows the testing sequence.) These figures show that, as with the transistors, there is no significant difference between the degradation with a negative gate voltage and with a zero gate voltage. There is a very pronounced difference between the degradation with negative



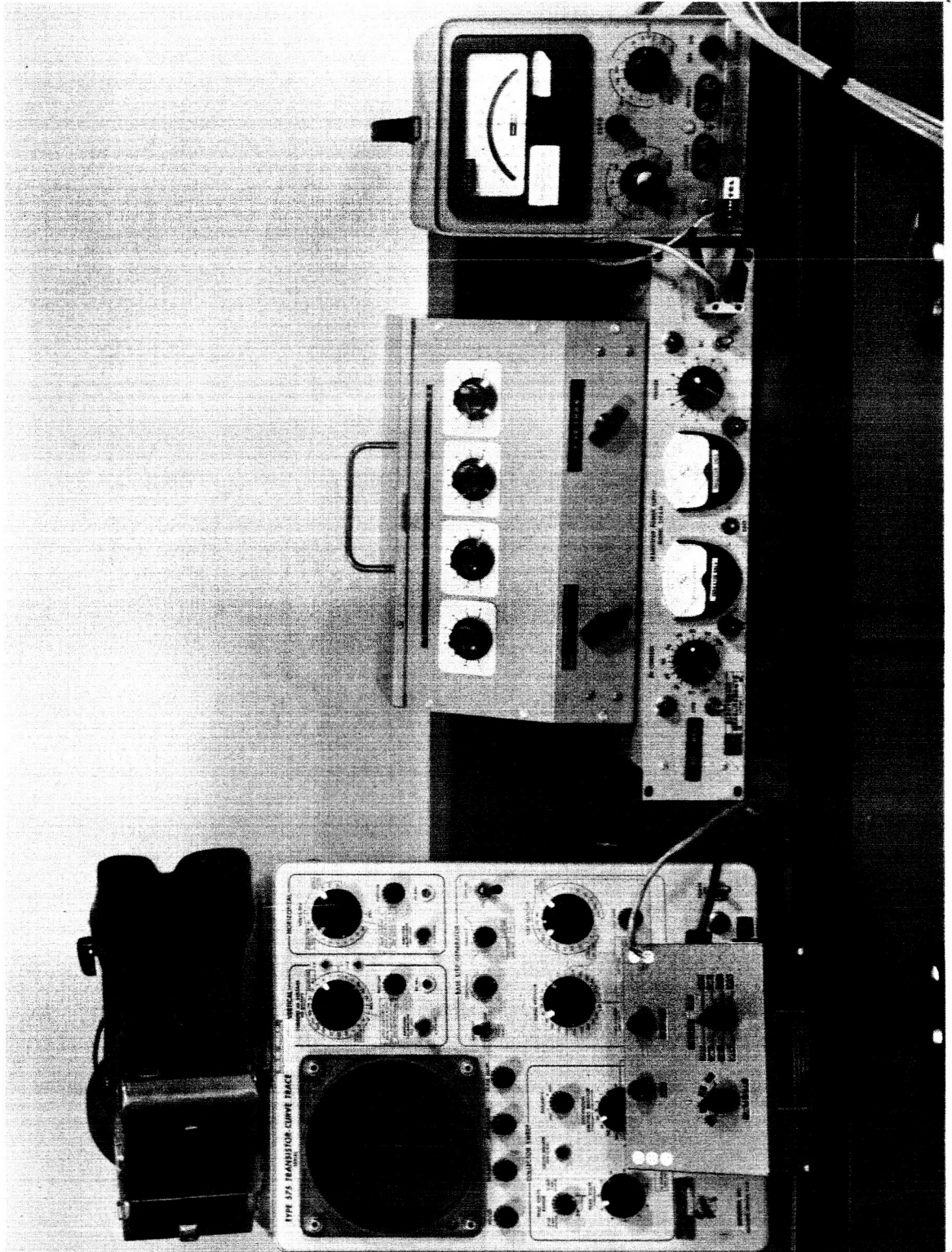


Figure 2. Equipment for testing MOS transistors during irradiation.

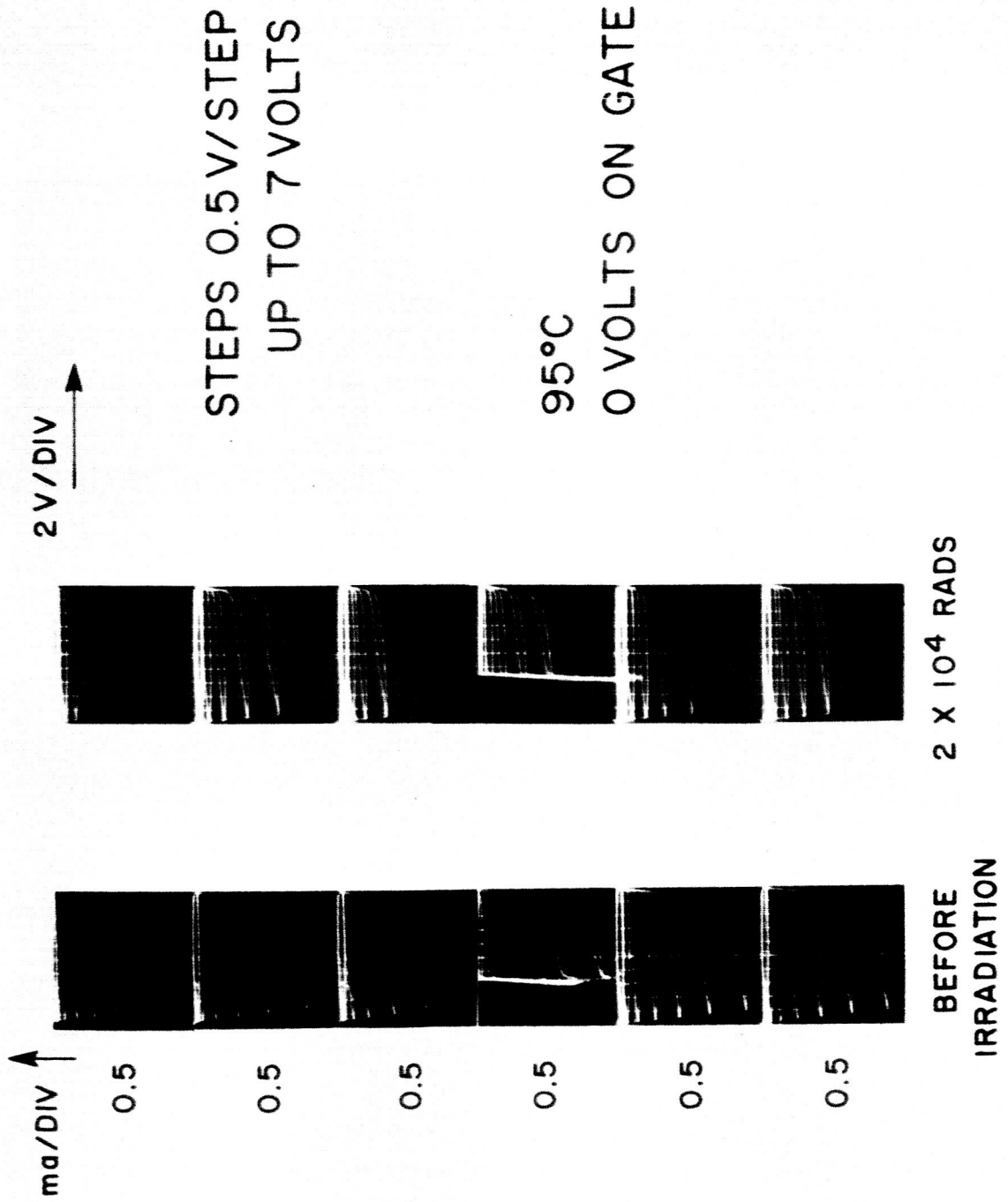


Figure 3. Effects of radiation on transistors, 95°C, 0 volts.

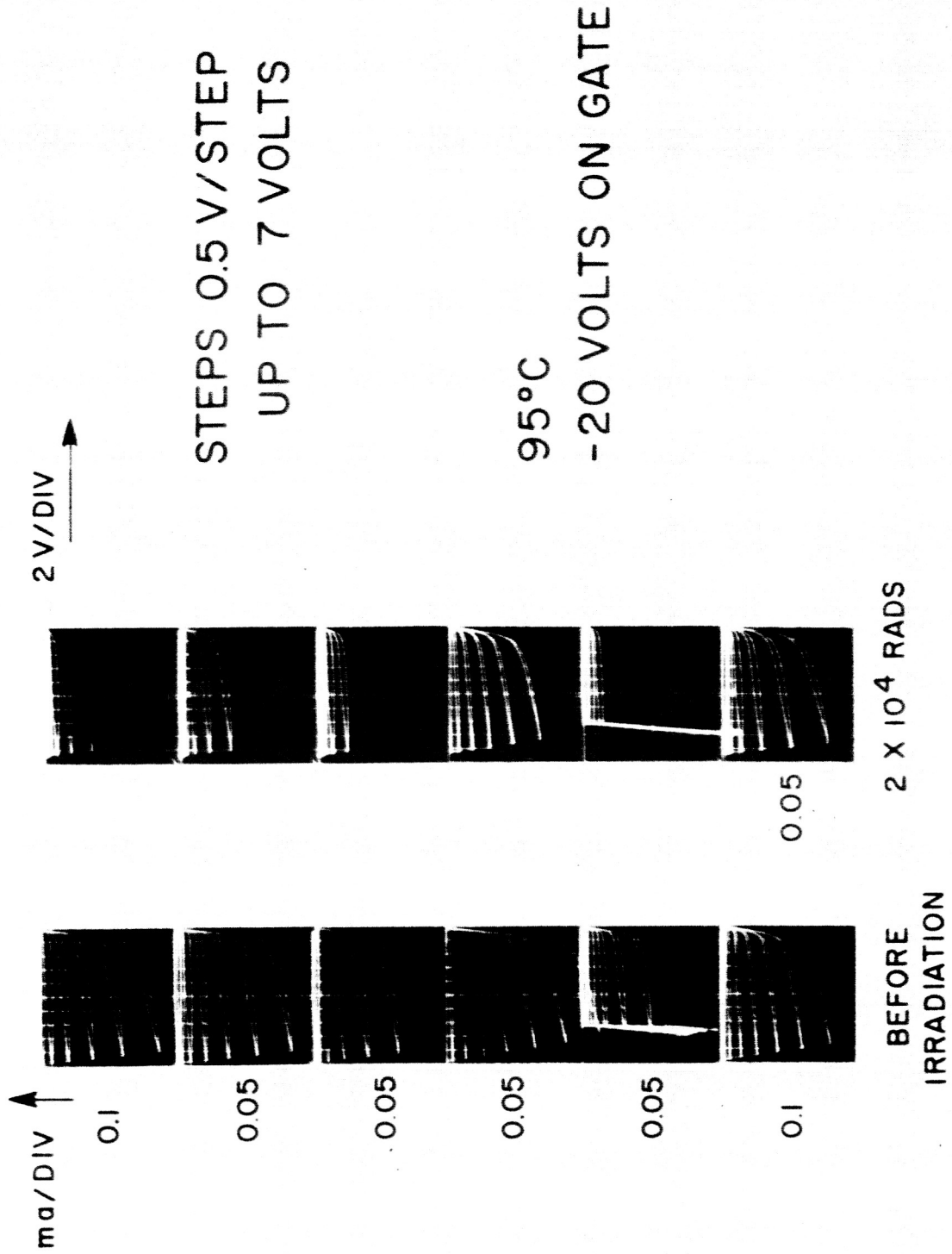


Figure 4. Effects of radiation on transistors, 95°C, -20 volts.

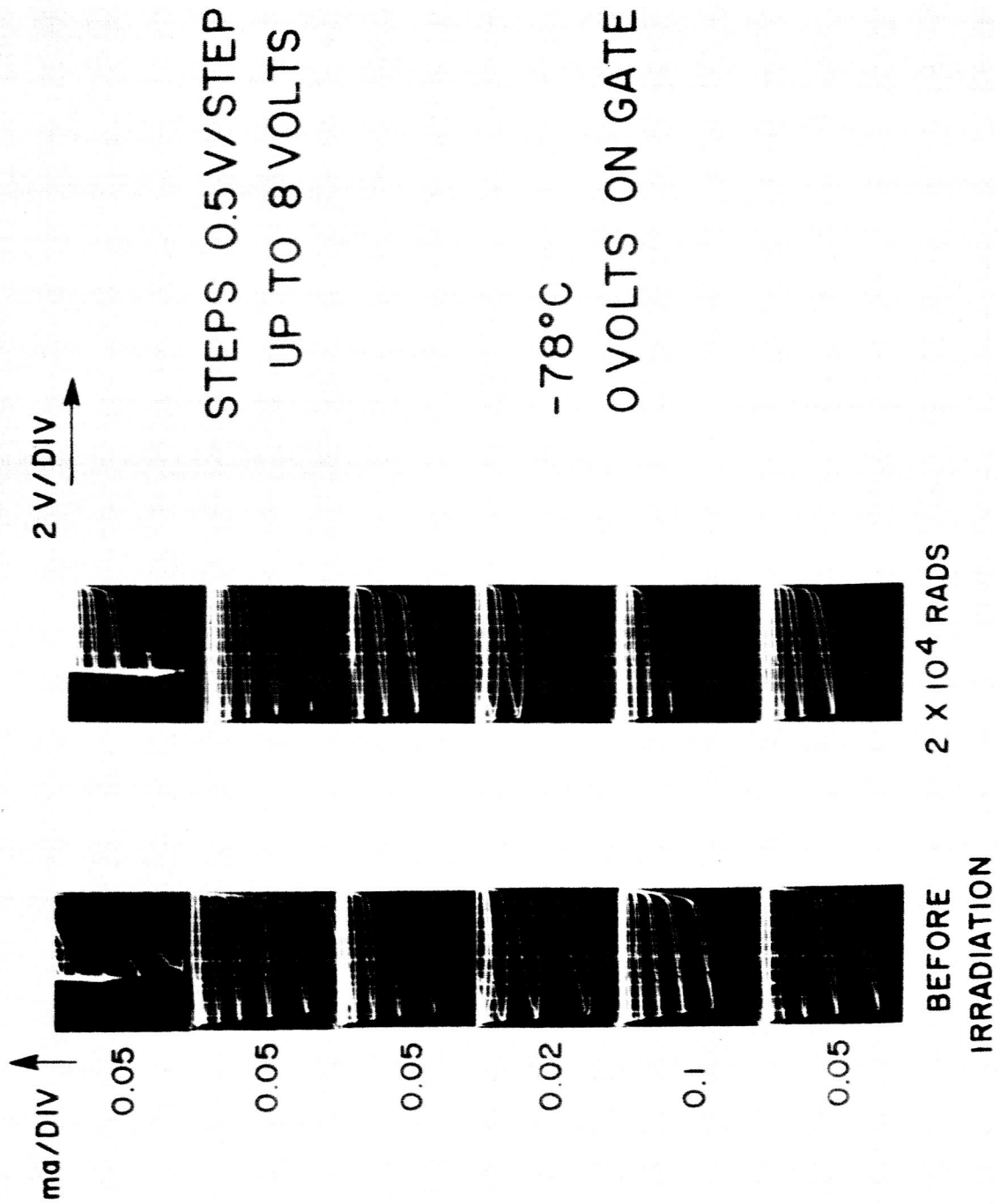


Figure 5. Effects of radiation on transistors, -78°C, 0 volts.

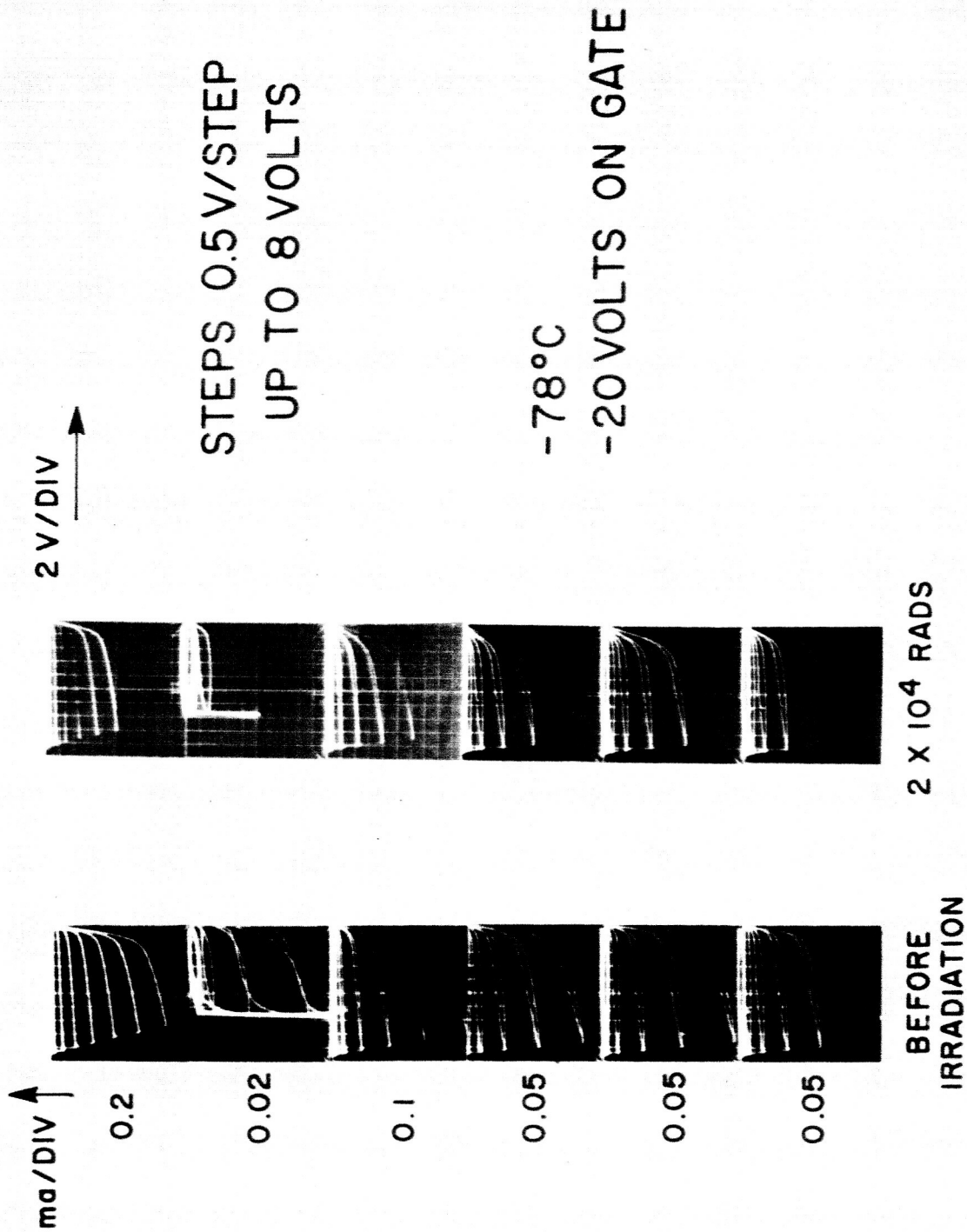
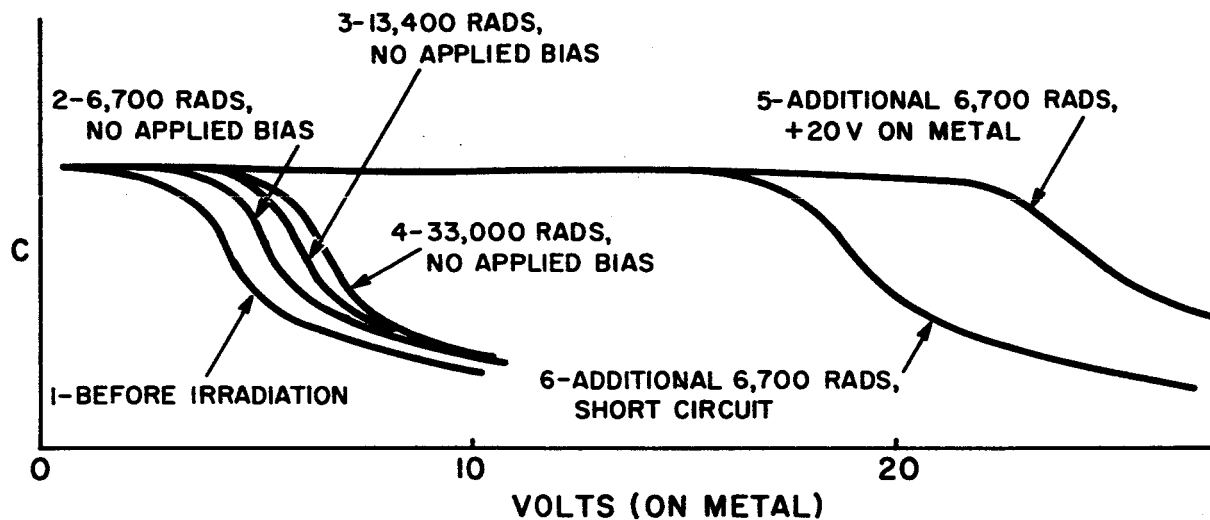
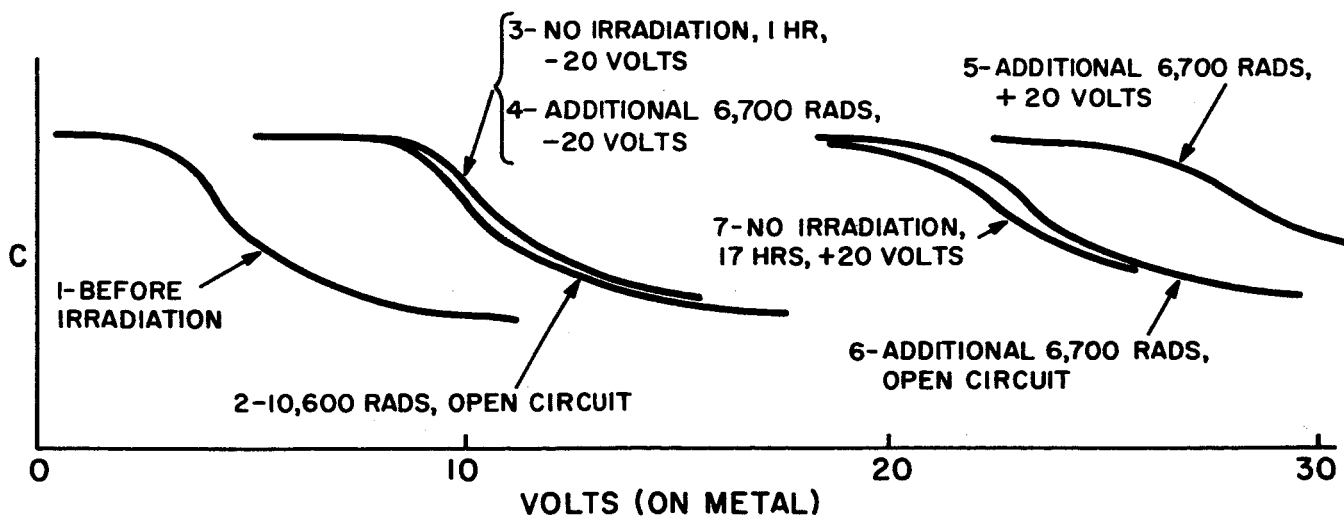


Figure 6. Effects of radiation on transistors, -78°C, -20 volts.



A.



B.

Figure 7. Typical effects of radiation on MOS capacitors.

bias voltage and that with positive. Following irradiation under positive bias, which introduces positive charge into the oxide, further irradiation with either a short or open circuit reduces the positive charge in the oxide. There is very little difference observed between tests with the capacitor terminals short circuited or open circuited at any stage of this testing. Recovery of the device characteristics following the irradiation does not occur at room temperature. Figure 8 shows a measure of the rate at which transistors do anneal after the irradiation. Good annealing in reasonable time periods are observed at temperatures above 200°C.

Tables 2a through 2g are a tabulation of the results of the testing of capacitors made of the various kinds of oxides. The test temperatures were -78°C, +20°C, and +108°C. The sequence of presentation is that in which the test was run. The dose in each case is the additional dose given at that step in the testing sequence. The inflection voltage is taken from the C-V curve. The thicknesses of these oxides are given in paragraph 2.1.4 of this report. Since the thicknesses of these oxides are all fairly close to 3000 Å, the voltages can be compared directly. The  $\Delta V$  column is included to make it easier to compare the effects of various doses and circuit conditions.

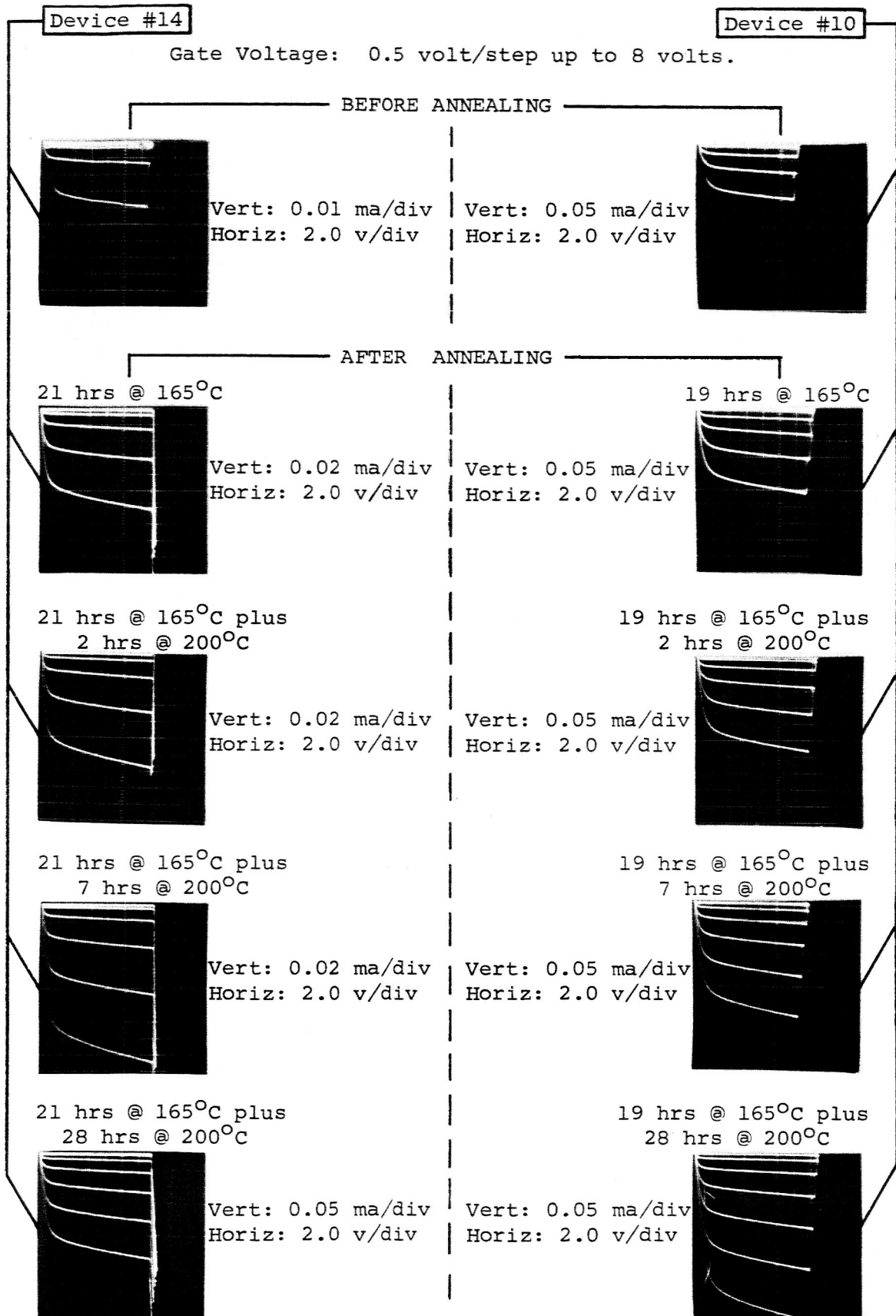


Figure 8. Annealing of MOS transistors after gamma irradiation.



Table 2a

## Results of Irradiation on Thermal Oxide

SAMPLE NO. and TEMP.	TEST CONDITIONS	CKT	INFLECTION VOLTAGE (Volts)	$\Delta V$	SAMPLE NO. and TEMP.	TEST CONDITIONS	CKT	INFLECTION VOLTAGE (Volts)	$\Delta V$
#1 +20°C	Initial		- 4.0	---	#6 +20°C	Initial		- 4.5	---
	1.2 x 10 <sup>4</sup> rads	open	-10.0	- 6.0		1.2 x 10 <sup>4</sup> rads	open	-10.0	- 5.5
	6.7 x 10 <sup>3</sup> rads	-20V	-10.5	- 0.5		6.7 x 10 <sup>3</sup> rads	-20V	-11.0	- 1.0
	6.7 x 10 <sup>3</sup> rads	open	- 8.5	+ 2.0		6.7 x 10 <sup>3</sup> rads	+20V	-30.0	-19.0
	6.7 x 10 <sup>3</sup> rads	open	- 8.5	0		6.7 x 10 <sup>3</sup> rads	open	-24.0	+ 6.0
#2 +20°C	Initial		- 4.5	---	#7 +20°C	Initial		- 5.0	---
	6.7 x 10 <sup>3</sup> rads	open	- 5.0	- 0.5		6.7 x 10 <sup>3</sup> rads	open	- 6.0	- 1.0
	6.7 x 10 <sup>3</sup> rads	open	- 6.0	- 1.0		6.7 x 10 <sup>3</sup> rads	open	- 6.5	- 0.5
	2 x 10 <sup>4</sup> rads	open	- 6.5	- 0.5		2 x 10 <sup>4</sup> rads	open	- 7.0	- 0.5
	6.7 x 10 <sup>3</sup> rads	+20V	-25.0	-18.5		6.7 x 10 <sup>3</sup> rads	+20V	-28.0	-21.0
6.7 x 10 <sup>3</sup> rads	open	-19.0	+ 6.0	6.7 x 10 <sup>3</sup> rads	open	-21.0	+ 7.0		
#3 +20°C	Initial		- 4.5	---	#8 +105°C	Initial		- 5.0	---
	1.2 x 10 <sup>4</sup> rads	open	- 9.0	- 4.5		5.4 x 10 <sup>3</sup> rads	-20V	- 6.5	- 1.5
	6.7 x 10 <sup>3</sup> rads	-20V	-10.0	- 1.0		1.5 x 10 <sup>4</sup> rads	-20V	-13.0	- 6.5
	6.7 x 10 <sup>3</sup> rads	+20V	-33.0	-23.0		-----	-----	---	-----
	6.7 x 10 <sup>3</sup> rads	open	-25.0	+ 8.0		-----	-----	---	-----
#4 +20°C	Initial		- 4.5	---	#9 -78°C	Initial		- 5.0	---
	1.2 x 10 <sup>4</sup> rads	open	-11.0	- 7.5		4 x 10 <sup>3</sup> rads	-20V	- 8.0	- 3.0
	6.7 x 10 <sup>3</sup> rads	-20V	-11.0	0		2.5 x 10 <sup>4</sup> rads	-20V	-18.0	-10.0
	6.7 x 10 <sup>3</sup> rads	+20V	-28.0	-17.0		-----	-----	---	-----
	6.7 x 10 <sup>3</sup> rads	open	-22.5	+ 5.5		-----	-----	---	-----
#5 +20°C	Initial		- 4.5	---	#10 -78°C	Initial		- 6.0	---
	6.7 x 10 <sup>3</sup> rads	open	- 5.0	- 0.5		1.9 x 10 <sup>4</sup> rads	-20V	-15.0	- 9.0
	6.7 x 10 <sup>3</sup> rads	open	- 5.5	+ 0.5		2.3 x 10 <sup>4</sup> rads	-20V	-22.0	- 7.0
	2 x 10 <sup>4</sup> rads	open	- 6.5	- 1.0		-----	-----	---	-----
	6.7 x 10 <sup>3</sup> rads	+20V	-25.5	-19.0		-----	-----	---	-----
6.7 x 10 <sup>3</sup> rads	short	-19.5	+ 6.0	-----	-----	---	-----		

Table 2b

## Results of Irradiation on Thermal Oxide with Phosphorus Deposition

SAMPLE NO. and TEMP.	TEST CONDITIONS	CKT	INFLECTION VOLTAGE (Volts)	$\Delta V$
#1 +20°C	Initial		-11.0	
	1.2 x 10 <sup>4</sup> rads	open	-15.0	+ 4.0
	6.7 x 10 <sup>3</sup> rads	-20V	-20.5	- 5.5
	6.7 x 10 <sup>3</sup> rads	+20V	-28.5	- 8.5
	6.7 x 10 <sup>3</sup> rads	open	-27.5	+ 1.0
#2 +20°C	Initial		-10.5	
	1.2 x 10 <sup>4</sup> rads	open	-15.0	- 4.5
	6.7 x 10 <sup>3</sup> rads	-20V	-20.5	- 5.5
	6.7 x 10 <sup>3</sup> rads	+20V	-28.5	- 8.0
	6.7 x 10 <sup>3</sup> rads	open	-28.0	+ 0.5
#3 -78°C	Initial		- 5.5	
	7 x 10 <sup>3</sup> rads	-20V	-15.5	-10.0
	2.4 x 10 <sup>4</sup> rads	-20V	-18.0	- 2.5
#4 -78°C	Initial		- 7.0	
	2.0 x 10 <sup>4</sup> rads	-20V	-27.0	-20.0
	2.1 x 10 <sup>4</sup> rads	-20V	-37.0	-10.0

Table 2c

Results of Irradiation on Thermal  
Oxide with 15 Hours, N<sub>2</sub> at 1200°C

SAMPLE NO. and TEMP.	TEST CONDITIONS	CTK	INFLECTION VOLTAGE (Volts)	ΔV
#1 +20°C	Initial		-20.0	
	1.2 x 10 <sup>4</sup> rads	open	-26.0	- 6.0
	6.7 x 10 <sup>3</sup> rads	-20V	-30.0	- 4.0
	6.7 x 10 <sup>3</sup> rads	-20V	-44.0	-14.0
	6.7 x 10 <sup>3</sup> rads	open	-39.0	+ 5.0
#2 +20°C	Initial		- 4.0	
	1.2 x 10 <sup>4</sup> rads	short	-10.0	- 6.0
	6.7 x 10 <sup>3</sup> rads	-20V	-10.0	0
	6.7 x 10 <sup>3</sup> rads	+20V	-28.5	-18.5
	6.7 x 10 <sup>3</sup> rads	open	-23.5	+ 5.0
#3 +105°C	Initial		-23.0	
	6.7 x 10 <sup>3</sup> rads	-20V	-28.0	- 5.0
	1.3 x 10 <sup>4</sup> rads	-20V	-36.0	- 8.0
#4 -78°C	Initial		-22.0	
	9 x 10 <sup>3</sup> rads	-20V	-33.0	-11.0
	2.4 x 10 <sup>4</sup> rads	-20V	-42.0	- 9.0
#5 -78°C	Initial		-24.0	
	2.1 x 10 <sup>4</sup> rads	-20V	-36.0	-12.0
	2.1 x 10 <sup>4</sup> rads	-20V	-43.0	- 7.0

Table 2d

## Results of Irradiation on Vapor Plated

Oxide, 1200°C, p-type Si

SAMPLES NO. and TEMP.	TEST CONDITIONS	CKT	INFLECTION VOLTAGE (Volts)	$\Delta V$
#1  +20°C	Initial		- 4.5	
	1.2 x 10 <sup>4</sup> rads	open	- 8.5	- 4.0
	6.7 x 10 <sup>3</sup> rads	-20V	-13.0	- 4.5
	6.7 x 10 <sup>3</sup> rads	+20V	-19.5	- 6.5
	6.7 x 10 <sup>3</sup> rads	open	-19.5	0
#2  +20°C	Initial		- 4.5	
	6.7 x 10 <sup>3</sup> rads	open	- 5.5	- 1.0
	6.7 x 10 <sup>3</sup> rads	open	- 6.0	- 0.5
	2 x 10 <sup>4</sup> rads	open	- 7.0	- 1.0
	6.7 x 10 <sup>3</sup> rads	+20V	-16.5	- 9.5
6.7 x 10 <sup>3</sup> rads	open	-16.5	0	
#3  +105°C	Initial		- 4.5	
	1.5 x 10 <sup>4</sup> rads	-20V	-16.0	-11.5
	4.5 x 10 <sup>3</sup> rads	-20V	-17.0	- 1.0

Table 2e

## Results of Irradiation on Vapor Plated

Oxide, 1200°C, n-type Si

SAMPLE NO. and TEMP.	TEST CONDITIONS	CKT	INFLECTION VOLTAGE (Volts)	$\Delta V$
#1 +20°C	Initial		- 5.0	
	$6.7 \times 10^3$ rads	open	- 5.5	- 0.5
	$6.7 \times 10^3$ rads	open	- 6.2	- 0.7
	$2 \times 10^4$ rads	open	- 7.5	- 0.7
	$6.7 \times 10^3$ rads	+20V	-21.0	-13.5
	$6.7 \times 10^3$ rads	short	-20.5	+ 0.5
#2 +20°C	Initial		- 4.5	
	$1.2 \times 10^4$ rads	open	-10.5	- 6.0
	$6.7 \times 10^3$ rads	-20V	-17.0	- 6.5
	$6.7 \times 10^3$ rads	+20V	-29.0	-12.0
	$6.7 \times 10^3$ rads	open	-29.0	0
#3 +105°C	Initial		- 5.0	
	$1.6 \times 10^4$ rads	-20V	-24.0	-19.0
	$3.4 \times 10^3$ rads	-20V	-24.0	0
#4 +105°C	Initial		- 6.0	
	$3.4 \times 10^3$ rads	-20V	-10.5	- 4.5
	$1.6 \times 10^4$ rads	-20V	-24.0	-13.5
#5 -78°C	Initial		- 7.5	
	$1.7 \times 10^4$ rads	-20V	-25.5	-18.0
	$2.2 \times 10^4$ rads	-20V	-37.0	-11.5

Table 2f

## Results of Irradiation on Oxide

Vapor Plated at 380°C

SAMPLE NO. and TEMP.	TEST CONDITIONS	CKT	INFLECTION VOLTAGE (Volts)	$\Delta V$
#1 +20°C	Initial		- 5.0	
	6.7 x 10 <sup>3</sup> rads	open	- 5.2	- 0.2
	6.7 x 10 <sup>3</sup> rads	open	- 5.2	0
	2 x 10 <sup>4</sup> rads	open	- 6.0	- 0.8
	2 x 10 <sup>4</sup> rads	+20V	-11.0	- 5.0
	6.7 x 10 <sup>3</sup> rads	open	-21.0	-10.0
#2 +20°C	Initial		- 7.2	
	6.7 x 10 <sup>3</sup> rads	open	- 7.5	- 0.3
	6.7 x 10 <sup>3</sup> rads	open	- 7.5	0
	2 x 10 <sup>4</sup> rads	open	- 8.0	- 0.5
	6.7 x 10 <sup>3</sup> rads	+20V	-13.5	- 5.5
	6.7 x 10 <sup>3</sup> rads	short	-13.5	0
#3 +105°C	Initial		- 7.3	
	8 x 10 <sup>3</sup> rads	-20V	-18.0	- 5.0
	1.2 x 10 <sup>3</sup> rads	-20V	-25.5	- 6.5
#4 -78°C	Initial		-13.0	
	1.6 x 10 <sup>4</sup> rads	-20V	-12.0	- 4.7
	2.2 x 10 <sup>4</sup> rads	-20V	-16.0	- 4.0

Table 2g

Results of Irradiation on  
Thermal Oxide, Wet Oxygen

SAMPLE NO. and TEMP.	TEST CONDITIONS	CKT	INFLECTION VOLTAGE (Volts)	$\Delta V$
#1 +20°C	Initial		- 4.3	
	6.7 x 10 <sup>3</sup> rads	open	- 5.3	- 1.0
	6.7 x 10 <sup>3</sup> rads	open	- 5.4	- 0.1
	2 x 10 <sup>4</sup> rads	open	- 6.4	- 1.0
	6.7 x 10 <sup>3</sup> rads	+20V	-28.0	-11.6
	6.7 x 10 <sup>3</sup> rads	short	-23.0	+ 5.0
#2 +20°C	Initial		- 4.0	
	6.7 x 10 <sup>3</sup> rads	open	- 5.3	- 1.3
	6.7 x 10 <sup>3</sup> rads	open	- 5.4	- 0.1
	2 x 10 <sup>4</sup> rads	open	- 5.4	0
	6.7 x 10 <sup>3</sup> rads	+20V	-28.5	-13.1
	6.7 x 10 <sup>3</sup> rads	open	-24.0	+ 4.5

The variability within each sample representing an oxide type is much the same as that among groups. There is little evidence that any of these oxide types offers a significant advantage over the others insofar as radiation resistance is concerned. There are several observations worth noting. The vapor plated (at 1200°C and at 380°C) oxides do not show an improvement when irradiation is continued without a positive bias after an irradiation with a positive bias.

The differences among the various oxides may be obscured by the effects of moisture and other possible contaminants.

### 3.1.3 Other Published Information

At the Silicon Interface Specialists Conference, A. S. Grove\* reported that when he irradiated devices with 35 keV X-rays at a dose rate of 5000 rads/sec, he found that the induced charge saturated with time at a level which depends on the voltage applied to the gate. He found that the induced charge is the same for zero voltage or any negative voltage. He found that the amount of induced charge is proportional to the square root of the positive applied voltage. He explained his data by assuming a uniform

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\* A.S. Grove, oral report at the Silicon Interface Specialists Conference, Las Vegas, Nevada, November 15-16, 1965.



distribution of electron traps in the oxide with a density of  $1.7 \times 10^{18} \text{ cm}^{-2}$ .

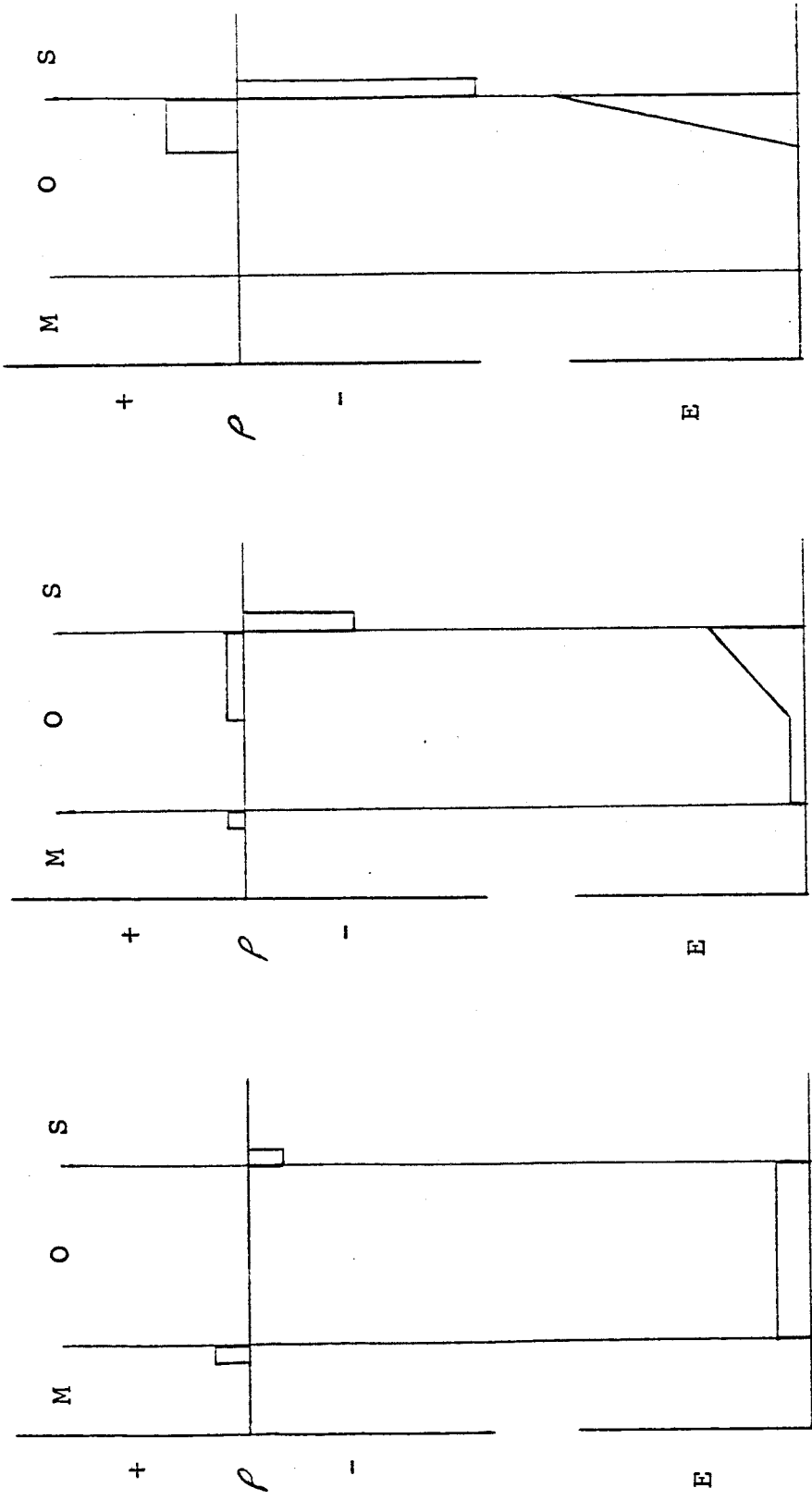
In a study of the effects of X-rays, gamma radiation, and ultraviolet light, Kooi<sup>17</sup> found that after X-ray or gamma radiation increases the density of positive charge in the oxide, an illumination with ultraviolet light with a photon energy of at least 4.2 eV reduces the positive charge in wet oxides but not in dry oxides. In wet oxides, the ultraviolet illumination decreases the positive charge density to a lower level if the oxide is first subjected to X-ray or gamma radiation rather than just being exposed to the ultraviolet light. The channel current of an n-channel MOS transistor was measured as a function of time in X radiation at a constant dose rate. The channel current first increased and then decreased as the irradiation proceeded. He finds that in many cases the presence of hydroxyl in the oxide appears to promote the formation of new defects during the irradiation.

### 3.2 Model

The model that is herein described is in agreement with our experimental observations. It is based on that originally proposed by A. S. Grove and includes modifications suggested by comments by M. Lambert (RCA) and others at the recent Silicon Interface Specialist Conference, and the recently reported observations of Kooi as noted in the previous subsection.

The oxide is assumed to contain a distribution of donor traps. The X or gamma irradiation ionizes the  $\text{SiO}_2$  and creates hole-electron pairs. Electrons in the donor traps can drop into empty levels in the valence band (holes), thereby forming positively charged donor traps. Whether a trap is filled or empty (neutral or positively charged, respectively) depends on the electrostatic potential at the location of the trap in the oxide.

Figure 9 shows how the charge density and the electrical field distribution in the oxide is affected by the irradiation. Assuming there is no net charge in the oxide before the irradiation, the charge distribution and field for a given applied voltage are as shown in Figure 9a. The charge densities on the two faces of the oxide are equal and opposite, and the field is constant throughout the oxide. As traps in the oxide are ionized, those above a certain potential, and therefore those to the right of a given plane in the structure remain ionized, while those at locations below this potential are fairly quickly refilled with electrons from the ionizations of other traps. Figure 9b shows an intermediate step, and when the situation shown in Figure 9c is reached, the field is zero to the left of a given plane, depending on the voltage, and all of the traps are ionized to the right of this plane.



a. Before Irradiation      b. After Some Irradiation      c. Saturation

Figure 9. The effect of irradiation on the distributions of charge density,  $\rho$ , and electric field,  $E$ , in the oxide.

For a given uniform trap density, the amount of charge contained in traps can be shown to be proportional to the square root of the voltage. After irradiation is ended, these ionized traps remain positively charged because the conduction band of the oxide is so far above the Fermi level that there are practically no electrons available to neutralize the traps. Electrons can be provided to neutralize these traps by an increase in temperature, an exposure to ultraviolet light of sufficiently short wavelength, or exposure to more X-ray or gamma radiation.

Kooi<sup>17</sup> showed that the channel current of a transistor first increases and subsequently decreases during a continuing irradiation. The increase is believed to be due to the ionization of donor traps in the oxide, which induces a higher density of electrons in the accumulation layer. Further irradiation causes a decrease in the channel current. This is believed to be due to the formation of states at the silicon surface which trap carriers and prevent them from contributing to the channel current. The observed fact that these states are formed in wet oxides and not in dry oxides might be due to the fact that they already exist in the silicon under dry oxides before the irradiation. In the wet oxides, hydroxyl groups may be bonded to silicon atoms. It may be that ultra-

violet light removes hydrogen from the hydroxyl groups, producing an oxygen ion. This ion may then be able to trap electrons.

The observed fact that ultraviolet light decreases the charge more in the wet oxides than in dry oxides might be due to the fact that dry oxides have many more electron traps at the oxide-silicon interface and therefore fewer electrons can be injected into the oxide.

In review, the effect of radiation appears to be that it ionizes various impurity and defect centers in the oxide. While the possibility exists that the radiation may induce some of the defect centers, it appears that most or all of the defect sites are due to impurities, such as sodium, and various lattice defects. Recognizing that the amorphous silica can be expected to have a high density of lattice defects, it would still be reasonable to reduce the density of impurities and the active defects by rigid control of the contaminant densities, including hydrogen and water.

### 3.3 Possibilities for Improvement

The evidence indicates that minute quantities of alkali ions and hydrogen and water may play a major role in determining the radiation-induced degradation of MOS devices. It is reasonable then to use very dry oxides as a starting point

to study the effects of minute quantities of introduced water. The results may provide the key to knowledge of whether MOS devices with improved radiation resistance can be made by more precise control of impurities.

Two kinds of experiments should be undertaken:

1. Very pure oxides should be prepared which are free of ionic impurities and of hydrogen and water. The effect of radiation on such oxides should be determined. Minute quantities of water and hydrogen should be introduced into similar oxides and the effect of radiation on these should be measured. It may be necessary to use tritium and tritiated water to determine more precisely the effect of hydrogen and water.
2. It may be impossible to reduce the density of active defect centers in the oxide. However, an attempt can be made to build barriers in the oxide layer to prevent electrons released from such donor sites from migrating into the metal or the silicon. If the electrons are confined to the oxide region, they can quickly return to neutralize the defect sites. Possibilities that might be explored for setting up such electron barriers include the

introduction of thin layers of material with a wider band gap, or of doped oxide designed to bend the energy band to form the proper barrier shape.

## 4. HIGH THRESHOLD VOLTAGE

### 4.1 Background Information

A wide variety of oxides formed in various ways and given a variety of post oxidation treatments in many laboratories contain a fixed positive charge density of about  $2 \times 10^{11} \text{ cm}^{-2}$  or higher.

#### 4.1.1 Low Temperature Post Oxidation Heat Treatments

Numerous experiments have shown that post oxidation heat treatments can influence the density of immobile charge. Figure 10 shows the results of such treatments at 200, 300, 400, and 500°C in dry hydrogen, dry nitrogen, and room air ambients for a 3000 Å thick oxide on 5 Ω-cm n-type silicon. The inflection voltage is defined as the voltage at the point of inflection in the C-V curve. The measurements were taken on unmetallized oxides using a gold ball probe. The charge was shown to be immobile at 400°C under a bias of ±20 volts for 10 minutes.

In view of the known effects of water on the properties of oxidized silicon, it now seems likely that water may be playing an important role in such observations as those shown in Figure 10.

#### 4.1.2 High Temperature Post Oxidation Heat Treatments

Experimental data given in the First Quarterly Progress Report (paragraph 3.4.6) show the effects of baking in nitrogen,



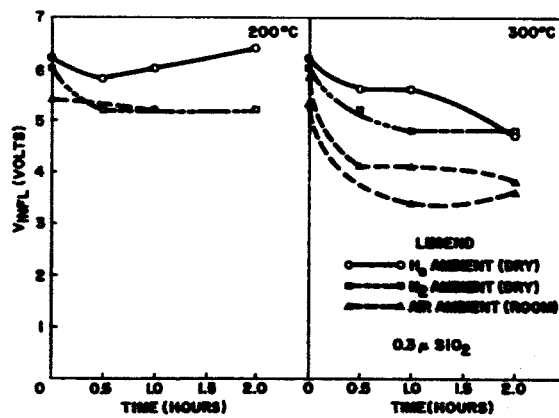
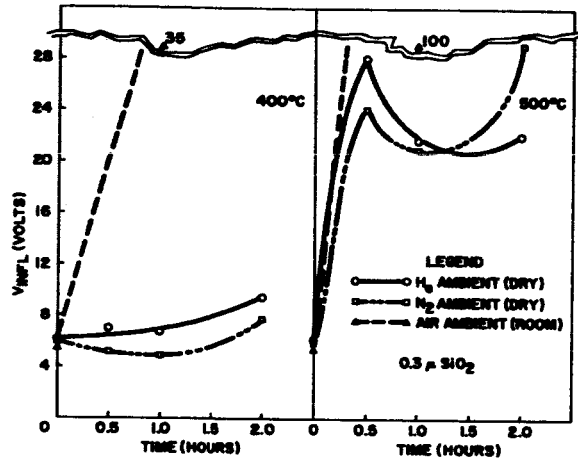


Figure 10. Effects of heat treatment.

helium, and oxygen at 1200°C, and of the effects of the cooling rate after such treatments. These data show that a considerably higher inflection voltage results from two hours at 1200°C in nitrogen than from the same baking conditions in helium. The inflection voltage was higher in all cases after one to two hours than after four or more hours. The cooling rate was shown to have an important effect on the inflection voltage, since slow cooling (over a period of from 1 to 2 hours) yielded higher values of inflection voltage. In retrospect, it now appears probable that all of these tests were influenced at least to some extent by the presence of uncontrolled amounts of moisture. When an oxide is put into a furnace, adsorbed room air moisture can diffuse into the oxide. When a furnace chamber is opened to remove an oxide after a heat treatment, a back-flow of moist room air occurs that can contaminate the oxide with water before the wafer is cool. The experiments involving slow cooling extended the time during which the oxide came in contact with moisture-containing room air and therefore probably increased the water content of the oxides.

#### 4.1.3 Comparison of Different Oxides

Further results of the study of threshold voltage are given in Table 1 where the fixed charge density is given for a number of oxides which were formed in various ways and given different post oxidation treatments.

Another experiment has shown that vapor plated  $\text{Al}_2\text{O}_3$  on silicon contains a negative charge in contrast with the positive charge in every other oxide tested. This indicates a possibility that a mixture of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in the proper proportion will yield a low threshold voltage. Several such oxides have been formed. They do in fact exhibit a range of threshold voltages, but seem to have so many mobile ions and fast trapping states that it is very difficult even to estimate the fixed-charge density. Dunavan and Lawrence<sup>6</sup> have found that gold diffusion also induces a positive surface potential in the silicon, indicative of a negative charge in the oxide.

#### 4.1.4 Surface States

Capacitance-voltage measurements of capacitors and channel conductance-voltage measurements of transistors can be combined to determine the density of states at or near the oxide-silicon interface. The basic information is derived as follows. The capacitance-voltage dependence shows the voltage at which the inversion layer forms in the silicon. Measurements of the conductance of the inversion layer show that the conductance increase due to the formation of the inversion layer may occur at voltages significantly different from those at which the capacitance-voltage curve shows the inversion layer to form. This is interpreted to mean that the first charges that make up the inversion layer go to fill states and do not contribute to the conductance

of the layer. This provides a means to measure the density of states at the oxide-silicon interface. Kooi has shown<sup>16</sup> that the density of states is very sensitive to the hydrogen, and therefore the water, content of the oxide. By means of this sensitive tool, Kooi has shown that hydrogen causes such states to disappear. Experimental data support the belief that water in an oxide reacts with the aluminum to form hydrogen. Moreover, a 300°C heat treatment in hydrogen with no aluminum present causes these states to disappear at a slower rate than a heat treatment in nitrogen at 300°C with aluminum present.

In some cases there seems to be a positive correlation between the density of states and the fixed charge in the oxide. That is, oxides containing minute amounts of water have fewer states and less fixed charge, ultradry oxides have more of each, and phosphorus doped oxides have even more of each.

#### 4.2 Model

The charge involved with the high threshold voltage is depicted in Figure 1 as fixed charge. It is positive for nearly all of the oxides tested (except for the Al<sub>2</sub>O<sub>3</sub> and the gold-doped oxide mentioned above.)

Because the oxide is not stoichiometric at the oxide-silicon interface, it is believed that there are silicon atoms with dangling bonds. A silicon atom with a dangling bond is a

silicon atom with only three covalent bonds with oxygen. There is one extra electron which can leave the silicon atom in the oxide and diffuse or drift to the silicon, leaving a positively-charged silicon atom. If an oxygen atom, or a hydroxyl, arrives at the site it can form a covalent bond, eliminating the dangling bond to form a stable neutral site.

The process of thermal oxidation requires a situation in which there is an abundance of silicon atoms and a deficiency of oxygen atoms in the oxide near the silicon. This proportion of atoms makes for a high density of silicon atoms having dangling bonds.

It is believed that oxygen, hydrogen, and hydroxyls are capable of forming covalent bonds and eliminating the dangling bonds and the fast states.

The observation that the state density decreases more rapidly during a 300°C bake in nitrogen when aluminum is present, than during a 300°C bake in hydrogen without aluminum, suggests a chemical reaction of aluminum and water at the oxide-aluminum interface. Such a reaction may form hydrogen atoms which live long enough to penetrate through the oxide before they recombine to form hydrogen molecules<sup>5</sup>. Such hydrogen atoms may be more mobile and more active chemically than hydrogen molecules which are conjectured to be involved in a bake in hydrogen.

The degree to which the various competing reactions occur to form states or to remove them depends on the chemistry and the electrochemistry of the MOS structure.

Chemically, oxygen or water at sufficiently high temperatures will oxidize the silicon. To permit this reaction to proceed, there must be an oxygen concentration gradient in the oxide to cause the net movement of oxygen toward the silicon. Although the solubility of oxygen in vitreous silica has been reported to be  $1.9 \times 10^{-3}$  at  $1078^{\circ}\text{C}$ , it is believed that at room temperature there is an oxygen deficiency near the silicon interface of the oxide.

The rate of oxidation can be accelerated, retarded or stopped by an applied electric field. Radio-chemical measurements provide evidence that a rapid rate of exchange takes place between oxygen atoms in the oxide and those in the ambient gas. Further, the oxidation rate has been observed to increase with increasing oxygen pressure. These three observations indicate that the oxygen moves through the oxide in the form of negative oxygen ions. After oxidation one finds only positive charge and therefore one can infer that these negative ions are neutralized as the temperature is decreased. The positive charge is believed to be oxygen vacancies that are located in the oxide near the silicon interface because in this region the oxide is not stoichiometric during the oxide growth.

The effects of different oxidation processes and post oxidation treatments are due to variations in the chemical and electrochemical reactions caused by differences in the impurities present in the temperature cycle. Various impurities must compete with each other for reactants. Some may have catalytic effects. The chemical equilibrium conditions of the competing reactions may be dependent on the temperature. The time schedules of the processing steps determine how far the reactions go. Cooling rates may influence the degree to which a high temperature chemical state is frozen after the structure is cooled.

There is no explanation at this time for the correlation between the trapping state density and the fixed-charge density.

#### 4.3 Possibilities for Improvement

Based on the preceding background information and the model discussed above, equipment and techniques will be developed to more precisely control minimal amounts of water in the oxides. Pure oxides (free of alkali ions and of water) will be characterized in terms of their fixed charge density. The study of the effects of exposing these oxides to water vapor in known concentrations for various times and temperatures should yield information concerning the effects of the handling and storage of oxides in room air. Heat treating such dry oxides in various

gaseous ambients for different times and temperatures may improve our understanding of the effects of both water and various heat treatments.



## 5. ANALYSIS OF RESULTS

During the past six months, significant progress has been made in gaining understanding of the effects of radiation. Radiation has been found to cause rapid degradation of MOS device characteristics. Most investigators agree that all kinds of oxides are degraded to about the same extent. There is evidence that the degradation rate is related to the hydroxyl content of the oxide. A model has been developed which is sufficiently accurate to enable explanation of the available data.

To study the problems of instability and high threshold voltage of MOS devices, MOS capacitors have been prepared from a variety of oxides and with various post-oxidation treatments. Within the limits of experimental accuracy, none of the oxides has been found to be significantly freer of charge than the thermally grown oxide. It is possible that the effects of minute quantities of water influenced the results.

Heat treatments at 300°C have yielded slight reductions in the fixed-charge density in oxides.

The effects of baking oxides in nitrogen, oxygen, and helium at 1200°C have been studied. Such baking can cause large changes in the fixed-charge density. The rate of cooling

from 1200°C was found to have an important influence on the fixed-charge density. The observed effects are now believed to have been affected by the presence of uncontrolled amounts of water.

An important part of the first six months of this program has been the collection, analysis, and review of the published or reported work done by other experimenters in the field of MOS devices. This has provided a broad base for the experimental analyses required in this program.

## 6. FUTURE WORK

Based on the information described in the preceding sections, the following work is planned:

The characterization and evaluation of various oxides will be continued.

Techniques and equipment will be developed to control to minimal levels the water content of oxides during oxidation, handling, and storage. Such dry oxides will be characterized for both fixed and mobile charge. The effects of exposure to water vapor for various times and at various temperatures will be studied to establish the effects of water introduced during the regular handling and storage of oxides.

Further work will involve the study of heat treatment effects on dry oxides to determine to what degree previous work was influenced by water. If the previous work is found to have been significantly influenced by water, some of that work will be repeated in a search for processing techniques that will yield improved devices and improved understanding.

## 7. CONFERENCES AND PUBLICATIONS

Personnel involved with this program have attended the following conferences, gaining information pertinent to the realization of the program objectives:

Electrochemical Society Spring Meeting, San Francisco, California, May 9-13, 1965,

Solid State Device Research Conference, Princeton, New Jersey, June 21-23, 1965,

IEEE Annual Conference on Nuclear and Space Radiation Effects, Ann Arbor, Michigan, July 12-15, 1965,

Electrochemical Society Fall Meeting, Buffalo, New York, October 11-14, 1965,

International Electron Devices Meeting, Washington, D.C., October 20-22, 1965,

Silicon Interface Specialists Conference, Las Vegas, Nevada, November 15-16, 1965,

Fourth Annual Symposium on the Physics of Failure in Electronics, Chicago, Illinois, November 16-18, 1965.

The Silicon Interface Specialists Conference is discussed in further detail on the following pages. A literature review derived from work done on this program and compiled by E. Schlegel was distributed at the conference. This literature review contained the list of references included in the First Quarterly Report plus the references that were added between September 10 and November 1, 1965. Appendix A of this report brings the list up to date to December 8, 1965.

Philco personnel participated in organizing and arranging a specialists' conference, the IEEE-sponsored Silicon Interface Specialists Conference, held in Las Vegas, Nevada, November 15 and 16, 1965. The purpose of the conference was to bring together a small group of specialists, actively engaged in the field of MOS physics, technology, or related areas, into an informal workshop atmosphere where a free exchange of ideas and discussion could lead to an increase in knowledge and understanding of silicon interface phenomena. Arrangements were made to have four technical specialists in the field of glass properties and ionic conductivity of glasses and of fused quartz attend the entire meeting, and to present invited review papers.

The invited specialists included: Professor A. E. Owen of the Department of Glass Technology of the University of Sheffield, England; Professor J. P. Roberts of the Ceramics Division of the University of Leeds, England; Dr. A. Herczog of Corning Glass Works, Research Center, Corning, New York; and Dr. M. E. Milberg of Ford Motor Company, Scientific Laboratories, Dearborn, Michigan.

The invited papers were presented subsequent to the sessions in which MOS device phenomena, theories and observations were covered, thus enabling the speakers to include pertinent comments relative to MOS phenomena in their discussions.

The four invited technical specialists performed several valuable functions. They reviewed their own work and that of other glass specialists, pointing out a number of significant references and experimental observations. They summarized available knowledge relative to the structure of glasses and concerning electrical conduction and ion migration in glasses. Considerable information about the properties of fused silica was presented. Perhaps most valuable was the emphasis placed upon the effects of water on the properties of vitreous silica. This included the differences between the effects of water introduced by various processes. Also, the interactions between cations such as hydrogen and aluminum or hydrogen and sodium were discussed. For example, hydroxyl formed by protons which replace Na in fused silica is much more stable than hydroxyl introduced by baking in hydrogen or water.

After the Silicon Interface Specialists Conference, Dr. Owen visited Lansdale and served, under NASA subcontract, as a consultant to Philco on ion migration in glass-like materials relevant to MOS device characteristics and stability.

## 8. REFERENCES

This section lists the actual references noted in the text of this report. Recent additions to the general bibliography begun in the First Quarterly Report are listed in Appendix A.

1. Carlson, H. G., C. R. Fuller, and J. Osborne, "Sodium Distributions in Thermally Grown Silicon Dioxide Films," presented at the 1965 Fall Meeting of the Electrochemical Society, Buffalo, New York, "Recent News" paper.
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## APPENDIX A

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

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