CASE FILE COPY

RESEARCH TRIANGLE INSTITUTE

NASA CR-66712

N 69 10711

CHARACTERIZATION OF SILICON OXIDE FOR A CAPACITANCE-TYPE METEOROID PENETRATION DETECTOR

Prepared for

Applied Materials and Physics Division
Langley Research Center, NASA
Hampton, Virginia

September 1968

(Prepared under Contract NAS1-7949 by the
Engineering and Environmental Sciences Division of the
Research Triangle Institute, Research Triangle Park
North Carolina)

RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

CHARACTERIZATION OF SILICON OXIDE FOR A CAPACITANCE-TYPE METEOROID PENETRATION DETECTOR

By K. S. Canady, L. K. Monteith,
and R. P. Donovan

Distribution of this report is provided in the interest of information exchange. Responsibility for the contents resides in the author or organization that prepared it.

Prepared under Contract No. NAS1-7949 by
RESEARCH TRIANGLE INSTITUTE
Research Triangle Park, N. C.

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ABSTRACT

Large area metal-oxide-silicon (MOS) capacitors have been fabricated and evaluated electrically and environmentally for use as micrometeoroid counters in space. The conclusion is that the present technology is capable of building capacitors that are suitable for performing this function. Capacitors have been fabricated with dielectric thicknesses from 2000 Å - 10,000 Å. These capacitors can be electrically stressed in excess of 10^6 V/cm and have been tested in air and vacuum at -150°C to +300°C without adverse effects.

CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

CHARACTERIZATION OF SILICON OXIDE FOR A CAPACITANCE-TYPE METEOROID PENETRATION DETECTOR

By K. S. Canady,* L. K. Monteith,** and R. P. Donovan

SECTION I

INTRODUCTION

A capacitor-type micrometeoroid detector operating as a cumulative counter of particles a micron or larger in diameter requires a dielectric with a thickness on the order of a micron. The mass of the particle of interest will determine the actual thickness of the capacitor dielectric and the front thin film electrode to be penetrated. The details of capacitor discharge during impact are not presently known. However, complete penetration of the dielectric region is generally accepted as necessary for reliable operation. To accomplish the design and testing of a detector where complete penetration is the order of a micron requires high quality thin films of an insulator and metal where the thickness of each can be easily varied.

Although the mechanism for capacitor discharge is not completely understood, there are certain desirable electrical characteristics of the capacitor structure which can be identified. The essence of operation is the ability of the detector to withstand applied electric fields on the order of 10^6 V/cm in severe environments. Upon penetration, a portion or all of the energy stored by the capacitor is dissipated through the impact region. For successful operation, the energy dissipation should clear the low impedance and restore the ability of the detector to withstand the applied field. To achieve this operation in severe environments of temperature, pressure, and vibration, a stable capacitor with respect to electrical performance is desirable. Excessive changes in leakage currents, capacitance, or field strength only compound the design problem for achieving a flight qualified detector. It is the purpose of this contract to study and characterize silicon oxide as a thin film dielectric material suitable for detecting low mass micrometeoroids in space. As part of a program to design and test a capacitor-type structure, thin film capacitors have been fabricated using metal-oxide-silicon (MOS) technology.

---

* Present address: Duke Power, Charlotte, N. C.

** Associate Professor of Electrical Engineering, North Carolina State University, Raleigh, N. C. (Consultant at Research Triangle Institute).

The MOS technology was chosen because (1) high quality insulating films of SiO_2 can be grown thermally with a thickness from 2000 to 10,000 Å, (2) aluminum metalization can routinely be accomplished in the same thickness range and (3) field strengths as high as 10^7 V/cm have been reported for SiO_2.

The MOS technology appears to provide the necessary attributes for a thin film capacitor type detector with one important exception. The micrometeoroid detector of interest requires a capacitor area of 10^3 cm^2 while MOS devices require areas on the order of 10^{-3} cm^2. As a result, a primary objective for the effort under this contract was to obtain large area MOS structures and characterize them as capacitors. The methods of fabrication and typical results of the electrical tests are included in this report. Also included is an assessment of these results as they relate to the design of a thin film capacitor-type detector.

As a parallel effort to the investigation of MOS structures, other methods for achieving thin film capacitors have been reviewed. The review is included as an appendix to this report. The primary considerations have been the details of the technology, properties of resulting films and state-of-the-art in obtaining large area films less than a micron in thickness. Special attention is given to pinhole free films in this thickness range.

SECTION II

FABRICATION OF MOS CAPACITORS

The substrate material in all cases was p-type silicon approximately 0.005 ohm-cm. The low resistivity silicon was chosen to avoid capacitance variations with applied voltage. This variable capacitance is necessary for field effect transistors but should be avoided in the application under consideration here. Preparation of the silicon wafer prior to thermal oxidation is of utmost importance in determining the electrical properties of the oxidized films. A dirty surface on a microscopic level can nucleate crystalline regions in an otherwise amorphous film. A rough surface may constrain oxidation in certain regions and result in substantial variations in film thickness. Dust particles on the surface may result in either pinholes or other unwanted structural defects in the oxidized film.

To build a thin film capacitor-type detector with a large area of silicon oxidized to form approximately 1/2 micron of SiO_2 places a premium on preparation of the silicon surface prior to oxidation. However, one must also exercise due caution to avoid degrading the electrical characteristics of the SiO_2 layer during the processes required after oxidation. In fact, each process step has been carefully considered for possible deleterious effects on the characteristics of the capacitor. A number of these considerations are included in the following discussion. The fabrication procedures are outlined in Fig. 1.

Cleaning Procedure

The cleaning procedures used to build the capacitors tested in this program are listed in Fig. 1. These were developed by a trial and error procedure starting with the commonly used procedures of silicon technology (Ref. 18). The initial step is to clean the wafer of all foreign metals, abrasives and other contaminants. The procedures include heating in sulfuric acid, a water rinse and a soak in hot nitric acid. Both these acids are strong oxidizing agents which should dissolve most organic greases and contaminants as well as dissolve many metal contaminants that might be on the surface. Step G of procedure I (HF etch) is to remove the native oxide layer caused by either exposure to air or the strongly oxidizing cleaning procedures of steps A and C. With the oxide removed, the wafer is copper plated to encase any adhering particles of alumina abrasive commonly used in the mechanical polishing of the silicon surface. These particles adhere tenaciously to the silicon surface but can be removed by a procedure such as copper plating in which these particles are actually encased in the copper layer that deposits on the silicon and then removed in the subsequent nitric acid etch. Step L, the hot Transene rinse, has been found to be an effective method of further removing metal ions on the silicon surface. Steps A through M have proved to be a more desirable

I. Clean Wafers.

A. Boil in H_2SO_4 - 10 minutes.
B. Rinse in DI water.
C. Boil in HNO_3 - 10 minutes.
D. Rinse in DI water.
E. Boil in DI water.
F. Rinse in DI water.
G. Etch in HF - 1 minute.
H. Rinse in DI water.
I. Copper plate.
J. Etch in HNO_3.
K. Rinse in DI water.
L. Rinse in hot Transene.*
M. Blow Dry.

II. Oxidize

Thickness		____	____	____
Temperature		____	____	____
Time:	Dry	____	____	____
	Wet	____	____	____
	Dry	____	____	____

III. Etch Oxide from Back Side.

A. Put $N_4HF \cdot HF$ (ammonium bifluoride) in plastic beaker and moisten slightly with DI water.
B. Place $N_4HF \cdot HF$ crystal on wafer and place one drop of water on crystal. Crystal should cover 1/4" diameter area minimum. Etch until all oxide removed from area under crystal.
C. Rinse in DI water.
D. Rinse in hot Transene.
E. Blow dry.

(Copper Plating Solution:
1. 100 grams $CuSO_4 \cdot 5\ H_2O$
2. Dissolve in DI water
3. Add 5 cc HF
4. Add DI water to make 500 ml.)

* Transene is the trade name of a versene marketed by Transene Corp.

Figure 1. Procedures for Fabricating MOS Capacitors

method of surface preparation than other chemical cleaning steps which are substantially similar to it but omit the copper plating. The number of oxide defects per unit area is reduced by following this procedure.

Oxidation

The oxidations were carried out in a diffusion furnace at 1100° (a few rare cases at 1200°C). The oxides were grown by 5-minute dry oxygen--x-minute steam--5-minute dry oxygen process. The steam time is determined by the desired oxide thickness. Some few oxides were grown totally in dry oxygen, usually at 1200°C; these, however, had lower breakdown field strengths than the steam oxides: 2×10^6 V/cm compared to 4×10^6 V/cm. The oxidizing species in steam oxidation is water which reacts with silicon to form SiO_2 and H_2 (Ref. 18). In dry oxygen, the oxidizing reaction is simply the combination of silicon and oxygen to form SiO_2.

Oxide Removal

The oxidation process grows an oxide on the back as well as the front of the wafer. Since the silicon wafer is the back contact to the capacitor, it is necessary to remove enough oxide from the back to make contact to the silicon. Initially, this was accomplished by covering the front oxide with black wax, then dipping the wafer in hydrofluoric acid to etch the oxide from the back. This procedure suffered from two disadvantages: (1) the acid could sometimes penetrate the wax on the front of the wafer, and (2) the wax itself is a foreign substance on the dielectric and may introduce undesirable effects.

The procedure listed in Fig. 1, part III, eliminated these undesirable effects. Ammonium bifluoride in water creates fluoride ions in an acid solution. The fluoride ion then etches the silicon dioxide in the same manner as HF. The advantages of this process are: (1) a small area of silicon dioxide can be etched away exposing the silicon which can then be covered with evaporated aluminum to have any desirable electrode area; (2) the only substance that touches the dielectric area is high purity water and Transene.

Evaporation

Aluminum. - All electrodes were made from evaporated aluminum. The aluminum was evaporated in an oil diffusion system; the vacuum chamber was pumped down to 5×10^{-5} torr before evaporation. The source used was high purity aluminum clips pressed into a tungsten filament. Normally, about 30 amps of filament current was needed to evaporate; the evaporation rate was approximately 40 Å/sec. Masks were used during the evaporation process to define the electrode areas. The substrate was unheated.

Holders

The first holder built for the micrometeoroid detector utilized a technique whereby contact was made to the electrode on top of the oxide by a one inch diameter metal ridged ring. This type of holder proved to be undesirable from both an electrical and a mechanical viewpoint. Since the wafer is held between two metal parts and the pressure on it determined by the screws, some wafers were broken by exerting too much pressure on the silicon. Also, the surface was frequently scratched and abraded by the metal ring contact.

The second generation holder was of the general design of Figs. 2 and 3 (for 2" wafers).

The spring was used to provide a more constant pressure on the silicon wafer. A hole halfway through the bottom plate aligns the wafer. The top plate contacts the wafer on the oxide only and does not touch the aluminum contact area. Contact to the wafer is made through the spring on the bottom side and through a gold lead thermocompression bonded to the top electrode. These holders were intended for use in laboratory tests of the capacitors only and are not designed to be flight type mounts.

Connections and Leads

One of the reasons a ring contact was not utilized was because of the clearing operation to be discussed in a later section. A second reason was that the ring scratched the aluminum contact. The holder shown in Fig. 3 was then used for the remainder of the contract. A 1 or 2 mil gold wire bonded to the aluminum electrode made contact to the top electrode. The top aluminum plate of Fig. 2 did not touch the evaporated aluminum electrode but contacted the oxide ring showing around the aluminum electrode. Since the top plate and bottom plate are at the same electrical potential, no arc can occur under the aluminum top plate.

Contact to the silicon was made by etching a hole in the oxide on the back of the silicon wafer and evaporating aluminum over the entire back surface. When mounted in the sample holder of Fig. 3, the stainless steel spring presses against the evaporated aluminum to establish a large area pressure contact.

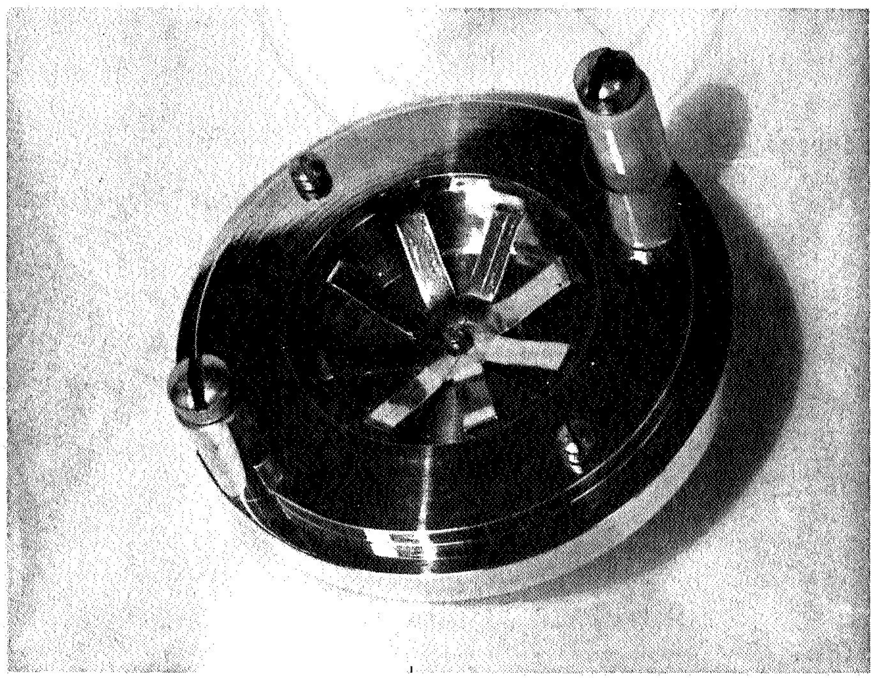


Figure 2. Assembled Capacitor Holder (without the capacitor)

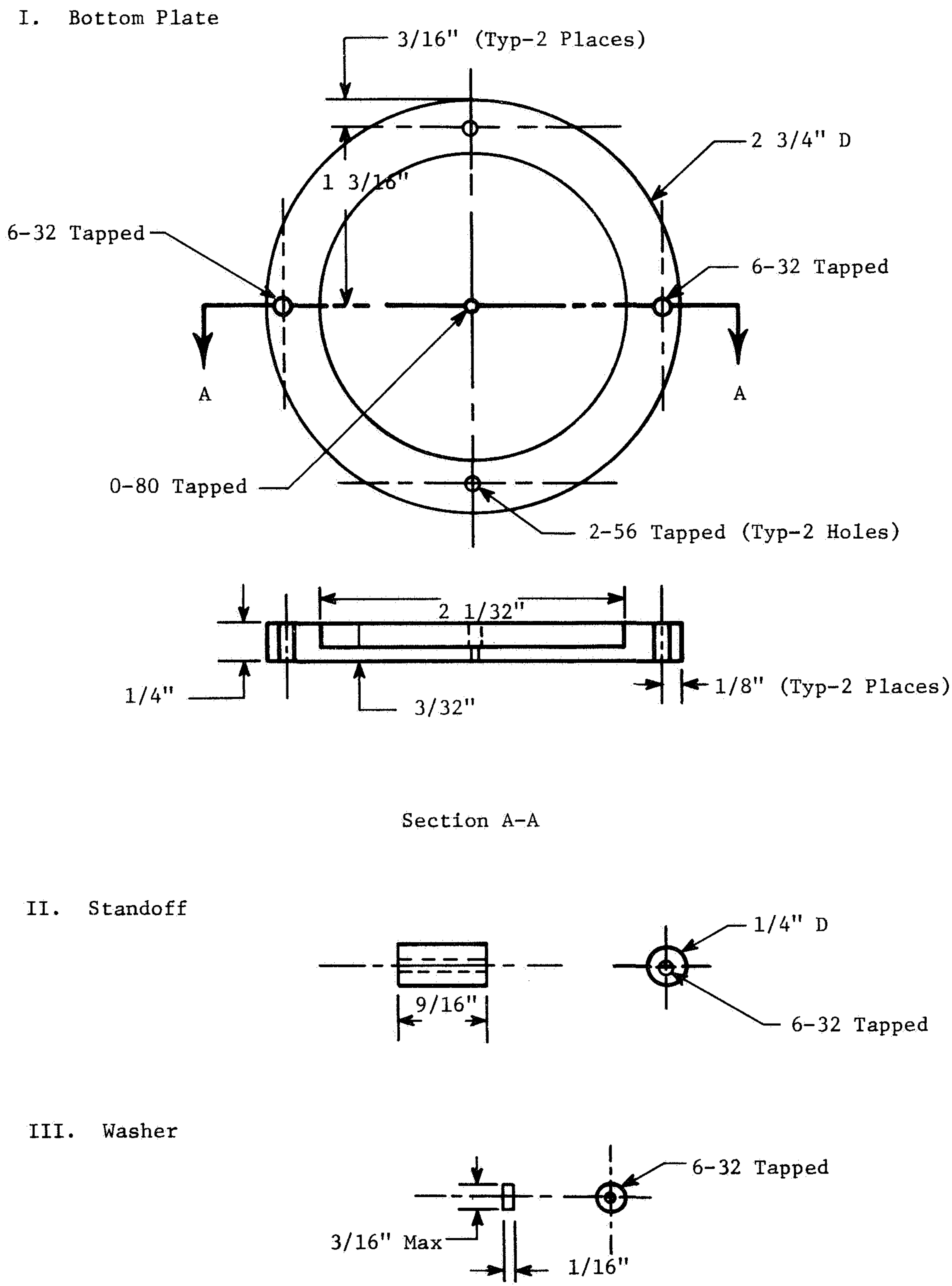
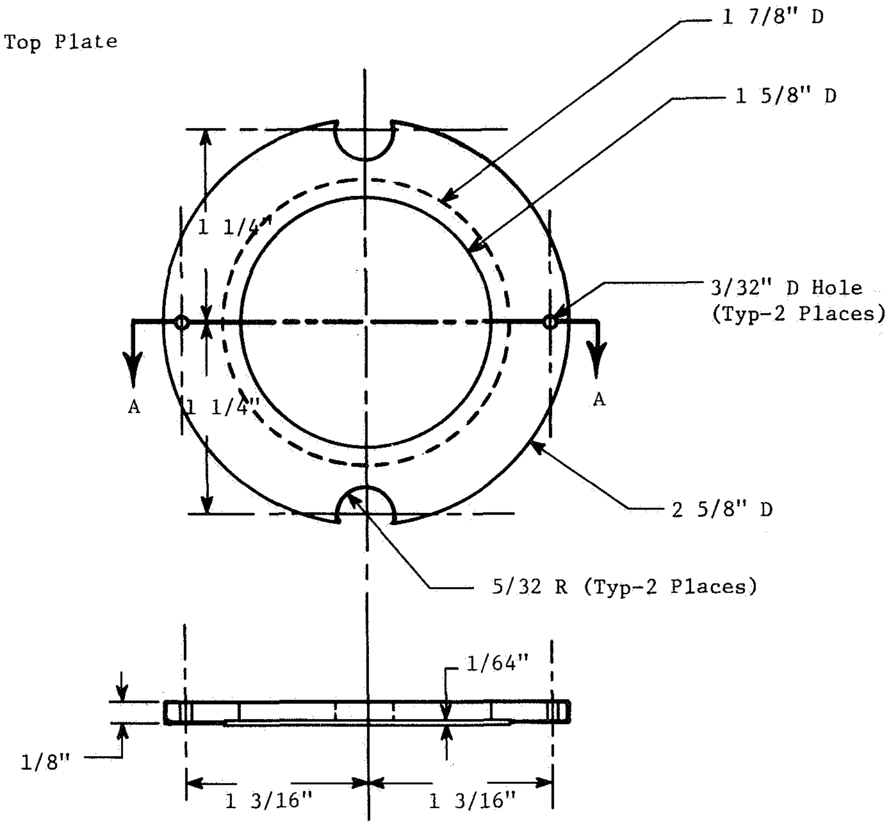


Figure 3. Detail Sketches of Wire Bonded Capacitor Holder

IV. Top Plate



Section A-A

V. Spring

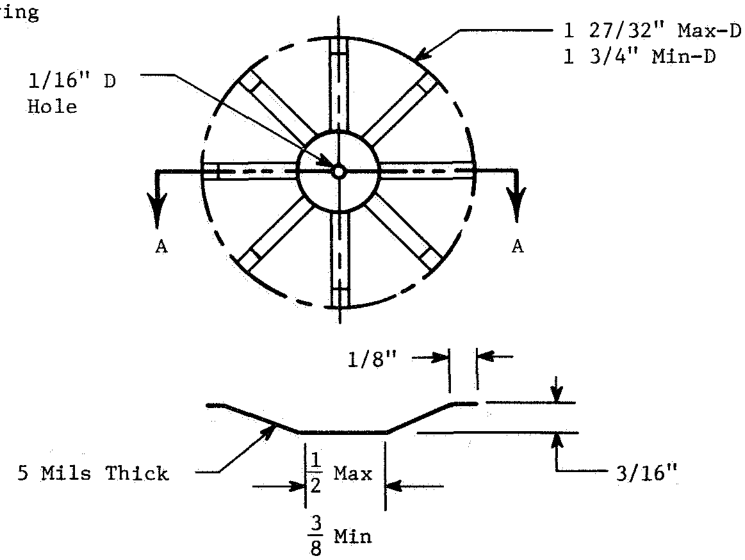


Figure 3 (continued)

SECTION III

ELECTRICAL TESTS OF MOS STRUCTURES

A capacitor-type detector requires a relatively stable capacitance capable of supporting a high field strength over the range of temperatures and pressures encountered in a flight application. The change in dissipation factor and dc resistance become important only if they result in appreciable power dissipation from the power supply which biases the capacitor. A 12 point matrix of oxide thicknesses - 2000 Å, 5000 Å, 10,000 Å--versus electrode thickness--300 Å, 1000 Å, 5000 Å, 10,000 Å were fabricated and tested to characterize these electrical properties and to demonstrate the ability to fabricate thin film capacitor type detectors with physical properties suitable for impact testing. The results of the electrical tests are discussed in the following sections.

Capacitance, Dissipation Factor, dc Resistance

The capacitance and dissipation factor were checked on samples varying in oxide thickness from 2000 Å to 10,000 Å and electrode thickness of 300 Å to 10,000 Å. It was observed that within the accuracy of the tests the capacitance generally did not change with temperature or with pressure. An example is the data in Table I.

The dissipation factor showed no definite temperature relationship. A key factor which influences this apparent random variation is the inability to accurately measure the dissipation factor to four decimal places. However, in some few cases, the dissipation factor increased with temperature. Table II is an example of typical data.

The dc resistance, if low enough to be measured, generally decreases with increasing temperature. Ordinarily, this decrease can only be seen at 300°C if at all. Table II is an example of this behavior.

As a capacitor the electrical characteristics of the MOS structure are rather insensitive to environmental changes representative of flight conditions. Routine measurements on a capacitance bridge were considered adequate for obtaining these data.

Although data are shown for only one thickness of SiO_2 and two aluminum electrode thicknesses, all the samples tested exhibited similar behavior. The capacitance is insensitive to environment. The dissipation factor and dc resistance exhibit measurable changes at temperatures approaching 300°C. As a result of these tests, it is apparent that the

Table I

Capacitance at Various Temperatures
and Pressures for MOS Structure

Sample 4-23-68A   10,000 Å SiO_2 (Steam Oxide)

300 Å Al

Capacitance	Temperature	Pressure
.0235μF	-150°C	160μ
.0234μF	-150	1 atm
.0236μF	-100	160μ
.0236μF	23°C	1 atm
.0236μF	23°C	150μ
.0236μF	100°C	1 atm
.0236μF	100°C	90μ
.0236μF	300°C	90μ
.0235μF	300°C	1 atm

Table II

Capacitance, Dissipation Factor and dc Resistance of MOS Structure at Various Temperatures and Pressures

Sample 4-30-68B 10,000 Å SiO_2 (Steam)
1000 Å Al

Capacitance	Dissipation Factor	dc Resistance	Temperature	Pressure
.0213μF	.002	5×10^9 ohms	-150°C	1 atm
.0213	.002	5×10^9	-150°C	500μ
.0213	.002	5×10^9	-100°C	1 atm
.0213	.002	5×10^9	-100°C	500μ
.0212	.002	5×10^9	23°C	500μ
.0212	.002	5×10^9	23°C	1 atm
.0213	.01	5×10^9	100°C	500μ
.0216	.02	1.2×10^7	300°C	1 atm
.0213	.02	1.6×10^7	300°C	500μ

MOS structure can be fabricated with SiO_2 thicknesses from 2000 Å to 10,000 Å and aluminum electrode thicknesses from 300 Å to 10,000 Å and behave as a stable capacitor under environmental changes representative of flight conditions.

Field Strength of MOS Structure

To fully characterize the MOS structure as a capacitor type detector, the field strength or breakdown voltage of the capacitor must be determined. Ideally, one would prefer a clearly identifiable bulk breakdown for the SiO_2 film. This is rarely realized for large area capacitor structures. Pinholes and thickness variations for thin films (less than 1 micron) result in less than ideal homogeneous insulating layers and field strengths less than true bulk breakdown are usually observed. Therefore, the emphasis in obtaining a thin film capacitor must be placed upon minimizing the pinholes and structural defects. Varying the growth kinetics of the thermal oxidation and surface preparation of the silicon wafer are two ways of influencing the structure of the oxidized layer. During this contract, there was no systematic attempt to minimize the pinholes and structural defects and thereby maximize the field strength. The primary concern was to identify the state-of-the-art in MOS technology as applied to a capacitor-type detector.

In the strictest sense of the word, breakdown for an insulator is usually defined as an irreversible process. However, for a capacitor-type detector, this definition may not be adequate. For example, the irregularities in thin films often burn-out as the field strength of the localized region is exceeded. The mechanism is quite analogous to capacitor discharge upon particle impact. After the defect is cleared the capacitor will usually sustain a higher field strength. Therefore, for the purposes of this contract, both the arcing potential and destructive breakdown field were considered.

Extensive efforts were made to obtain breakdown voltage versus temperature. A method was found to determine breakdown voltage in the absence of arcing or transient breakdown. The method consisted of analyzing the current-voltage characteristics where electrode injection is suspected as the supply of current carriers. A plot of log current versus voltage or square root of voltage should be near linear at moderate voltages. A sharp upturn in current indicates a threshold for destructive breakdown. Figures 4 and 5 are an example of this behavior. When the current carriers are supplied by electrode injection, the current should increase with increasing temperature at a given voltage. Figure 6 is an example of this behavior.

The temperature dependence did not always behave in a predictable fashion. Often the current was noted to be rather insensitive to temperature and the threshold for breakdown was not clearly defined. Likely

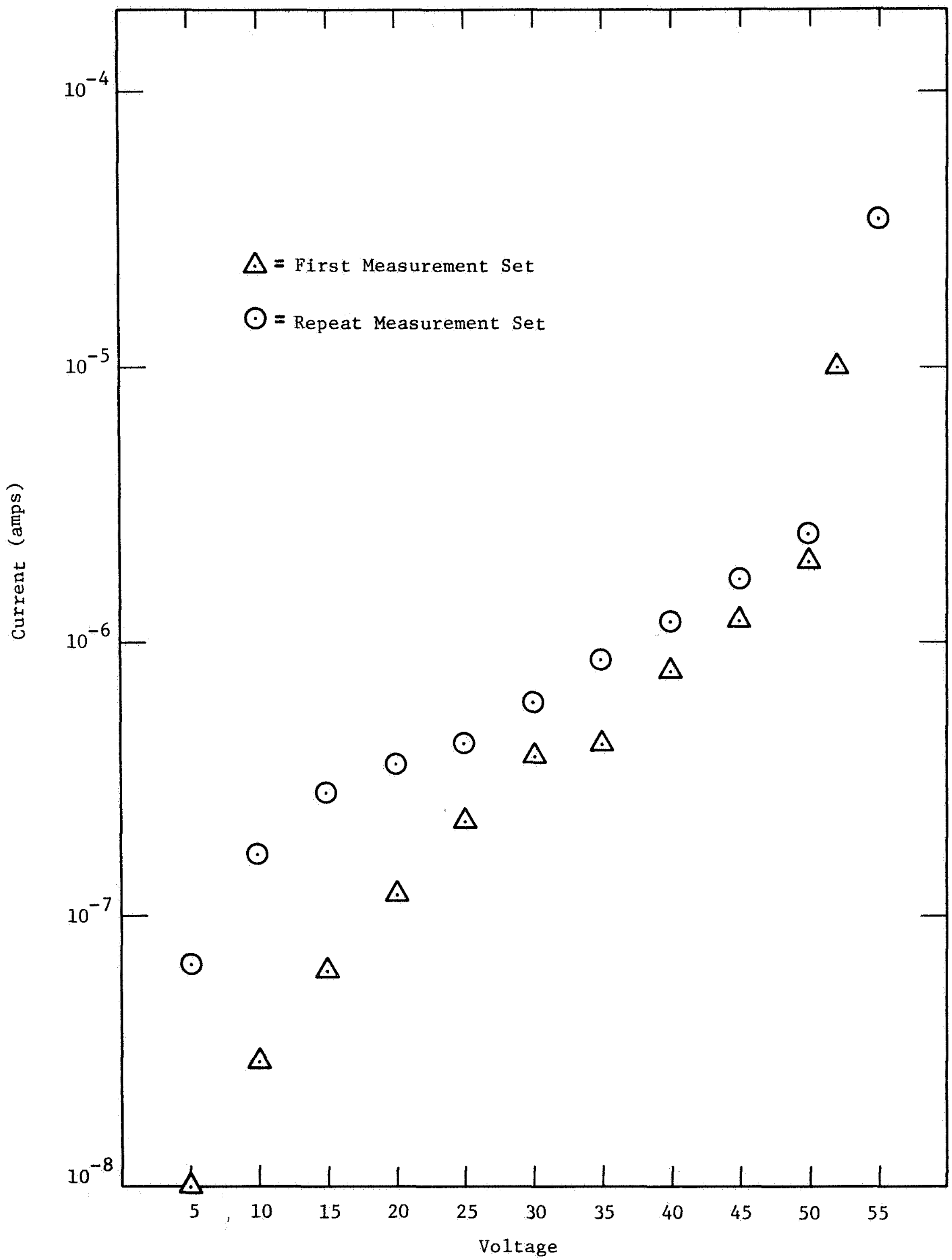


Figure 4. Current-voltage Plot of a Large Area MOS Capacitor; Oxide Dielectric Thickness, 2000 Å

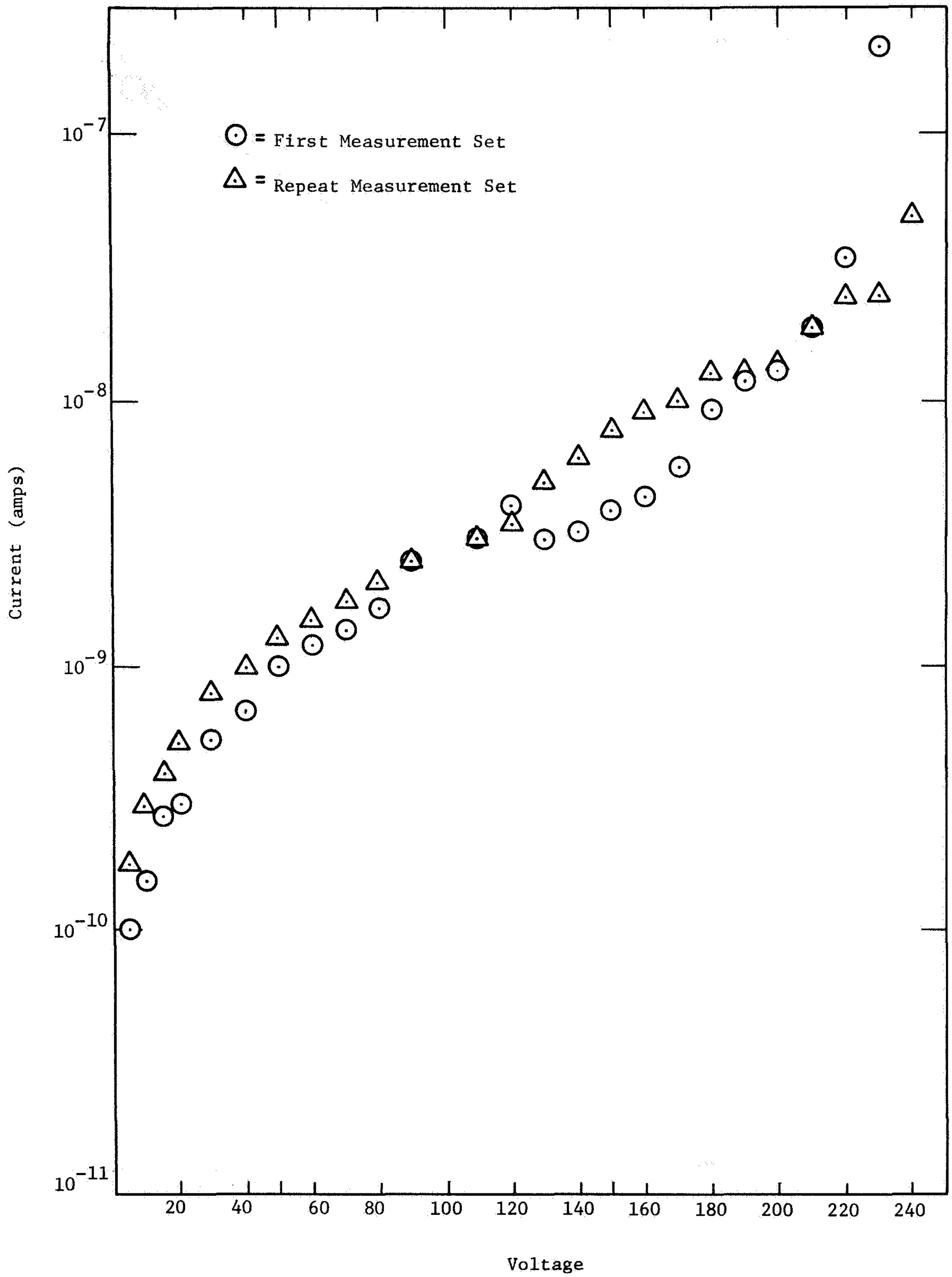


Figure 5. Current-voltage Plot of a Large Area MOS Capacitor; Oxide Dielectric Thickness, 5000 Å

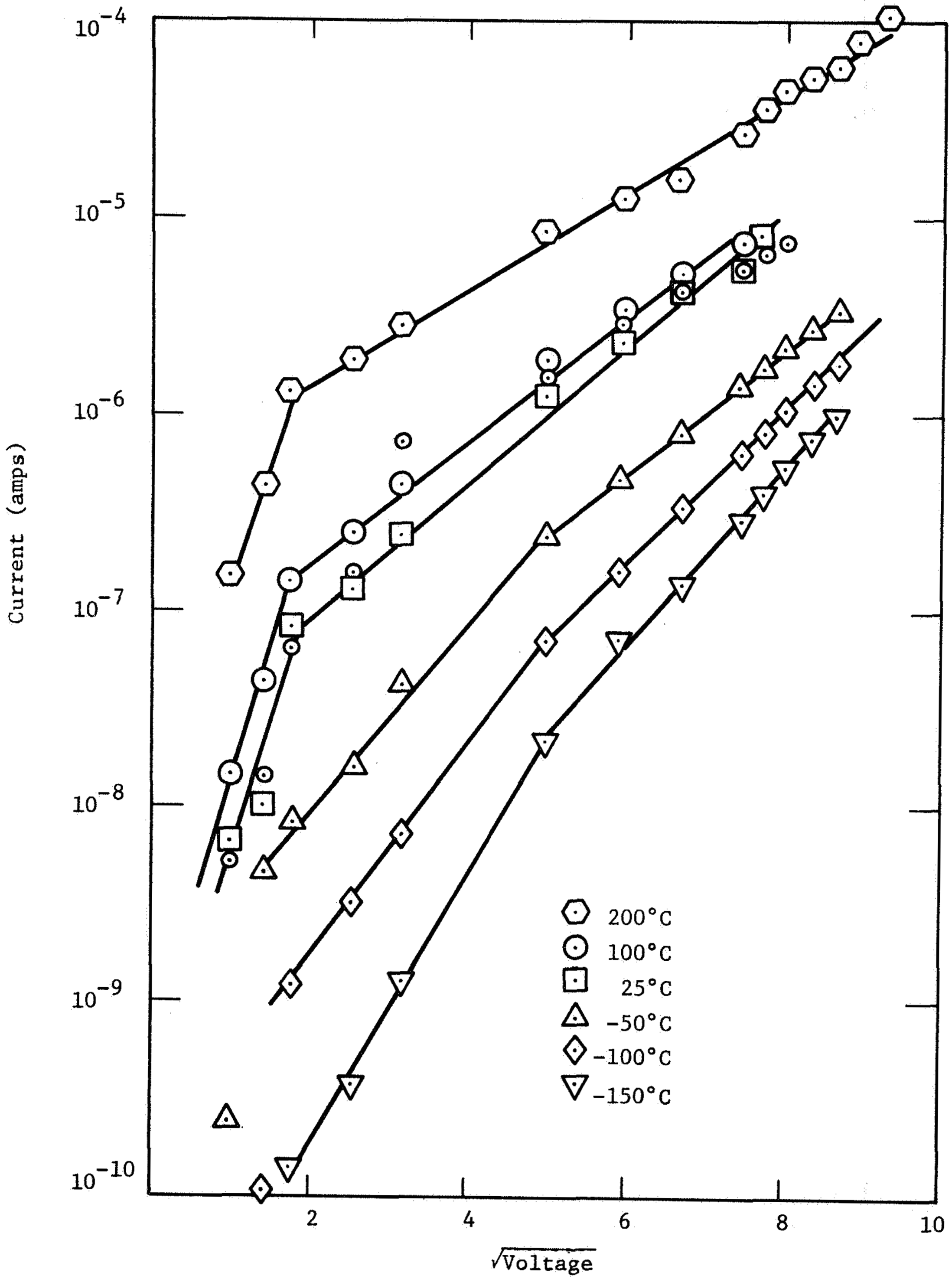


Figure 6. Current vs. Square Root of Voltage for an MOS Capacitor (oxide thickness, 2000 Å) at Various Temperatures

suspects for this behavior are polarization effects near the electrodes in bulk SiO_2 and leakage currents which depend not only on temperature but on other environmental factors as well. These effects should be more carefully considered before definitive remarks concerning bulk field strength of large area SiO_2 capacitors can be made.

More realistic data for the intended application is the arcing potential and the ability to clear the capacitors to field strengths in excess of 10^6 V/cm. Freshly prepared samples could nominally withstand applied fields near 10^5 V/cm. Shown in Table II and Fig. 7 is the arcing voltage as temperature is varied. These data are difficult to analyze due to the fact that once a capacitor has been cleared of defects at a given field strength, the applied field can be increased. However, this is true to a certain field strength where further arcing will in fact decrease the achievable field. This is presumably due to defect creation during the arcing process itself. The technique used in Fig. 7 was to first clear the capacitor to the field strength where further arcing had little effect on the ability to achieve higher fields. The data indicate a decrease in arcing voltage with increasing temperature. However, there is still a tendency for the arcing voltage to increase as a result of previous arcing history. This is shown by a second set of data in Table IV for the sample used for Table III. Presently, the arcing phenomena is not well understood and further investigation should be conducted. One would prefer the arcing voltage to be near 10^6 V/cm for freshly prepared samples. This would permit a more versatile biasing capability for the capacitor detector to insure reliable operation.

Technique for Clearing Defects in MOS Structure

The nature of the clearing operation involves the application of a high field resulting in a current density through the defect region sufficient to vaporize or burn-out the low field strength region. Almost all dielectrics made at RTI and those obtained commercially were cleared to obtain field strengths in excess of 10^6 V/cm. A few exceptions were noted for the 9500 Å commercial oxides. These exceptions certainly indicate that high field strengths for freshly prepared samples can be obtained. However, details for achieving this desirable feature are not known.

There were two methods employed during the contract to clear the capacitors: The first was to mount the wafer between a metal plate and a metal ring. Then power as supplied by a 110 volt variac was applied in one or two volt increments starting at about three or four volts. The variac was rapidly switched on, then off at each increment. To see if the clearing was successful at each voltage, the variac was disconnected and dc resistance of the capacitor checked with an electrometer. There are two disadvantages with this method. One, if a pinhole or fault occurs

Table III

Arcing of MOS Structure over a Range of Temperatures

Sample 7-25-68A — 10,000 Å SiO_2

1000 Å Al

Temperature	Capacitance	Dissipation Factor	Current at 1V (amp)	Current at 50V (amp)	Arcs
25°C	.048865µF	.0044	1.9×10^{-8}	5×10^{-7}	240 V
300°C	.048975µF	.0056	2.25×10^{-8}	1.5×10^{-7}	220 V
200°C	.049532µF	.0460	3.1×10^{-9}	1.5×10^{-9}	227 V
100°C	.048861µF	.0169	4.2×10^{-12}	1×10^{-10}	300 V
25°C	.048710µF	.0489	2.5×10^{-11}	2.9×10^{-9}	278 V
-50°C	.048600µF	.0134		1.5×10^{-12}	380 V
-100°C	.048530µF	.0033	1.24×10^{-11}	1.5×10^{-11}	400 V
-150°C	.048475µF	.0027		6×10^{-11}	440 V
25°C	.048610µF	.0104	8.62×10^{-11}	7.3×10^{-9}	250 V

Table IV

Arcing of MOS Structure over a Range of Temperatures
(Repeat of Table III)

Sample 7-25-68 10,000 Å SiO_2
1000 Å Al

Temperature	Capacitance	Dissipation Factor	Current at 1V (amps)	Current at 50V (amps)	Arcs
25°C	.048573μF	.0081	5.2×10^{-12}	2×10^{-10}	390 V
300°C	.048643μF	.0020	1.4×10^{-10}	2.3×10^{-8}	370 V
200°C	.048540μF	.0031	2.4×10^{-11}	1×10^{-7}	365 V
100°C	.048582μF	.0052	4.5×10^{-12}	8×10^{-10}	390 V
25°C	.048393μF	.0245	6×10^{-12}	2×10^{-10}	395 V
-50°C	.048342μF	.0051	4.7×10^{-13}	2.2×10^{-11}	400 V
-100°C	.048287μF	.0032		4×10^{-11}	440 V
-150°C	.048219μF	.0044			460 V
25°C	.048356μF	.0093		5×10^{-10}	380 V

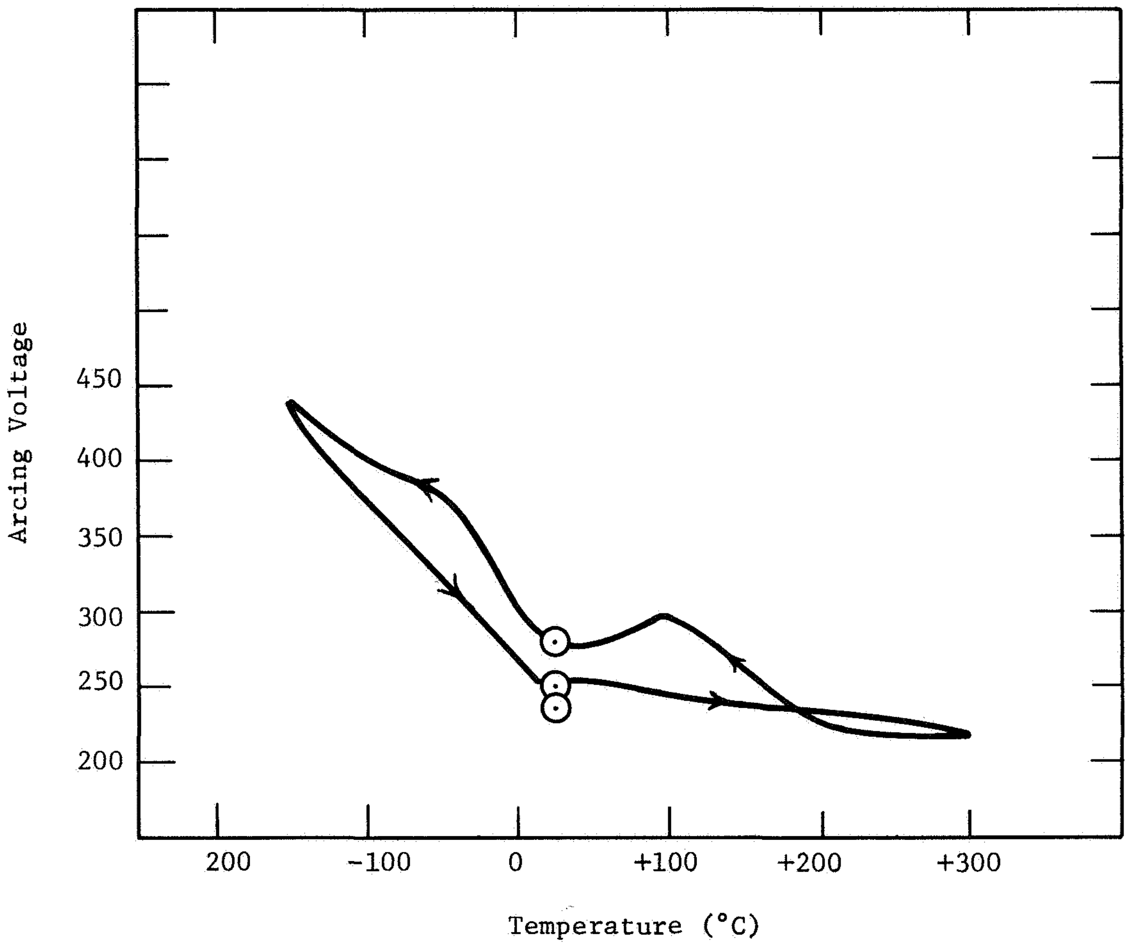


Figure 7. Initial Arcing Voltage during Temperature Cycling (data from Table III)

under the contacting metal ring, the capacitor shorts to the plate when an arc occurs. Secondly, the power applied to the capacitor is not as controllable as it should be. The least possible power that will accomplish the clearing operation should be used since excess power will cause more faults.

The second method, designed to eliminate these two disadvantages, is as follows: a point probe contact is used, either a platinum wire or a gold bonded lead. The 575 Tektronix curve-tracer is used to burn-out the faults. The curve tracer allows good current-voltage control. The capacitor is connected between collector and emitter terminals of the curve tracer with the emitter grounded. The polarity switch can be either plus or minus. There is sometimes a difference in breakdown voltage depending on polarity; however, the top electrode was usually chosen positive which is the severer test. In use the silicon should be positive. The range voltage switch is set to 0-400 volts. Sometimes if a large area short is encountered, more current is needed to clear and the 0-20 or 0-200 volts range is selected. The horizontal scale is set at 10 V/cm and the vertical scale set on .5 mA/cm. The dissipation limiting resistor is set to 100K. Voltage is gradually applied to the peak volt range pot. If the capacitor is good, a semi-circular trace is seen; if it is resistive, a line is traced. A straight horizontal line indicates an open circuit or no contact.

The procedure to burn-out a fault on the curve tracer is as follows:

1. Set horizontal scale to 10 V/cm.
2. Set vertical scale to .5 mA/cm.
3. Dissipation limiting resistor to 100K.
4. Increase voltage from 0 to a value high enough to observe the state of the capacitor.
5. If a semi-circular trace is not observed, return voltage to zero and decrease dissipation limiting resistor and increase vertical current scale.
6. Increase voltage again.
7. Continue steps 5 and 6 until arc occurs.
8. Capacitor has then been cleared of at least one fault.

Experience has shown that many capacitors can be cleared of faults up to voltages of approximately 4×10^6 V/cm. Careful observation will indicate that for each arc encountered the voltage or field strength can be increased slightly, up to a point. At some point, further arcing or clearing will not increase the ultimate field strength; in fact, it will decrease.

Almost all capacitors could be cleared by the second method regardless of their original condition, whereas the yield by the first method was low.

Life Test

The process of clearing a MOS structure to achieve high field strength must be seriously examined if used in the fabrication of capacitor-type detectors. Arcing is observed during the breakdown of most dielectrics over a wide range of thicknesses. For thin films the effect is amplified by the small range of voltages usually encountered for operation. For 2000 Å films a 20 volt bias results in a field of 10^6 V/cm which is a rather high field. One usually thinks of voltages in excess of 1 volt for biasing the capacitor-type detector. Therefore, the range of bias is compressed compared to 1/4 mil Mylar capacitors where 600 volts is required for a field of 10^6 V/cm. Arcing at 600 volts for 1/4 mil Mylar capacitors would create few problems for obtaining an operative detector. However, for the thin film capacitor, life tests designed to gain confidence in the ability of the detector to withstand the bias required for reliable operation should be a necessary part of flight qualification. To pursue the matter further, two preliminary tests were conducted under this contract.

A 2000 Å oxide capacitor was placed in a holder with 20 volts across it to determine if any arcs would occur during a long life test. Over a one month period, no deviation occurred on the chart paper that could be definitely attributed to arcing. Three small deviations did occur about eighteen days after the beginning of the run. These did not have the same shape and amplitude as testing arcs. Power line fluctuation or low frequency noise environment such as induction motor start-up are likely explanations.

After one month at 20 volts, the voltage was increased to 35 volts. Here arcing occurred routinely at about 5 minute intervals. Therefore, the voltage was decreased to 30 volts where one arc occurred in a seven day period and that during the first hours of operation.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this contract are that capacitors made of thermally grown silicon oxide constitute a satisfactory capacitor electrically to perform the micrometeoroid detection function. The parameters of the capacitor--dielectric constant, dissipation factor, dielectric breakdown strength--do not vary appreciably over the temperature range of -100°C to 300°C; that is, they do not vary appreciably enough to adversely influence the performance of the capacitor in the micrometeoroid detection role. Certainly, they do exhibit variations with temperature; these have been measured and presented in this report.

Assuming that the capacitors do satisfactorily perform the desired micrometeoroid measurement, other recommendations are:

(1) The minimum oxide thickness investigated in the course of this contract was 2000 Å. Yield at this thickness was not as great as that of the 10,000 Å oxides and the number of defects that had to be burned-out was greater. The yield and defect density were clearly technique dependent. Oxides grown on surfaces prepared by the alkali ion etch generally performed better in both respects (yield and burn-out densities) than did those prepared either by chemical cleaning or by the cupric ion technique, also designed to eliminate aluminum oxide particles (Ref. 19). A brief investigation of thinner dielectrics was made and in general yields continued to decreas until, at 500 Å oxide, the yield was zero. There is no reason to believe that this is a fundamental limitation although it does represent the present state-of-the-art, as far as RTI is concerned. The survey of the literature indicates that very little work has been published on the techniques for improving the defect density of large area thermal oxides while a great deal of information has been published on methods for reducing ions and electrical contaminants in the oxide. A higher yield will probably result from an investigation of techniques for preparing and growing oxides with reduced defects for the purpose of making large area MOS capacitors.

(2) The clearing phenomena referred to throughout the report is closely related to yield. Processes which gave higher yields invariably resulted in fewer defects that required clearing. The number of defects also varied inversely with oxide thickness. Consequently, most of the 2000 Å oxides had to be cleared before reaching what might be assumed to be operating field strength (10^6 V/cm or greater). The same was true

for some of the 10,000 Å oxides although many of these units required no burn-out at all before reaching these high field strengths. The initial wet chemical cleaning process involving neither the alkali ion etch or the cupric ion etch resulted in 100% of the wafers requiring burn-out. Toward the end of the contract, both the cupric ion and the alkali ion etch resulted in more wafers exhibiting no observable defects until field strengths in excess of 10^6 were reached. Better results generally came from the alkali ion etch process than with the cupric ion etch. Further work to improve this technique seems worthwhile if these capacitors are to be flown in space.

(3) Packaging of the capacitor has been largely arbitrary. Most of the samples examined under this contract were spring mounted in holders held down from the top. A few were bonded with epoxy cement. The response of either type of mounting to impact from a high velocity particle must be assessed for future housing designs.

(4) The role of breakdown, either electrically initiated or mechanically initiated, is still unclear. Consequently, the capacitors being fabricated for the micrometeoroid detection are based solely on empirical considerations. A fundamental study of the physics and mechanics of mechanically initiated breakdown could contribute much to the thoughtful design of future capacitors. At present, the role of many variables is simply not known; i.e., top electrode composition and thickness, substrate thickness, substrate mounting, dielectric mechanical properties (amorphous versus crystalline), etc.

(5) Similarly, the physics of impact and fracture are not well understood. Investigation of the responses of crystalline and amorphous substrates to high velocity impacts would furnish useful information for future capacitor designs.

Of the various materials now being used to form thin film dielectrics in microelectronic capacitors, the thermal growth of silicon oxide on silicon seems as suitable as any for use as a micrometeoroid capacitor. Should this structure prove unsatisfactory, the most promising other material is perhaps the polymer film poly-p-xylylene

APPENDIX 1

REVIEW OF TECHNIQUES FOR FABRICATING THE DIELECTRIC OF A THIN FILM CAPACITOR

This appendix gives a brief state-of-the-art review of the various solid state technologies that might be capable of manufacturing capacitors with dielectric thicknesses in the 1000 - 10,000 Å range. This range of thickness is that usually associated with thin film technology. Many techniques exist for depositing or growing thin films. The most promising of the technologies will be briefly described in principle and some of the results that might be obtained using these techniques are summarized. A brief evaluation of the suitability of each technology for building the type of capacitor sought for micrometeoroid detection is made and an estimate of the potential for future development is also included.

Most practical methods for building thin film capacitors consist of depositing an insulator upon a conducting substrate which makes up one electrode of the capacitor. The second electrode is deposited on the opposite side of the insulator to make up the finished capacitor. In the thin film thickness range, the most common deposition technique has been evaporation, sputtering, or other vacuum dependent process. Many useful capacitors have been and are still being made by these techniques; however, their fabrication is highly technique dependent because of the many variables associated with a vacuum deposition process. Much time and effort has already been devoted by the industry to developing and optimizing these processes. Consequently, the present state-of-the-art is not one that is likely to be changed dramatically by further research and/or development.

A second general class of techniques for building thin film capacitors consists of converting the surface layers of a metal or semiconductor into an oxide dielectric. In this structure, the original metal serves as one electrode. The oxide formed by the oxidation process is the capacitor dielectric and a second metal electrode is deposited on top of the oxide to finish the capacitor structure. The thermal oxidation of silicon is an example of this method as is the anodization of aluminum, tantalum, and other metals. The general advantage of this type technique over the straight deposition process is that the starting substrate participates in the dielectric formation and hence small variations or non-uniformities in the substrate surface can be healed or accommodated for in the formation of the dielectric. A rough starting substrate does not necessarily guarantee a poor capacitor. On the other hand, the composition of the dielectric will be dependent on the substrate cleanliness and certain imperfections or impurities on the surface being oxidized can create defects or imperfections in the resultant oxide.

Building thin film capacitors with dielectrics composed of polymers or other plastics constitutes a third general fabrication technique. This technique is newer than the others but striking performance claims have already appeared in the literature. Pinhole free dielectrics have been described in the 200 Å and lower region by using this method. Because of its relative newness, evaluation of these techniques for the micrometeoroid capacitor program are more tentative.

Vacuum Deposition Techniques

Vacuum deposition techniques are divided into two general categories: 1) thermal vaporization, and 2) ion bombardment. Within these two broad categories many variations exist, the most important of which will be discussed in the following paragraphs.

Vacuum Evaporation by Thermal Vaporization. - This technique is the most common vacuum deposition technique in use; it has been used for the longest time as well. The principles of operation are quite simple: a material heated in vacuum to boiling will spew forth its constituent atoms which then proceed in a straight line path to deposit on the first surfaces intercepting the atom's line of sight, providing the vacuum is low enough that the mean free path between atomic collisions is large with respect to the chamber dimensions. The commonly used heat sources are tungsten filaments through which large currents are passed. The filaments become hot through resistance heating and any material in contact with the hot filament is also heated and can be boiled off as described. This technique is quite suitable for metals such as gold, aluminum, silver, and a large host of materials with relatively low boiling temperatures (under 1500°C). Some dielectrics are also deposited by this technique, the most common of which is probably silicon monoxide. The source material for silicon monoxide is usually a fine brown powder or chunks of a material with essentially the stoichiometry of SiO. Precise composition of the starting sources is generally somewhat in doubt. Spectrographic analysis indicates that the same absorption properties are exhibited by finely divided mixtures of silicon and silicon dioxide as are exhibited by the commercially available powders sold under the name silicon monoxide. Technique is highly important in the growth of silicon oxide films formed by the evaporation of this silicon monoxide powder. Heating rates, residual pressure in the vacuum chamber, and source composition all influence the electrical properties of the resultant film. In addition, small particles of solid matter can be spewed forth from the hot mixture and form gross particles in the growing film. These large chunks of material that are deposited are referred to as meteors and specially designed evaporation boats have been built so as to eliminate them from the deposited film.

Films of silicon monoxide evaporated from a hot tungsten filament are probably among the more common dielectrics used to make capacitors.

The dielectric constant of films made in the 1000 to 10,000 Å thickness range is on the order of 5 to 6. Breakdown voltage of these films is on the order of 2 to 4 $\times 10^6$ V/cm. As is general for thin films, the breakdown voltage is not a true bulk breakdown phenomena but more a measure of a defect or pinhole density. Breakdown events generally initiate at field strengths of 1 to 5 $\times 10^5$ V/cm (Ref. 1). By using thin electrodes these initial defect-related breakdown events are generally self healing. In general, these films can be deposited down to 1000 to 2000 Å in thickness with yields that would seem to be acceptable for micrometeoroid detectors. "Burn-out" phenomena occur in that defects and weak spots must be eliminated by a "clearing" operation. A serious problem in some applications, not necessarily micrometeoroid sensors, would be changes of properties with temperature. Operating silicon monoxide capacitors at 200 to 300°C generally causes drift in the capacitance of the unit and changes the dissipation factor by a greater magnitude than comparable capacitors built with thermally grown silicon dioxide dielectric.

Other thermally vaporized materials can also be used as the dielectric of a thin film capacitor. Common dielectrics include magnesium fluoride, lanthum fluoride, cerium fluoride, cerium dioxide and zinc sulfide (Ref. 2). Magnesium fluoride is particularly recommended because of its dielectric constant of 6.5 and its dielectric strength of 2.2 $\times 10^6$ V/cm.

The oxides of rare earth and transition metals have been used to make capacitors (Ref. 3). These materials are suitable but possess no major advantage over silicon monoxide or magnesium fluoride. They are less familiar and do not warrant further consideration in building micrometeoroid capacitors at present.

All the materials discussed so far can be deposited with an electron gun heater instead of the resistance heater that has been in use for the past 20 years. In general, film properties are comparable between the two methods, although some evidence suggests an electron gun deposits a higher density film and one with higher dielectric constant (Ref. 4). No major advantage seems to accrue other than cleanliness from using the electron gun. Electron gun heating of source material does make possible direct thermal evaporation of many insulators such as synthetic quartz, sapphire, and others (Ref. 5). The dielectrics produced by these means are comparable to those produced by the other techniques and in general no advantage or disadvantage accompanies this method.

<u>Sputtering</u>. - Sputtering is a vacuum deposition process in which the source material is vaporized because of bombardment by high energy ions. The ions acquire high energy by acceleration in an electric field existing between two electrodes, normally operating in the kilovolt potential difference range. Diode sputtering consists simply of these two electrodes accelerating the ions that exist between them

in a system evacuated to the 10^{-2} torr pressure range. Efficiency of the process can be improved by adding a third terminal whose function is simply to inject electrons into the vacuum chamber. The additional electron-injecting electrode permits sputtering to take place at lower absolute pressures. The added electrode converts the diode sputtering process into the triode sputtering system. The material to be deposited is generally one electrode of the system (the negatively biased electrode) and the sputtering action depends upon the impact of high energy ions upon it. If the material is an insulator a space charge builds up on the surface of this electrode after a very short period (because of the positively charged ions impacting on it), reducing the energy and number of subsequent impacts. This substantially ends the sputtering cycle. To prevent this action, a method of biasing the electrode with an RF potential has been developed which permits the space charge to be neutralized on alternate half-cycles. This is the RF sputtering modification. In any of these systems--diode, triode, or RF sputtering--the residual gas composition and pressure can be controlled to cause further modification in the nature of the deposited film. For example, if silicon is sputtered in an oxygen atmosphere the composition of the resultant film can be either silicon oxide or silicon dioxide depending on the sputtering rate and the residual gas pressure. When the film material is different from the source material because of a modifying reaction occurring during the sputtering, the process is classified as a reactive sputtering. Commercial vacuum systems now make possible the incorporation of all these features into a single system; that is, a single bell jar and pumping system can do either diode, triode, or RF sputtering which is itself either reactive or nonreactive depending on the rates and residual gas composition selected.

Silicon oxide films deposited by the reactive sputtering process are typically more like thin films of thermal silicon dioxide than evaporated films of silicon monoxide. The dissipation factor and dielectric constant typically are close to that of amorphous bulk silicon dioxide (Refs. 6-8).

Conclusions. - Vacuum deposition of inorganic insulating films is highly developed for producing insulating layers and capacitor dielectrics in contemporary microelectronics. These uses are generally confined to relatively small areas, compatible with the dimensions of microelectronics, and hence are not directly assessable in terms of a large area micrometeoroid detecting capacitor. The common shortcomings of vacuum deposited dielectric thin films are defects or pinholes in the dielectric layer which cause localized regions of poor performance and result in low breakdowns. Many of these low breakdowns can be healed by passing large currents through the region and vaporizing the surrounding metal and dielectric. This action is probably very similar to the discharge accompanying micrometeoroid impact. It is important to be able to distinguish between the two events and to be able to eliminate all such defects prior to using such a capacitor as a meteoroid capacitor, although the ability to perform this self-healing operation does suggest that the particular capacitor under test would be suitable as the meteoroid counter as well.

Techniques for vacuum depositing thin films have been under development for a long time. Substrate preparation is unquestionably very important in film preparation as are the many variables that describe a particular deposition process. A satisfactory micrometeoroid detector could probably be constructed from a parallel array of many small identical capacitors, each of which was preselected from a much larger quantity initially fabricated. This solution is not the best solution available with present technology.

Vapor Deposition Techniques

Vapor deposition describes the general class of film formation techniques in which the film is formed by a decomposition, oxidation, or other chemical reaction. The advantages of this process are that it requires no expensive vacuum equipment to maintain and operate. It can be carried out in relatively simple every day laboratory apparatus. In silicon technology, the quality of vapor deposited silicon oxide films have proven superior for many applications than similar films formed by vacuum evaporation.

While vapor deposition has been used for over half a century to form various types of refractory metal coatings such as carbide, nitride, borides and silicides, the most common use of vapor deposition at present is in the growth of high quality silicon epitaxial layers. Such layers are not useful for dielectrics but the techniques that have been perfected over the past ten years to grow such silicon layers have been extended to form silicon oxide layers. Two common methods for depositing silicon oxide are as follows: (1) the thermal oxidation of silane (Ref. 9), and (2) the pyrolytic decomposition of tetraethylorthosilicate (Refs. 10-12), The reaction between silane (SiH_4) and oxygen occurs at low rates even at room temperature. For uniform high quality layers, the reaction is generally carried out in the vicinity of 300 to 400°C. The thermal decomposition of tetraethylorthosilicate on the other hand requires a temperature in the 700 to 1000°C range. In both cases, the reacting gases are mixed in the vicinity of a heated substrate which catalyzes the reaction. Glow discharges have also been employed to carry out essentially the same type of reaction (Ref. 10).

The properties of these films are similar in general quality to those formed by vacuum deposition. High quality capacitors with dielectric thicknesses less than 500 Å have been fabricated successfully (Ref. 10). Breakdown field strength, dissipation factor and dielectric constant are similar to that of thermally grown SiO_2. Consequently, this source of dielectric film formation is suitable for the MOS capacitor fabrication. Uniformity of deposit is an ever present problem, however. To cover large areas uniformly requires not only good temperature control but good control of the gas flows from which the oxide is deposited. As before, the film quality is dependent upon the substrate preparation and cleanliness.

Polymer Dielectric Films

Polymer thin films are prepared in a manner very similar to the inorganic vapor deposited films just described. One major difference is that the film itself is a polymer and that the reaction used to form it must involve a polymerization as well as a simple decomposition or chemical reaction. The chief advantage of plastic polymers as capacitor dielectrics is their low residual stress. These films are able to flow plastically under stress and capacitors made from them withstand stresses that crack or shatter the inorganic dielectrics and oxides previously discussed. Thin polymer films have been prepared to thicknesses as small as 100 Å and in general exhibit low electrical conductivity, a small dissipation factor, and a high dielectric breakdown strength. Their primary disadvantage is their relative instability, both with respect to temperature and to certain chemical ambients. Most polymer films must operate at temperatures below 150°C; most films are affected by exposure to water particularly at high temperatures.

Formation of a plastic polymer thin film requires some methods of initiating polymerization. Common techniques for doing this are gaseous discharge and pyrolysis, although various photo-initiated reactions also are commonly used (Refs. 12-13). A whole host of materials have been deposited by these methods, including polystyrene, polyethylene terephthalate, polytetrafluoroethylene, polycarbonate, photoresist, and collodion. Often, these are self-supported films and are processed so as to be inserted between two aluminum foils. With such manufacturing methods, the minimum film thickness is in the range of .15 to 1 mil. A notable exception is the recent polymeric thin film developed by Union Carbide and marketed under the name of Parylene. These films are deposited from a gas phase of p-xylene vapor which impinges on a room temperature surface such as aluminum. The p-xylene polymerizes to form poly-p-xylylene. The properties of the deposited polymer are quite impressive. The most important is that of pinhole free coatings in the 50 to 100 Å range. Such film perfection implies a high suitability for use as a large area capacitor to detect micrometeoroids. The other dielectric properties of poly-p-xylylene are certainly suitable for forming such a capacitor. Its dielectric strength is on the order of 3×10^6 V/cm; the dielectric constant is low (on the order of 2.7), the dissipation factor is also very low (~ 0.0001). The ability to manufacture large sheets of this type capacitor would seem to make it highly suitable for the micrometeoroid capacitor application. It could well prove superior to any of the inorganic capacitor dielectrics. A chief drawback is its newness and the lack of data from the field to judge its performance.

Anodically Grown Dielectrics

Anodically grown dielectrics refer to those electrochemical techniques in which a dielectric is grown on a substrate by chemically combining a species from the surrounding gas or liquid, usually oxygen, with the substrate material, forming an oxide or other insulating material. It differs from thermal oxidation in that the chemical reaction is initiated electrically. Two common classifications exist: the wet electrolytic method in which the substrate is immersed in an electrolyte and the electric field applied between it and an inert counter electrode; and 2) the dry plasma anodization technique in which the substrate is placed in a chamber in the vicinity of a gas plasma which serves as the reservoir of oxygen ions. It is primarily the second technique that is of most interest for the formation of high performance capacitors, the wet electrolytic technique having been studied longer and shown to be subject to the usual uncertainties and shortcomings such as pores and defects that plague most thin films. The gaseous anodization technique has not become so common as to have had the contempt heaped upon it that such familiarity seems to breed in thin films. Most reports concerning gaseous anodization are glowing reports, praising the high perfection and lack of defects in comparison with the wet electrolytic (Ref. 15). Among the dielectrics formed commonly in this manner are silicon dioxide, titanium dioxide, tantalum pentoxide. Probably the most striking results are those claimed by Miles and Smith for the gaseous anodization of aluminum (Ref. 15). They claim essentially pinhole free films in the 100 to 200 Å thickness range over areas of 1 to 2 cm^2. These areas however are the sum of many small dots rather than one continuous large capacitance electrode. Silica deposition has been developed by Ligenza (Ref. 16) and pursued further by Kraitchman and Handy (Ref. 17) using silicon as a substrate for the formation of anodized silicon oxide. No claims for unusually good perfection or defect free films were made by either of these investigators. The films were represented as a convenient low temperature method for depositing silicon oxide. The dielectric properties and physical properties of these films so deposited are comparable to the thermally grown oxide which they were designed to replace. Indeed the apparatus and the design of the electrodes to maintain the discharge might make the uniform coating of a large area more difficult than many of the other techniques discussed. The one advantage of this method of dielectric film preparation is that it would tend to be somewhat self-healing since the dielectric film formed consumes the substrate in its formation. Defects or areas of uneven or nonuniform structure tend to be smoothed out or otherwise massaged into a minimum damage configuration by such methods. This feature though is also shared by the technique to be discussed next, thermal oxidation.

Thermal Oxidation of Silicon

The thermal oxidation of silicon is a well-studied much performed technique in silicon technology (Ref. 18). It consists of placing highly polished silicon wafers into an oxidizing atmosphere--either 100% oxygen or oxygen plus steam--at a high temperature for a controlled time. The film thickness is proportional to time and temperature for a given oxidizing atmosphere and is reproducible to better than 5% over most of the range of thicknesses used in silicon technology. One of the more recent uses of silicon oxide in silicon technology is as the gate dielectric of the MOS field-effect device. In this role, the oxide is grown approximately 800 to 1200 Å thick, is over coated with an aluminum electrode and then subjected to electric fields on the order of 10^6 V/cm for device operation. These requirements are very similar to those encountered in the micrometeoroid capacitor. The one major difference is that of area. The gate of the MOS field-effect transistor may have an area of 10^{-3} cm^2; the area of the micrometeoroid detector requires an area of 10^3 cm^2. This factor of 10^6 increase in area does not make the task 10^6 more difficult. It does place a premium on being able to grow oxides on silicon that are at least the present state-of-the-art.

In principle, any surface placed into the furnace at a uniform temperature can be uniformly oxidized. Therefore, the maximum area attainable in the present state-of-the-art is a question of the maximum practical size silicon surface that can be prepared and inserted into a furnace. In contemporary production, the circular wafer is in use; its maximum readily available diameter is 2 inches. However, there is no reason why one can't go to a 6 to 12 inch diameter disc if the need is important enough. There is nothing fundamentally difficult about growing this large a substrate crystal, particularly if the requirement for having the entire wafer a single wafer is relaxed. For the micrometeoroid capacitor, this accommodation seems quite permissible. No added failure mode is anticipated by switching from a single crystal to a polycrystalline substrate.

Thermally grown silicon oxide has not been overly popular as a dielectric for a capacitor in integrated circuits or other silicon devices, primarily because of its rather low dielectric constant. To build a capacitor out of silicon oxide requires an inordinately large area. Ofttimes the preferable course in constructing an electronic function is to simply append an external capacitor to the active components and forget about integration. People have spent time and money developing high dielectric constant dielectrics such as the tantalum oxides and titanium oxides previously mentioned. For the micrometeoroid application, however, the low dielectric constant is of no consequence. The properties most sought after are the ability to fabricate a capacitor with a thin dielectric, which will not short out upon initial fabrication and which will retain the self-healing properties exhibited by Mylar and other thick film capacitors upon impact by a hard, high energy object. In addition, it would appear desirable to have the dielectrics exhibit a high dielectric strength. On all these scores, thermally grown silicon oxide comes off quite well. No information is yet available on its response to high velocity particle impact but from laboratory studies of over-voltage signals, the self-healing action would certainly seem to be reasonable to expect.

Table A-1

Properties of Various Dielectric Thin Films

Dielectrics	Dielectric Constant (at 25°C)	Dissipation Factor (at 25°C unless otherwise noted)	Minimum Thickness (Å)	Max. DC Breakdown Strength (volts)
Evaporated SiO	5 to 10	.001 to .01	500 to 1000	$3\text{-}4 \times 10^6$
Evaporated MgF	6 to 7	.001 to .01	1000	2×10^6
SiO_2 (Thermal)	3.2 to 3.8	< .001	500 to 1000	$1\text{-}2 \times 10^7$
Sputtered SiO_2	1.8 to 3.4	~ .001	1000	$6\text{-}10 \times 10^6$
Vapor Deposited SiO_2	4.5 to 5.5	.01 (at 100°C 1 kc)	500	$5\text{-}10 \times 10^6$
Parylene	2.7	.00015 (25°C 1 kc)	100 to 1000	3.2×10^6
Anodic Ta_2O_5	14 to 28	.01 to .02	700	1×10^6

REFERENCES

1. Klein, N.; and Gafni, H.: "The Maximum Dielectric Strength of Thin Silicon Oxide Films", IEEE Trans. on Elect. Dev., ED-13, Feb. 1966, pp. 281-289.

2. Maddocks, F. S.; and Thun, R. E.: "Properties of Evaporated Film Capacitors", J. Electrochem. Soc., Vol. 109, Feb. 1962, pp. 99-103.

3. Carr, H. E.; Foster, W. D.; Harbuck, T. A.; and Fromhold, Jr., A. T.: "An Experimental Investigation of Properties of Dielectric Materials for Use in Thin Film Capacitors", Final Report, Contract NAS8-20061, (N 68-11024), Auburn University, Alabama, Jan. 25, 1967.

4. Shimoda, R. Y.; Hsieh, E. J.; and Mayeda, K.: "Comparison of Some Physical Properties of Resistance-heat and Electron-gun Evaporated SiO Films", Vacuum, Vol. 18, May 1968, pp. 269-272.

5. Lewis, B.: "The Deposition of Alumina, Silica, and Magnesia Films by Electron Bombardment Evaporation", Microelectronics and Reliability, Vol. 3, Sept. 1964, pp. 109-120.

6. Peters, F. G.: "Dielectric Properties of Silicon Dioxide and Lead Tellurium Oxide Glass Films", Ceramic Soc. Bull., Vol. 45, Nov. 1966, pp. 1017-1021.

7. Clark, R. S.: "Reactively Sputtered SiO_2 Capacitors", Trans. AIME, Vol. 233, March 1965, pp. 592-596.

8. Sinclair, W. R.; and Peters, F. G.: "Preparation of Oxide Glass Films by Reactive Sputtering", J. Am. Ceramic Soc., Vol. 46, Jan. 1963, pp. 20-23.

9. Goldsmith, N.; and Kern, W.: "The Deposition of Vitreous Silicon Dioxide Films from Silane", RCA Rev., Vol. 28, 1967, p. 153-165.

10. Ing, S. W.; and Davern, W.: "Glow Discharge Formation of Silicon Oxide and the Deposition of Silicon Oxide Thin Film Capacitors by Glow Discharge Techniques", J. Electrochem. Soc., Vol. 112, March 1965, pp. 284-288.

11. Alt, L. L.; Ing, S. W.; and Laendle, K. W.: "Low Temperature Deposition of Silicon Oxide Films", J. Electrochem. Soc., Vol. 110, May 1963, p. 465.

12. Gregor, L. V.: "Polymer Dielectric Films", IBM Journal, March 1968, pp. 140-162.

13. Valley, D. J.; and Wagener, J. S.: "ML-1 Capacitors, A New Miniaturized Type of Plastic Film Capacitor", IEEE. Trans. on Comp. Parts, Vol. CP-11, June 1964, pp. 205-211.

14. Piera, J. T.; and Pritchard, J. P.: "Dielectric Properties of Thin Insulating Films of Photoresist Material", IEEE Trans. Comp. Parts, Vol. CP-12, March 1965, pp. 8-11.

15. Miles, J. L.; and Smith, P. H.: "The Formation of Metal Oxide Films using Gaseous and Solid Electrolytes", J. Electrochem. Soc., Vol. 110, Dec. 1963, pp. 1240-1245.

16. Ligenza, J. R.: "Silicon Oxidation in an Oxygen Plasma Excited by Microwaves", J. Appl. Phys., Vol. 36, Sept. 1965, pp. 2703-2707.

17. Kraitchman, J.; and Handy, R. M.: "Silicon Oxide Films Grown and Deposited in a Microwave Discharge", Prepared under Contract No. NAS8-11931, (N 66-32305), Westinghouse Research Labs., Pittsburgh, Pa., June 1966.

18. Fundamentals of Silicon Integrated Device Technology, Vol. 1 Oxidation, Diffusion and Epitaxy, ed. by R. M. Burger and R. P. Donovan, Prentice-Hall, Inc., Englewood Cliffs, N. J., (1967).

19. Regh, J.; and Silvey, G. A.: "Silicon Planar Chemical Polishing", Electrochem. Tech., Vol. 6, Mar/Apr 1968, pp. 155-158.