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Semi-Annual Technical Report No. 1 | *April 1 to August 31, 1964*

RELIABLE DIELECTRIC FILMS FOR MICROCIRCUITS

Prepared for:

U.S. ARMY ELECTRONICS LABORATORIES
FORT MONMOUTH, NEW JERSEY 07703

CONTRACT NO. DA 36-039-AMC-02204(E)
TECHNICAL REQUIREMENTS NO. SCL-7600B
DATED 24 OCT. 1962

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By: SAUL W. CHAIKIN GILBERT A. ST. JOHN

SRI Project PMU-4919

Object of the Research: To attempt to improve the capability of thin dielectric films used in making film capacitors in microcircuitry.

Approved: A. E. GORUM, DIRECTOR
MATERIAL SCIENCES DIVISION

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CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

I PURPOSE AND BACKGROUND

In the field of thin film electronic circuits, vacuum-deposited metals and dielectric films are used in making capacitors. For military applications, improved capability of thin dielectric films is necessary. Stanford Research Institute is studying ways of improving an existing dielectric, SiO, and methods of making new film dielectrics. The present contract is an extension of one (DA-36-039-SC-87460) aimed at increasing the dielectric breakdown strength of thin film capacitors.

Silicon monoxide is by far the most widely used film dielectric in microcircuitry. However, the limits of performance of the material are only moderately well known. The main problem seems to be that the properties of the SiO film depend on preparation conditions. We are endeavoring to expand the knowledge of the interrelationship between preparation conditions and dielectric properties. This will broaden the base of understanding of the material and, in addition, should aid in preparation of a military specification on film capacitors using reasonable values for electrical and physical performance.

Silicon monoxide is not an ideal material--reproducibility, dielectric constant, and temperature capability are among the features in which it falls short. Thus, we are seeking new film dielectrics with improved properties using the technique of sputtering, particularly reactive sputtering. This technique offers the greatest promise for chemical variation in the deposited material by compound formation and should permit deposition of desirable, but otherwise unobtainable, materials.

Finally, we are studying a dielectric breakdown problem which is related more to the properties of the electrodes than to the dielectric. This is the "edge effect" where premature dielectric failure occurs at edges of capacitor electrodes and crossing conductors.

II ABSTRACT

Edge Effect. By means of electron microscope study techniques, important properties of aluminum electrode edges were determined. It was established that (1) the surface of the film at its edge is smoother than in the planar area, (2) aluminum crystal size becomes smaller as the edge becomes thinner, (3) edge slope of practical electrode thicknesses and mask spacings is probably 5° or less, partly because diffusion of aluminum atoms on the substrate surface occurs. Through these findings, two candidate explanations for edge breakdown were ruled out: field enhancement by prominent aluminum crystals which might be expected to grow at the edge because of the slower growth rate; and significant thinning and weakening of the dielectric deposited on a sharply sloped edge. The most likely explanation at the present is that the sharp, chisel edge of a conductor or electrode causes a field enhancement of perhaps 3- to 5-fold, and, at field values far from breakdown on the planar portion of a capacitor, the edge may be near or at breakdown.

SiO Capacitor Performance. It was found that electrical leakage of SiO capacitors is enormously sensitive to deposition rate and somewhat sensitive to thickness; and that deposition rate and thickness interact in their effect on leakage. Slow (2 Å/sec) and fast (20 Å/sec) deposited films in the 2000 Å thickness range exhibit almost a million-fold difference in leakage while similar rates, for 10,000 Å films, show only a thousand-fold difference. Dissipation factor and temperature coefficient of capacitance (TCC), under the same conditions, also show extreme variation: dissipation factor from 0.003 (slow films) to 0.075 (fast, thin films), and TCC from $\lesssim$ 40 ppm/°C (slow films) to 5700 ppm/°C (fast, thin films).

It was concluded that low deposition rate and high residual gas pressure will favor the incorporation of oxygen into the film and will shift the oxygen/silicon ratio from SiO toward SiO_2. This will confer

SiO_2 electrical properties on the film resulting in reductions in dielectric constant, dissipation factor, leakage, and TCC.

Life tests of SiO capacitors at 85 and 125°C are in progress; the former for periods between 336 and 472 days (for 1300 Å and 10,000 Å capacitors) and the latter for 76 days. No pattern of dielectric failure is developing. There are only minor problems due to attachment of electrical leads.

Sputtered Dielectric Films. Reactive sputtering of metals to produce dielectric films offers an attractive route to the fabrication of materials with high dielectric constants. Initial attempts to make silicon nitride (Si_3N_4) by reactive sputtering of silicon in argon-nitrogen gave dielectric films whose infrared spectra showed the presence of an Si-N bond but also an Si-O bond through contamination.

III PUBLICATIONS, LECTURES, REPORTS, AND CONFERENCES

No publications, lectures, or reports were prepared during this period except for two scheduled letter-type reports.

Two conferences were held with U.S. Army Electronics Laboratories representatives for the purpose of reviewing plans and progress under the contract. On April 29th, Saul Chaikin and Gilbert St. John of Stanford Research Institute visited William Weintraub and Isaac Pratt of the Electronics Laboratories. On July 6th, Mr. Weintraub visited Messrs. Chaikin and St. John.

IV FACTUAL DATA AND DISCUSSION

A. Dielectric Breakdown at Conductor Edges -- The Edge Effect

Failure of a dielectric layer often occurs at the edge of a conductor. Thus, in a capacitor configuration, dielectric breakdown may occur between the edge of one electrode and a portion of the other electrode. One explanation offered is that a sharp step exists at the edge of a conductor vapor-deposited through a mask.[1] The dielectric layer at the corner of this step will be especially thin and therefore quite vulnerable to breakdown at a voltage lower than that of the planar section of the dielectric.

In a later paper,[2] another author substantiated the edge breakdown effect, ascribed it to the high electric fields which occur at sharp step at the lower electrode edge, and offered a solution based on (a) electropolishing of the first electrode, and (b) slight shifting of the dielectric mask during deposition to make the dielectric edge more diffuse.

In our study of the edge breakdown problem we decided it was necessary to learn of the actual structure of the edges of aluminum electrodes. Is there really a sharp step at the edge? What is the mask shadow width (penumbra) of the electrode edge? Is there an aluminum crystal growth effect at an edge which could influence breakdowns?

Toward this end, electron microscope techniques were applied for examining aluminum film edges by replicas, transmission, and cross-section methods. Figure 1 shows an aluminum deposition setup which emphasizes the critical relationship of source width, mask spacing, and penumbra. The inset in the figure shows the information gained by the three electron microscope techniques.

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[1] G. Siddall, "Vacuum Deposition of Dielectric Films for Capacitors," Vacuum, 9, 279 (1960).

[2] A. E. Lessor, Jr., "Fabrication and Reliability of Thin Film Cross-overs and Terminations," I.E.E.E. Transactions on Component Parts, Vol. CP-11 (No. 2) 49 (1964).

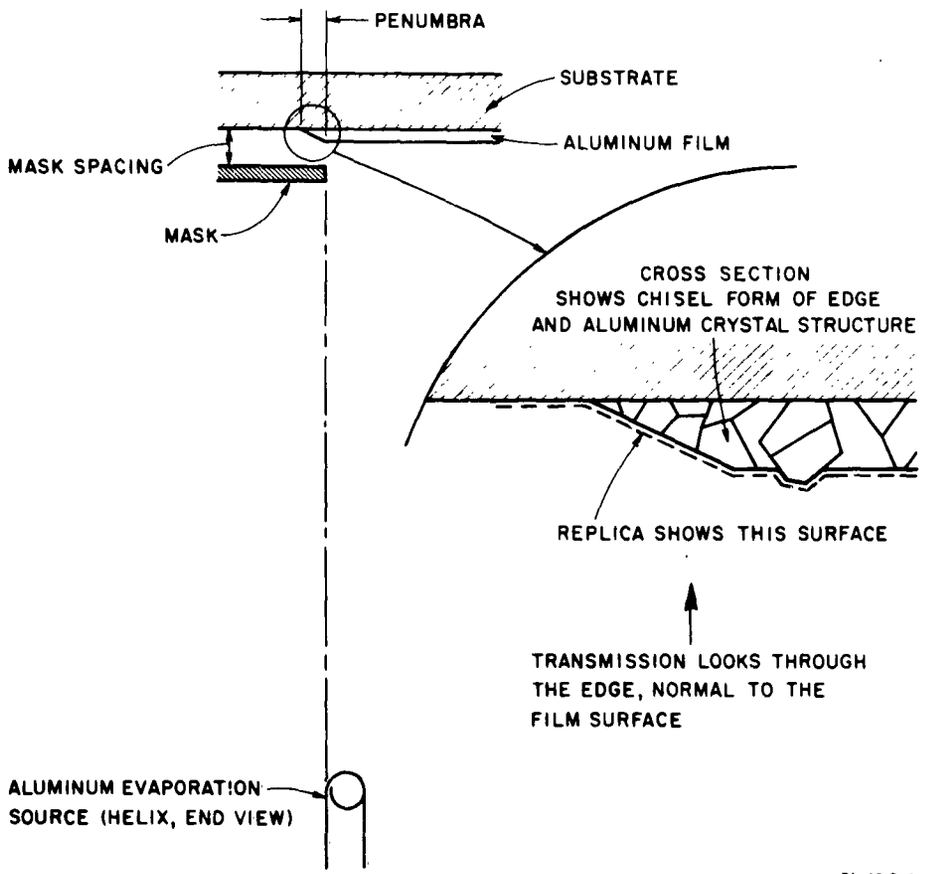

FIG. 1 FORMATION OF A TAPERED ALUMINUM EDGE (Penumbra) DURING EVAPORATION
Inset: Application of Electron Microscope Techniques to Study of Edge Structure

The penumbra is the region at the edge of the film where the thickness diminishes to zero. It occurs because the electrode evaporation source is not a point source and because the mask edge is a finite distance from the substrate, in practice, 25 to 75 microns.

Edge granularity hypothesis--Because edges of film conductors are thin the deposition rate must be lower. A low deposition rate is known to produce a granular deposit, and therefore, a rougher surface.[3] Asperities on rough surfaces can act to enhance electric fields and, therefore, it seemed reasonable to suspect that the higher fields at prominent crystal grains in edges are the source of premature dielectric failure.

We studied the crystalline character of aluminum films at edges and on the planar portions looking for prominent crystals at the edges. Electron micrograph replicas of the planar portions of two aluminum films are shown in Figs. 2 and 3. The films were deposited at comparable rates (1000 Å/min) and are of comparable thickness (about 2000 Å) but were deposited at different substrate temperatures: room temperature and 150°C. To the naked eye both are good, specularly reflecting aluminum mirrors. With intense lighting at grazing incidence, a faint bluish tinge is apparent, characteristic of light scattering by fine particles. Both films show a generally fine-structured deposit of aluminum crystals but with a random scattering of larger crystals. The heated substrate produced fewer but larger and better formed crystals.

Figure 4 shows a surface replica of the edge of the film of Fig. 2, but at a lower magnification in order to include the entire penumbra. The population of layer crystallites diminishes, almost discontinuously, only a short distance away from the edge of the planar section. The fine aluminum crystals, which form the bulk of the film, become smaller as the edge of the penumbra approaches. A half-tone reproduction

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[3] L. Holland, "Vacuum Deposition of Thin Films," 5th Printing, Chapman and Hall, Ltd., 1963, p. 207, 327.

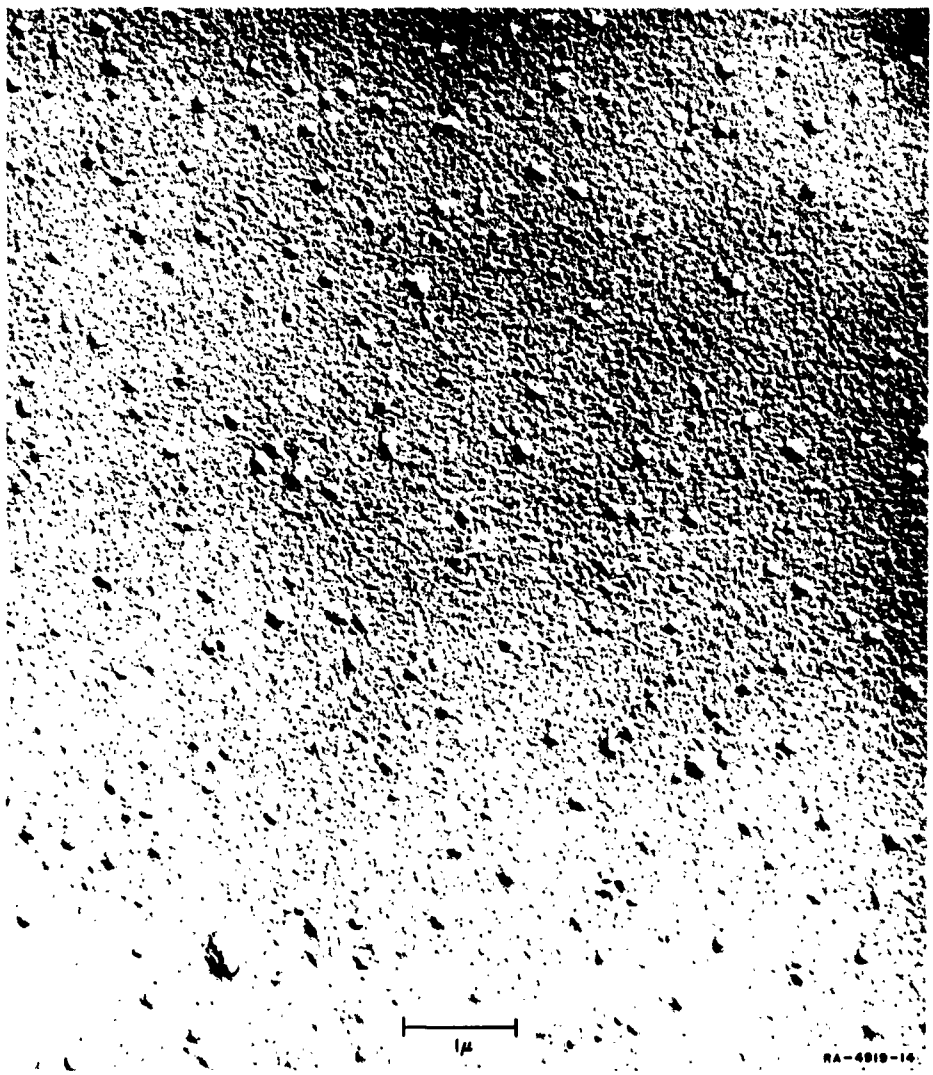

FIG. 2 SURFACE REPLICA OF ALUMINUM FILM DEPOSITED ON SUBSTRATE AT ROOM TEMPERATURE

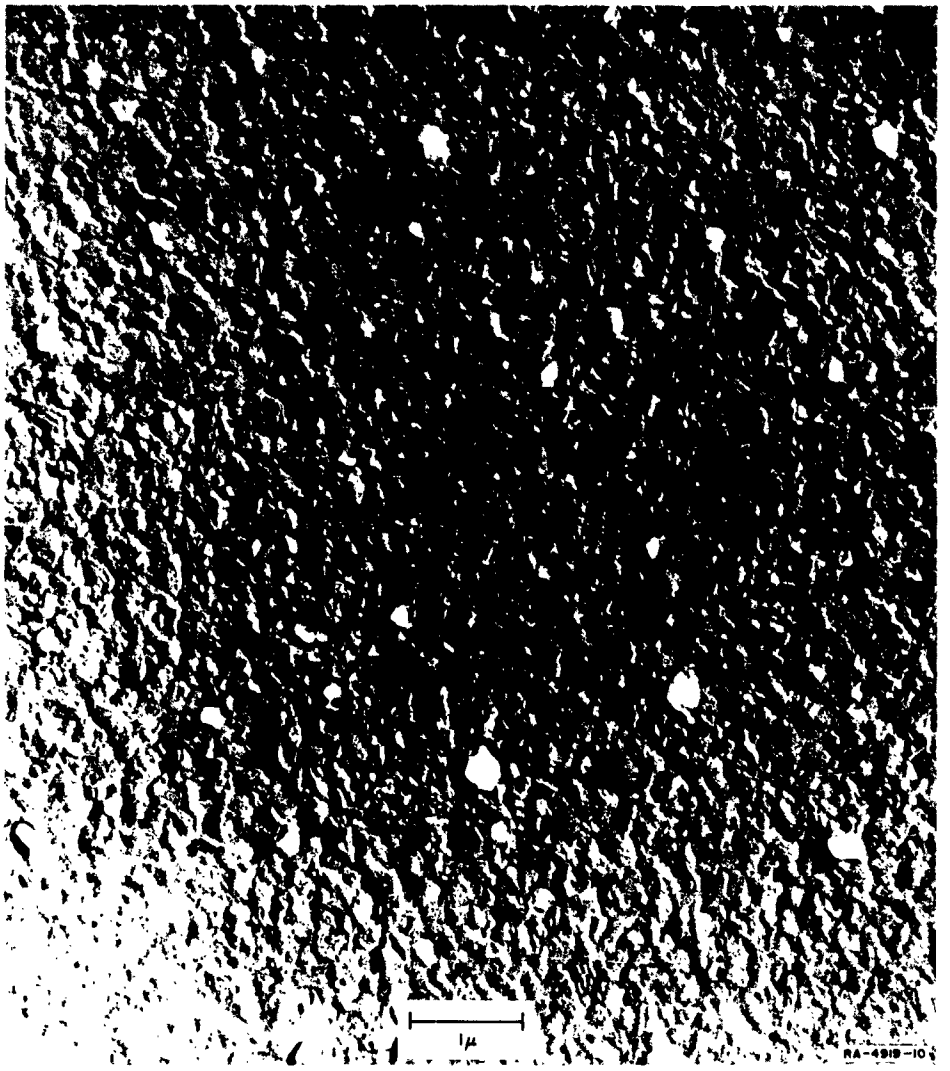

FIG. 3 SURFACE REPLICA OF ALUMINUM FILM DEPOSITED ON SUBSTRATE AT 150°C

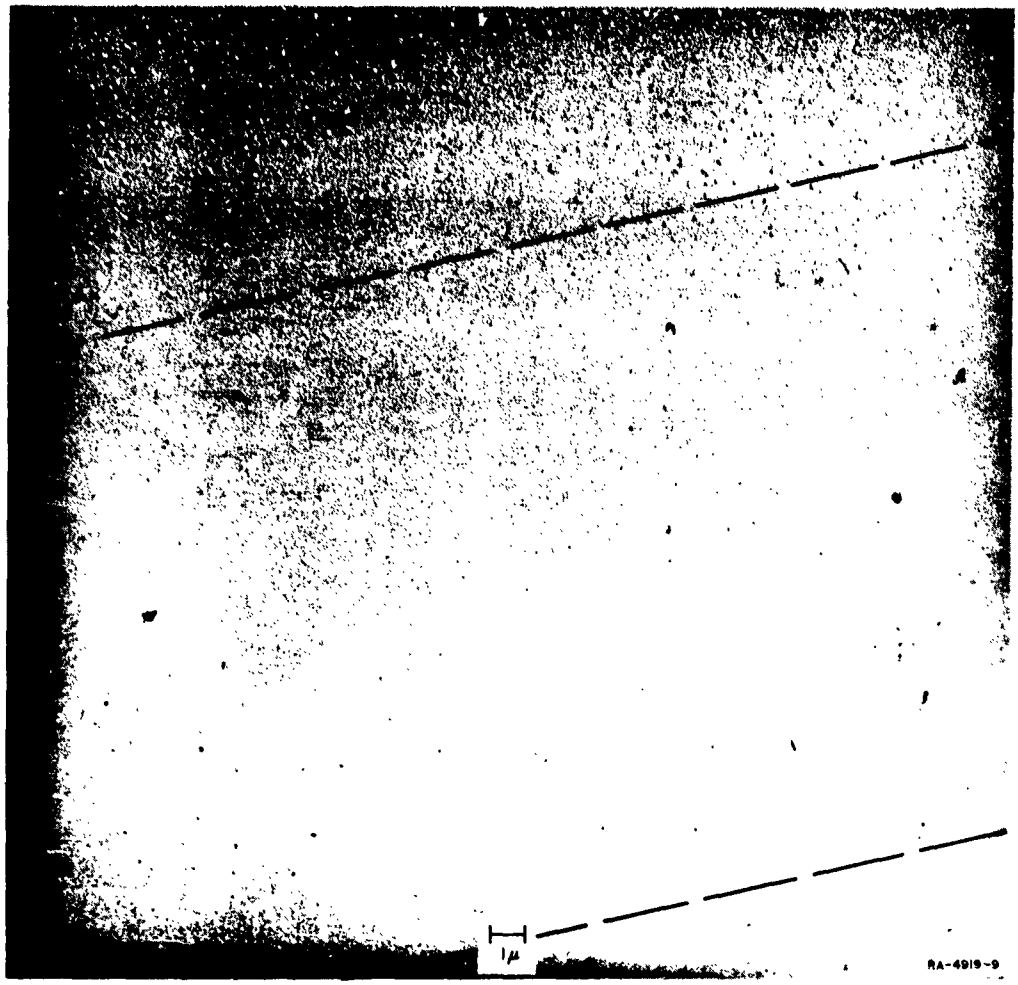

FIG. 4 SURFACE REPLICA OF ALUMINUM FILM PENUMBRA OF FIG. 2

obscures this fine detail somewhat. However, it is obvious that the lower deposition rate in the penumbra does not favor granularity. Possibly the tendency to grow larger crystals at the slower deposition rate is overridden by the low thickness at the edge. The film deposited at elevated temperature behaved in a similar manner.

In Fig. 4 the mask spacing was 0.007-inch (175 μ), the source-to-substrate distance was 203 mm, and the source coil diameter was 15 mm. Assuming that the evaporating metal atoms behave like light rays, the calculated penumbra is 12.9 μ. The observed penumbra, the distance

between the dashed lines in Fig. 4, is about 20 μ. The discrepancy might be due either to surface migration of aluminum atoms during deposition, or to rebounding of aluminum atoms from the substrate and the mask backside.

The same general pattern of small and large crystals was also seen by means of transmission electron microscopy of a 4000 Å aluminum film deposited on a thin (est. 500 Å) SiO film mounted directly on an electron microscope grid. (SiO is structureless in the electron microscope).

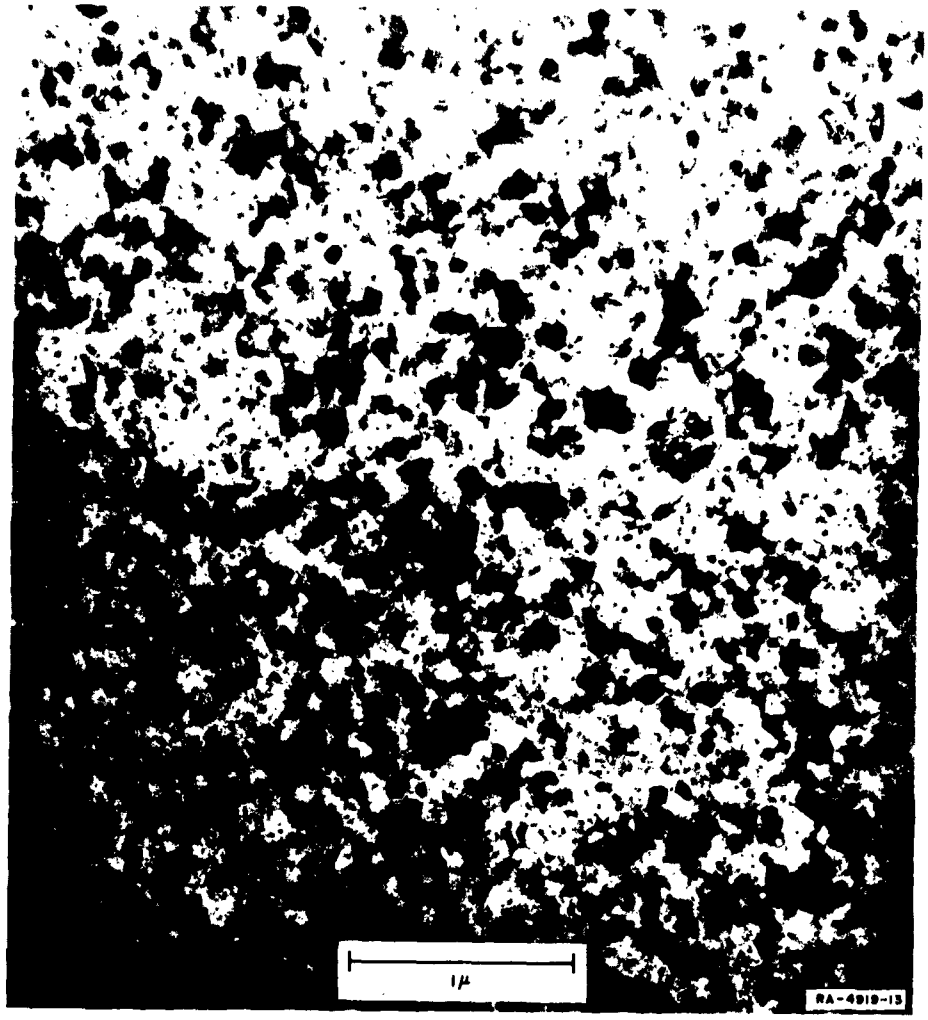

FIG. 5 TRANSMISSION ELECTRON MICROGRAPH OF 4000 Å VACUUM-DEPOSITED ALUMINUM FILM

Figure 5 is a view through the aluminum film. The dark and light shapes about 1000 Å in size are individual crystals of aluminum. Various crystal orientations to the electron beam will result in different contrast. The banded structures in some of the crystals are diffraction effects, most likely due to thickness variations. An important point is that a number of much larger than average crystals, around 2000 to 3000 Å, may be seen. These correspond to the prominent crystals of Fig. 2. Another feature, not easily visible on the replica picture, is tiny crystallites about 100-250 Å in size.

The edge of the same film is shown in Fig. 6, also in transmission, but at lower magnification in order to show the entire penumbra. The abrupt disappearance of the larger crystals as the film begins to become

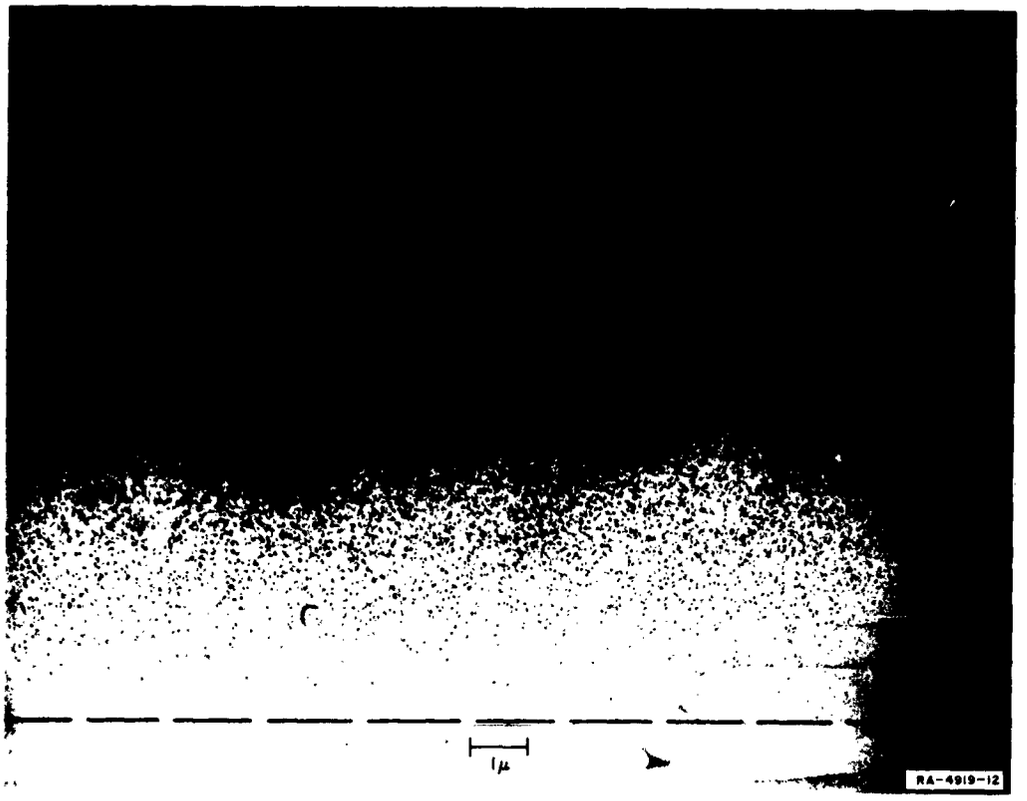

FIG. 6 TRANSMISSION ELECTRON MICROGRAPH OF EDGE OF 4000 Å VACUUM-DEPOSITED ALUMINUM FILM

thin is very apparent. The gradual reduction in size of the smaller crystals throughout the taper may easily be seen. The water mark in the lower right area of the picture should be disregarded.

The penumbra in Fig. 6 is about 6.5 μ compared to a calculated value of 3.8 μ (mask spacing 51 μ, source-to-substrate distance and coil diameter as before).

Related experiments were carried out at IBM with evaporated tin films.[4,5] For magnetic reasons it is desirable to eliminate the sloping edges of vacuum-deposited superconducting tin films. It was found that elevation of the substrate temperature or deposition in ultra high vacuum solved the problem by grossly increasing the crystal size of the resulting deposit. The crystals were large relative to the film thickness so that, at edges, where less metal was available, the film consisted of isolated crystals.

Edge slope hypothesis--Schematic sketches of conductor edges always suggest a considerable slope,[1,2] say 30 to 60°; one author even proposed a vertical step. A dielectric deposited on such a slope would suffer a reduction in effective thickness. Thus, its thickness in the direction normal to the substrate would be the same as on the planar portions of the conductor, but its thickness in the direction normal to the slope (the important direction for dielectric breakdown) would be diminished by the cosine of the slope angle. For a 45° slope the thickness would be reduced by the factor 0.71. This would make a significant differential in breakdown strength between the planar and sloped portion of the dielectric. Furthermore, deposition of SiO on a sharply sloping surface results in a highly stressed and mechanically unstable film.[6] One would expect that these factors will reduce the breakdown strength of SiO.

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[4] M. E. Behrndt, R. H. Blumberg, and G. R. Giedd, "On the Influence of Aggregation on the Magnetic Phase Transition of Evaporated Superconducting Thin Films," IBM Journal, 4, 184 (1960).

[5] H. L. Caswell, "Effect of Residual Gases on Superconducting Characteristics of Tin Films," J. Appl. Phys., 32, 105 (1961).

[6] J. Priest, H. L. Caswell, and Y. Budo, "Stress Anisotropy in Silicon Oxide Films," J. Appl. Phys., 34, 347 (1963).

The edge slope is thus an important quantity in determining breakdown strength. High values ($> 30^{\circ}$) will yield stressed films which are significantly thinner than adjacent, planar portions. Calculated values for slopes based on light ray behavior are not necessarily reliable because of the mobility of atoms on surfaces during deposition. The slope of the edge shown in Fig. 4 is about 0.5° (film thickness 0.2 μ, penumbra 20 μ). The mask spacing for Fig. 4 (0.007 inch) is probably greater than generally employed.

Figure 6 represents a more realistic mask spacing: 0.002 inch. The film thickness is 0.4 μ and the penumbra width estimated as 6.5 μ. Thus the slope is 3.5°.

The dielectric thickness reduction on a slope of even as much as 5° will be about 0.5%, an entirely insignificant quantity, with respect to premature breakdown. Anisotropy effects,[6] on mechanical properties at least, are not large at 5°. It was concluded that great slope is not the factor which promotes dielectric breakdown at edges.

Field enhancement hypothesis--The finding that conductor edges have very low angle slopes gave rise to the hypothesis that the sharp edge of the conductor can enhance an electric field. Thus, if the potential across the planar portion of crossing conductors, or of a capacitor, is 50 v for a 10,000 Å thick dielectric, the field will be 5 v/1000 Å. In the previous contract period it was shown that the average dielectric breakdown strength of SiO was 20 v/1000 Å. If a four-fold enhancement of the 5 v/1000 Å electric field occurred at the edge of the conductor the SiO at the edge would be stressed to its maximum average breakdown strength.

Field enhancement has been well studied in recent years in connection with field emission cathodes.[7] For a sharp tungsten needle of tip

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[7] L. Marton, "Advances in Electronics and Electron Physics," Academic Press, Inc., 1956, Vol. VIII, p. 89.

radius 1000 Å, and a plane anode spaced 100 μ away, a field enhancement factor of 4000 may be achieved.

For the case of an electrode edge, the field enhancement cannot be so great because the needle is replaced by a structure akin to a razor edge and the reference anode is parallel to the conductor plane. W. Hansen of SRI's Applied Physics Laboratory has derived a formula for field enhancement, ρ, in the conductor edge situation:

$$\rho = \frac{1}{\sqrt{2}} \left(\frac{D}{r_0} \right)^{\frac{1}{2}}$$

where D = distance between edge and anode and r_0 = edge radius.

For example, if r_0 = 200 Å and D = 4000 Å, then a field enhancement of 3.2 will occur at the edge.

Partially successful attempts have been made to determine the edge radius by examining cross-sectioned aluminum conductors in the electron microscope. Two views of such a section from a 1500 Å thick film are shown in Figs. 7 and 8 . The fragility of the sectioned edge has made it difficult to obtain a continuous length. Figure 7 at low magnification shows much of the tapered edge, but has a break in the section. The tip of the edge is best seen in the high magnification picture. Because the growing film has an unsmooth surface it is hard to arrive at a figure for edge radius. If an envelope is drawn around the edge, a radius of 200-250 Å is obtained. However, if the irregularities at the edge are active in field enhancement, then the effective radius will be smaller and the field at the surface higher.

No experimental tests of the field enhancement hypothesis of edge breakdown have been undertaken. Edge breakdown should depend on the aluminum film thickness, the mask spacing , and dielectric thickness in a predictable manner if the hypothesis is correct.

The electron microscope cross-sectioning technique has yielded interesting pictures of capacitors and of the planar portions of aluminum films. Because they do not relate to edge breakdown, they are presented in the Appendix.

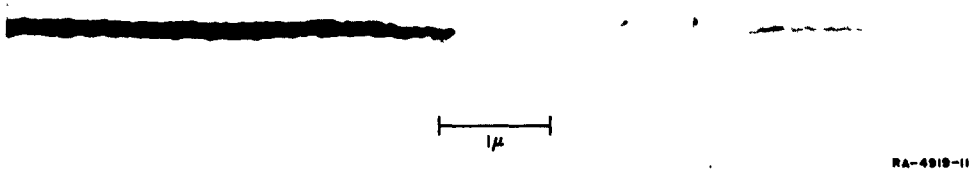

FIG. 7 CROSS SECTION OF 1500 Å ALUMINUM CONDUCTOR EDGE AT LOW MAGNIFICATION

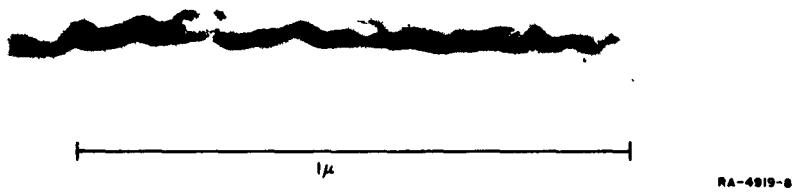

FIG. 8 CROSS SECTION OF 1500 Å ALUMINUM CONDUCTOR EDGE AT HIGH MAGNIFICATION

B. Properties and Performance of SiO Capacitors

1. Interrelation of Deposition Parameters (Rate and Dielectric Thickness) with Dielectric Properties

The influence of SiO deposition rate on its dielectric properties is fairly well known. The fact that film thickness is a related parameter is not as well known. The purpose of the investigation described below was to confirm and to obtain quantitative details regarding these interrelationships.

The vacuum system and deposition equipment used in this study are the same as that used in the preceding contract, No. DA-36-039-SC-87460 and they are described in the Final Report on that contract (April 15, 1964). Briefly, a Consolidated Vacuum Corporation unit, Model PS-40A, with a 6-inch baffled diffusion pump and an 18 x 30-inch glass bell jar was used. The system will reach 10^{-5} torr in 30 minutes and 10^{-6} torr in about four hours with the usual apparatus load.

Deposition equipment consists of a single substrate, four-position rotary mask changer and a source cluster 15 inches below the substrate. Substrate heating may be carried out with an aluminum contact heater block.

a. Leakage Resistance

During the present report period a comprehensive study was made of leakage resistance of silicon monoxide capacitors at various voltages. The SiO was deposited at three different rates: about 2, 6, and 20 Å/sec. Two dielectric thicknesses, 2000 Å and 10,000 Å, were studied. All capacitors had aluminum electrodes about 500-1000 Å thick and were deposited at a pressure of about 10^{-5} torr on a heated substrate: 100-150°C for the aluminum and 200-235°C for the SiO. The pattern was the "tab" pattern of the previous contract. Each capacitor had an area of 0.117 cm^2.

Leakage was measured using a multitapped battery and a 100 K Ω series resistance. A microvoltmeter measured the voltage across the resistor caused by the leakage current. Contact to the capacitor electrodes was made by indium soldered leads. The sensitivity of this combination was 5 x 10^{-11} amperes leakage at voltages from 3 to 22 volts.

Leakage of the SiO film was found to be enormously sensitive to deposition rate and somewhat sensitive to thickness (Figs. 9 and 10). The slowly deposited films in both thickness series were the best, having resistances in the range of 10^5 to 10^6 M Ω at 3 v. The fastest films (3-105 and 3-109) in the 2000 Å series were very leaky, 5 M Ω at 3 v and 2 M Ω at 9 v; the intermediate films (3-103 and 3-108) had values in between. The fast (3-110) and intermediate (3-107) films in the 10,000 Å series were appreciably superior to their thin counterparts. Thus, increasing the thickness will permit a faster deposition rate for the same leakage.

At test voltages up to 22 volts the resistance behavior was non-ohmic: values fell to between one-half and one-twentieth the 3-volt values. The slower films tend to be somewhat more ohmic than the faster ones.

b. Dissipation Factor

Inspection of Figs. 9 and 10 will show that dissipation factor is also very sensitive to deposition rate and, for the highest rate, to thickness. For convenience those values are tabulated below:

	Dissipation Factor		
Dielectric Thickness	Slow Rate ~ 2 Å/sec	Medium Rate ~ 6 Å/sec	Fast Rate 20 Å/sec
2,000 Å	0.004	0.006	0.07
10,000 Å	0.003	0.007	0.033

Again, the greater dielectric thickness appears to ameliorate the degradation of a physical property which accompanies a faster deposition rate.

c. Temperature Coefficient of Capacitance (TCC)

The effect of temperature on capacitance and dissipation factor was measured on 2000 Å and 10,000 Å SiO capacitors. Once more, a very

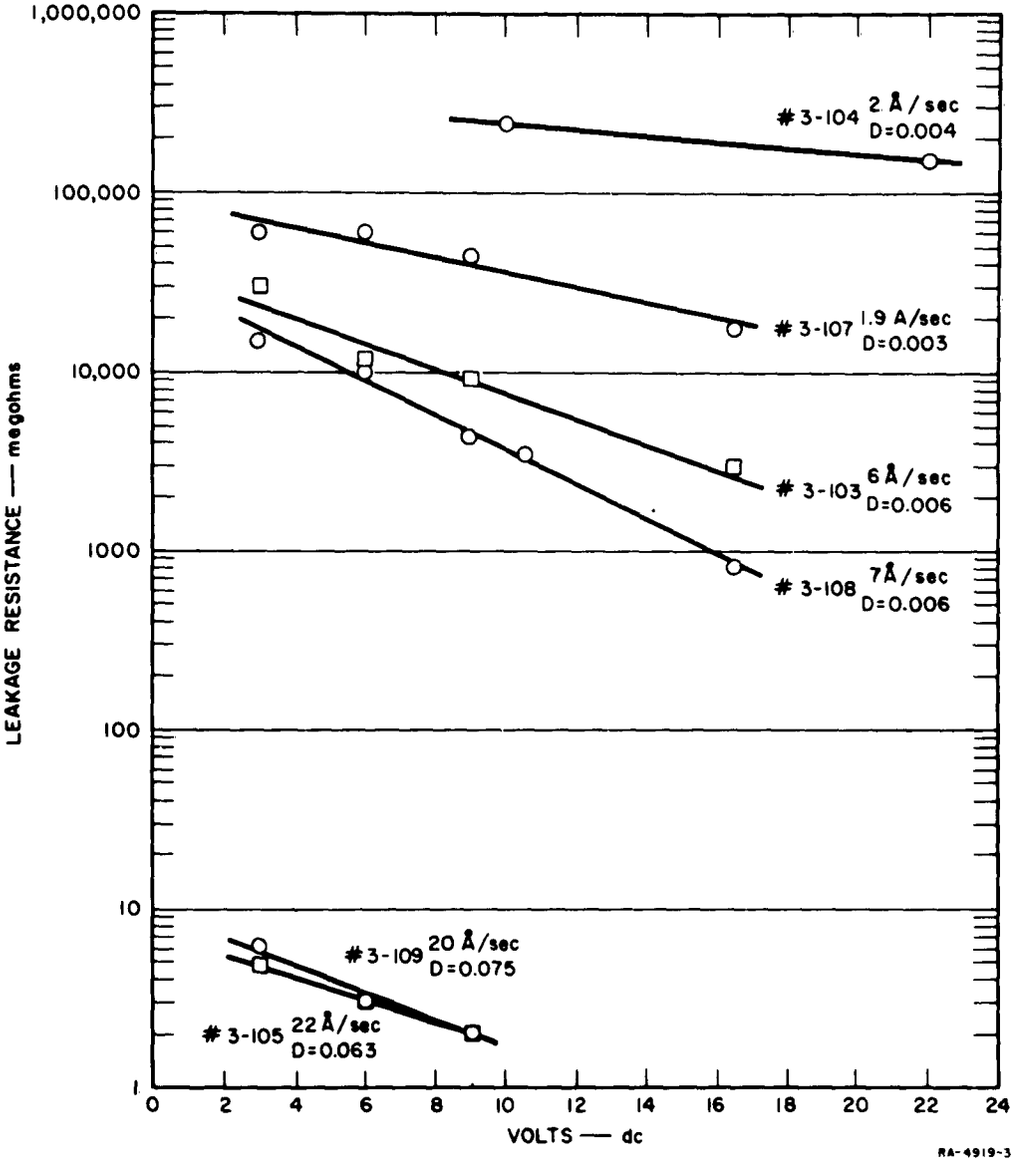

FIG. 9 LEAKAGE RESISTANCE OF THIN (2000 Å) SiO FILMS AS A FUNCTION OF DEPOSITION RATE

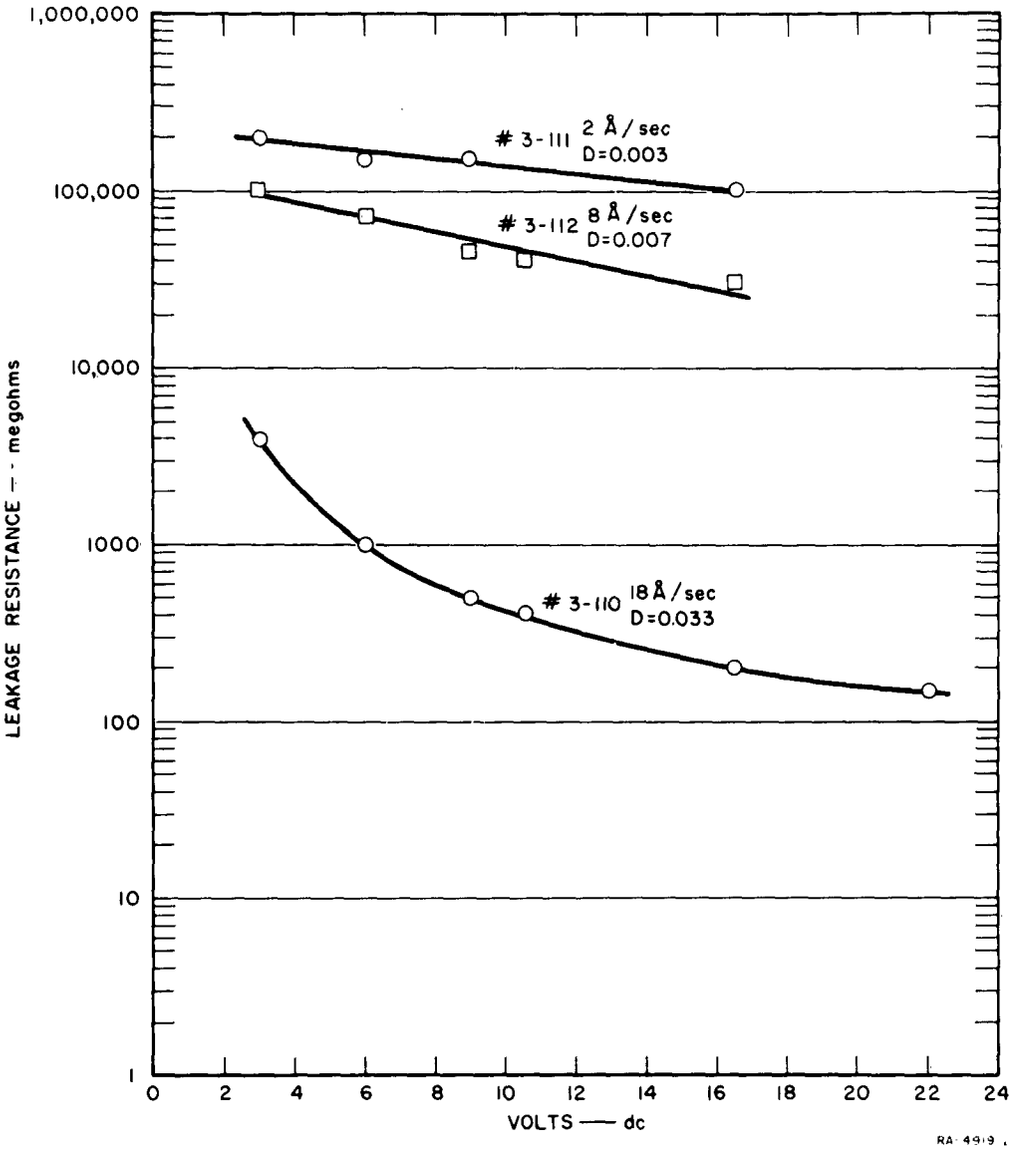

FIG. 10 LEAKAGE RESISTANCE OF THICK (10,000 A) SiO FILMS AS A FUNCTION OF DEPOSITION RATE

large difference in behavior between slow- and fast-deposited films was observed (Table I). The capacitance of the slowly-deposited 2000 Å film was virtually unchanged over the temperature range 25° to 125°C, whereas the fast film had a high TCC which worsened rapidly as the temperature was raised. Dissipation factor also suffered with temperature, more for the fast film than the slow one. Leakage resistance of the fast film deteriorated rapidly to 300 K Ω at 125°C.

For the 10,000 Å capacitors TCC, dissipation factor, and leakage were not so sensitive to temperature, in a fast deposition, as the thinner films.

Practically speaking, a fast-deposited film would probably be suitable if it were 10,000 Å or more and if the ultimate in TCC, dissipation factor, and leakage were not required. Thin (2000 Å) films may freely be employed but it is imperative that the deposition be slow.

d. Literature Comparison and Discussion

Some of the findings given above are not new. Listed below are a number of papers in the literature dealing with deposition rate effects. However, a comprehensive study such as this one permits consolidation of a number of related parameters. At least one benefit would be the additional insight needed for preparation of a military specification on capacitors.

G. Siddall, "Vacuum Deposition of Dielectric Films for Capacitors," Vacuum, 9, 274 (1960). Increasing deposition rate from 0.55 to 29.5 Å/sec resulted in elevation of the loss angle tangent from 0.010 to 0.037. Leakage resistance was lower for faster rates of deposition.

D. B. York, "Properties of Evaporated Thin Films of SiO," J. Electrochem. Soc., 110, 271 (1963). Deposition rates from 10 to 101 Å/sec produce dielectric films with dissipation factors from 0.002 to 0.12, respectively, and leakage resistance from 10^5 M Ω to 1 M Ω, respectively. Leakage resistance is ohmic up to 1 volt and non-ohmic between 1 and 10 volts. The higher the oxygen pressure up to 10^{-4} torr during evaporation, the lower the leakage current.

Table I

EFFECT OF TEMPERATURE ON CAPACITANCE, DISSIPATION FACTOR, AND LEAKAGE FOR THIN AND THICK SiO CAPACITORS

Temp. °C	Thin (2000 Å) Capacitors							Thick (10,000 Å) Capacitors							
	Capacitance and TCC				Dissipation Factor		Leakage Resistance, MΩ, of Fast Capacitor at 3 v	Capacitance and TCC				Dissipation Factor		Leakage Resistance, MΩ at 9 v	
	Fast (20 Å/sec)		Slow (2 Å/sec)		Fast	Slow		Fast (18 Å/sec)		Medium (8 Å/sec)		Fast	Medium	Fast	Medium
	Cap, pf	TCC ppm/°C	Cap, pf	TCC ppm/°C				Cap, pf	TCC ppm/°C	Cap, pf	TCC ppm/°C				
25	3130	1600	2640		0.054	0.002	10	720	714	635	260	0.023	0.007	2000	50000
55	3310	2400	2640	≤ 40	0.096	0.003	3	735	1130	640	260	0.038	0.009	500	15000
85	3500	5700	2650		0.14	0.0035	1.5	760	1880	645	390	0.066	0.015	--	5000
125	4400		2650		0.35	0.005	0.3	810		655		0.125	0.024	35	850

H. Hirose and Y. Wada, "Dielectric Properties and DC conductivity of Vacuum-Deposited SiO Films," Jap. J. Appl. Physics, 3, 179 (1964). Leakage and dielectric loss decrease with decreasing deposition rate. Degree of vacuum is a strong influence in the range 10^{-5} to 10^{-3} torr: better vacuum will produce films with higher dielectric loss.

F. W. Schenkel, "Thin Film Capacitor Parameter Studies," Proceedings of the Electronic Components Conference, May, 1964, p. 194. TCC of a 40 Å/sec film can be improved from 1150 ppm to 110 ppm by a 30 minute 400°C treatment.

The film dielectric called "silicon monoxide" can range from SiO possibly to, or close to, SiO_2. The film with low oxygen content has high dielectric constant, dissipation factor, leakage, and TCC. Any deposition or processing procedure which favors incorporation of oxygen into the film will shift the oxygen/silicon ratio toward SiO_2 and will yield a film with reduced dielectric constant, dissipation factor, leakage, and TCC.

There are three important parameters for the oxygen enrichment of a film. Two pertain to the bell jar and one outside. Low deposition rate will permit reaction of evaporating SiO with residual gas molecules, particularly oxygen and water:

$$SiO + \tfrac{1}{2}O_2 \rightarrow SiO_2$$

$$\text{or } 2SiO + \tfrac{1}{2}O_2 \rightarrow Si_2O_3 \text{ (that is, } SiO_{1.5})$$

$$\text{and } SiO + H_2O \rightarrow SiO_2 + H_2$$

The other parameter, obviously, is high residual gas pressure. High gas pressure, practically, means 10^{-3} to 10^{-5}. Outside the bell jar heat treatment will permit reaction with atmospheric oxygen.

The low oxygen material is thought to be conducting via ionic impurities, such as silicon ions. This is consistent with a high dissipation factor, dielectric constant, and TCC. Oxidation may lower all these quantities by tending to immobilize the silicon through formation of silicon-oxygen bonds in a glassy network.

The beneficial effect of increasing dielectric thickness of fast films (low oxygen content) may be simply the usual one of increasing the current path, thus reducing both leakage and dissipation.

2. Progress of Life Tests at 85° and 125°C

Two series of life tests of SiO capacitors are in progress at the present time. An 85°C series was started on April 30, 1963 and was intended to test the effectiveness of methods of improving capacitor reliability, developed under the previous contract.

A 125°C series, started on July 13, 1964, was intended to last a few days or weeks to determine whether or not 10,000 Å SiO capacitors could operate at that temperature with a standing potential of 50 volts or more. They did operate through this short period, with 67.5 volts, but it was decided to continue the monitoring through the life of the present contract.

a. 85°C Life Tests

A full description of capacitor construction and the test circuitry is given in the Final Report (April 15, 1964) under the previous contract. There are two SiO thickness series under test: ~ 1300 Å and 10,000 Å. The former are under 10 v and the latter under 47 v dc standing potential. Both have aluminum electrodes in the standard tab pattern. Lead attachment to the aluminum was initially by silver-epoxy cement and then by indium solder. The latter method was far more satisfactory and, in fact, the major problem in this life test program has been intermittent lead failure, probably through a polarization effect at a connection interface. The last complete report on these life tests was in the Final Report of April 15, 1964 and those results covered the period through March 19, 1964 (up to 277 test days).

At that time the results for the 10,000 Å capacitors were as follows: of the 100 capacitors on test, 90 experienced no dielectric breakdown whatsoever. The 11 breakdowns which occurred on 10 capacitors were of the self-healing transient type. No capacitor had permanently shorted. For 88 of 100 capacitors, capacitance and dissipation factor (C and D) were in excellent agreement with the values obtained

immediately after fabrication. For most of the other 12 capacitors, the lead problem interfered with an accurate reading but experience with restoring lead integrity (indium soldering over the old silver-epoxy and pulsing with AC) has suggested that these capacitors are as good as those for which acceptable readings were obtained. It is still possible that at the conclusion of the test a method for re-establishing good contact will be found and final valid readings can be taken.

For the present report, readings of C and D for both the thick and thin series were taken on 9/29/64. The results are presented in the form of a comparison of the status on 3/19/64 with the status on 9/29/64 (Tables II and III). The only changes in status are due to leads re-establishing contact through AC treatment, or breaking contact. Capacitors called "OK" exhibited no significant change in C or D since fabrication.

To illustrate the use of the Tables, Substrate No. 352 (Table II) on 3/19/64 had 6 capacitors OK out of the 10 on the substrate; the remaining 4 suffered bad contact. On 9/29/64, 3 of these 4 capacitors were restored to a satisfactory condition and one of the previously OK capacitors now had open circuit, leaving a net of 8 OK capacitors.

For the thick series, a net gain in satisfactory capacitors was observed: on 3/19/64, 88 out of 100 were satisfactory; on 9/29/64, 99 out of 100. Of the 7 unsatisfactory, 2 were OK but were lost through substrate breakage.

The status on the thin capacitors on 3/19/64, that 57 out of 60 were OK. On 9/29/64, 10 capacitors on 2 substrates exhibited a rise in D from 0.004 up to 0.010-0.035. In all likelihood this is a lead problem and should not be counted as a failure. Perhaps in a later measurement satisfactory connection will be accomplished.

Table II

PROGRESS OF 85°C LIFE TESTS OF 10,000 Å SiO CAPACITORS

Substrate No.	Status on 3/19/64		Status on 9/29/64			Total No. of Days Under Test
	Of 10 Capacitors, No.OK	No. with Faulty Contact	No. which Reestablished Good Contact	No. of Newly Developed Faulty Contacts	Total No.OK	
320	10	0	–	0	10	472
323	10	0	–	0	10	471
325	10	0	–	0	10	465
352	6	4	3	1	8	378
353	9	1	1	0	10	377
354	9	1	1	2*	8	372
361	6	4	2	1	7	339
363	9	1	1	0	10	337
364	9	1	1	0	10	336
365	10	0	–	0	10	336

* Lost through substrate breakage on handling.

Table III

PROGRESS OF 85°C LIFE TESTS OF 1300 Å SiO CAPACITORS

Substrate No.	Status on 3/19/64		Status on 9/29/64			Total No. of Days Under Test
	Of 10 Capacitors, No.OK	No. with Faulty Contact	No. which Reestablished Good Contact	No. of Newly Developed Faulty Contacts	Total No.OK	
335	10	0	–	0	10	415
337	10	0	–	7*	3	413
338	10	0	–	3*	7	410
339	9	1	1	0	10	410
355	8	2	1**	0	8	358
366	10	0	–	0	10	336

* Faulty contact symptom is high dissipation factor, about 0.01 to 0.035.

** Formerly open circuit; contact reestablished but with D = 0.15.

b. 125°C Life Test

For a cursory look at the performance of SiO at 125°C, a unit of 10 capacitors was fabricated using our tab pattern (capacitor area = 0.117 cm^2). The SiO deposition rate was 8 Å/sec and the thickness was 10,000 Å. The capacitance values of the 10 capacitors ranged from 625 to 655 pf and the dissipation factor was 0.007. Three of these capacitors were wired into a test circuit with 67.5 v standing potential from a dry cell. Leads were attached with indium solder. The unit was placed in an oven at 125°C and the test initiated on July 13.

On first raising the temperature the capacitance values rose about 3% and the dissipation factors increased to the 0.02 to 0.03 range. No significant change in these values was detected in almost daily checks through July 29. On that day the unit was removed from the oven for a microscope check of transient, self-healing shorts and only one capacitor had one such short. No sign of degradation, such as peeling or discoloration, was apparent. The unit was returned to the test condition within one hour.

After July 29, checks were made every week or two and the C and D values remained stable. The most recent measurement was made on 9/29/64 (76 days). The test is still in progress and all three capacitors are functioning normally.

C. Sputtered Dielectric Films

Cathodic sputtering is a gas discharge process in which metal is removed from the cathode. The positive ions of the gas, formed in the discharge, bombard the cathode (target) and this causes atoms of the cathode to be ejected into the plasma. They deposit, by diffusion, on surfaces which are accessible, including clean substrates. It is, therefore, a method of forming metal films for microelectronic purposes.

Argon is the gas usually used for sputtering because it is the heaviest, inert gas of reasonable price. Atomic weight is important because ejection of target atoms involves impact. Inertness is important when it is desired to sputter a reactive metal. However, incorporation of small amounts of reactive gases in the argon will yield a compound of the metal. For example, titanium sputtered with argon containing about 0.2% of oxygen produced a titanium dioxide film.[8] This variation of the sputtering technique is called reactive sputtering.

Reactive sputtering of metals to produce dielectric films is carried out at reduced pressure in a vacuum system and thus is a vacuum process, readily compatible with vacuum evaporation and glow discharge cleaning. Its main attraction is that it offers a route to the fabrication of materials with dielectric constants higher than SiO (ϵ = 5 to 6) or SiO_2 (ϵ = 3.8).

1. Silicon Nitride

Our initial attempt to produce a new sputtered dielectric involved silicon nitride (Si_3N_4). This material had been made in thin film form by a pyrolysis technique at 800°C.[9] The film's dielectric properties were attractive: dissipation factor < 0.0001 at 1 kc,

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[8] T. K. Lakshmanan, C. A. Wysocki, and W. J. Slegesky, IEEE Trans. on Component Parts, Vol. CP-11, 14 (1964).

[9] C. R. Barnes and C. R. Geesner, "Silicon Nitride Thin Film Dielectric," J. Electrochem. Soc., 107, 98 (1960).

dielectric constant 12.7 at 25°C, leakage resistance of a 0.5 mil film (area unspecified) 150 M Ω at 100 v dc, temperature capability 600°C.

Sputtering of silicon was attempted in argon-nitrogen mixtures, 5% and 50% in nitrogen. Films were sputtered onto sodium chloride crystals for infrared analysis, and onto 7059 substrates with aluminum electrodes for capacitor tests. Gas pressure was 10-20 μ and discharge conditions 2.5 to 3.5 kv at 2 to 5 ma. Deposition periods ranged from 45 minutes to 2 hours and film thicknesses were around 1000 to 2000 Å.

Infrared spectra of films confirmed that silicon nitride was formed; however, an absorption band suggesting contamination by a silicon oxide was also observed. Two capacitor runs using the tab pattern were made yielding capacitance values of 5800 and 3500 pf and dissipation factors of 0.004 and 0.021. Thickness varied over the surface of the deposit, preventing an accurate determination of dielectric constant. If future effort in this direction is made, contamination from residual gases will be reduced. (We believe that contamination by silicon monoxide may be raising the dissipation factor).

2. Other Reactively Sputtered Dielectrics

Only a literature study has been carried out in this area and possibilities for achieving high dielectric constant materials are so attractive that further sputtering efforts will probably be concentrated here. For example, the dielectric constants of TiO_2 are 85 and 200 in the two major crystal directions.[10] Randomly oriented crystallites should give a value of 114.[11] Lakshmanan et al[8] achieved a value of 55 in exploratory studies. Anodic oxidation of titanium yields a dielectric constant of 40 for the oxide film.[12]

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10 A.R.Von Hippel, "Dielectric Materials and Applications," John Wiley and Sons, Inc., New York, 1954 , p. 302.

11 R. G. Breckenridge and W. R. Hosler, "Electrical Properties of TiO_2 Semiconductors," Phys. Rev. 91, 793 (1953).

12 F. Huber, "Thin Films of Titanium and Titanium Oxide for Micro-miniaturization." IEEE Trans. on Component Parts, Vol. CP-11, 38 (1964).

Possibly the main attraction of the reactive sputtering technique is the class of very high dielectric constant materials--the titanates. Values ranging in the thousands have been obtained for ceramic forms of $BaTiO_3$ and of $BaTiO_3$ mixed with $SrTiO_3$ (Ref. 10, pages 305, 306). Lead titanate films have been prepared by sputtering from a titanium cathode with electroplated lead dots; however, a maximum dielectric constant of only 33 was obtained (bulk ceramic = 50 to 200).[13]

3. Future Plans

Subject to approval at a forthcoming Steering Committee meeting at the U.S. Army Electronics Laboratory, it is planned to emphasize the fabrication of high dielectric constant materials of the type described. The work to date has been carried out using a cathode cooled only by conduction through a base plate post, and by radiation. A water-cooled cathode is being constructed. Improvements in substrate temperature, heating, and control are being made because crystallization of amorphous films of reactively deposited dielectrics at elevated temperatures may be a key factor.[14]

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[13] N. Schwartz, "Reactive Sputtering," Trans. Amer. Vac. Soc. (1963), p. 325.

[14] E. Sekine and H. Toyoda, "Experimental Study of Evaporated $BaTiO_3$ Films," Review of the Electrical Communication Laboratory (Nippon Telegraph and Telephone Public Corporation) 10, 457 (1962).

V CONCLUSIONS

1. Dielectric breakdown at conductor edges is not caused by edge roughness due to slower deposition rate, nor is it caused by a sharp slope at a conductor edge. The most likely explanation is that the sharp, chisel edge of a conductor causes a significant field enhancement at that location.

2. SiO deposition rate and film thickness are interrelated parameters. Rapid deposition is suitable if film thickness is 10,000 Å or more and if the ultimate in TCC, dissipation factor, and leakage is not required. Thin (2000 Å) films may be employed but it is imperative that the deposition be slow.

3. SiO capacitors will function at 85° and 125° under standing potential for long periods: for the lower temperature, at least one year for 1300 Å dielectric (with 10 v dc) and for 10,000 Å dielectric (with 57 v dc); for the higher temperature, at least two months for 10,000 Å dielectric with 67.5 v dc.

4. Reactive sputtering of metals to produce dielectric films offers an attractive route to the fabrication of materials with high dielectric constants. Initial attempts to make silicon nitride (Si_3N_4) by reactive sputtering of silicon in argon-nitrogen gave dielectric films whose infrared spectra showed the presence of an Si-N bond but also an Si-O bond through contamination.

VI PROGRAM FOR NEXT INTERVAL

1. Improve apparatus for sputtering by providing water cooling for cathode and by increasing the temperature limit for substrate heating.

2. Reactively sputter TiO_2 to attempt to raise the reported film dielectric constant nearer to the theoretical value of 114. An oxygen-poor product has been described in the literature and perhaps improvements can be made by elevating the oxygen/argon ratio in the sputtering gas by substrate heating during deposition, and by annealing.

3. Reactively sputter titanates using a multiple cathode or a single bimetallic cathode of controlled relative area. Elevated substrate temperature for deposition may promote crystallization or may permit crystallization at a low annealing temperature.

VII IDENTIFICATION OF PERSONNEL

Name	Title	Man-Hours Worked
Saul W. Chaikin	Manager, Surface Chemistry Section	395
Gilbert A. St. John	Chemist	506
Donald K. Stellman	Senior Chemical Technician	260

Details of the work reported herein are recorded in SRI Notebooks Nos. 5717 and 6727.

Appendix

CROSS-SECTIONING OF THIN FILMS

In the course of developing a sectioning technique to show conductor edge structure, interesting electron micrographs of cross sections of capacitors and of the planar portion of aluminum films were made.

The sectioning technique involved coating a substrate (usually Corning 7059) with a material which later would allow stripping of the deposited layers. Formvar plus SiO, each about 500 Å, and also Victawet, a surface-active material,* permitted stripping. It was accomplished by painting a stripe of 3M Company's Scotchcast No. 2 epoxy resin on the deposited layer and curing it at 60°C for 2 hours. The cured resin adhered to the layer and the composite could easily be removed from the slide. Formvar was removed by solvent rinsing and Victawet by rinsing in water. The composite was then potted in more epoxy resin in a gelatin capsule mold and sectioned with an LKB ultramicrotome having a diamond knife. Sections were usually about 1000 Å thick.

Representative micrographs of aluminum films are shown in Fig. 11 The individual crystals of aluminum which make up the film may easily be distinguished. Most crystals are rectangular and extend the full thickness of the film, from one interface to the other. Banded structure exhibited by some crystals is an effect of diffraction. The film surfaces appear generally smooth except for projections which appear occasionally. These correspond to the bumps seen on the surface replicas of Figs. 2 and 3. Film thicknesses measured from the micrographs check exactly with values obtained from the piezoelectric crystal thickness monitor during deposition.

Figure 12 is a cross section of a capacitor deposited on a heated substrate (110°C for aluminum and 210°C for SiO). The first aluminum

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* E. F. Fullam, Inc., Box 444, Schenectady, New York.

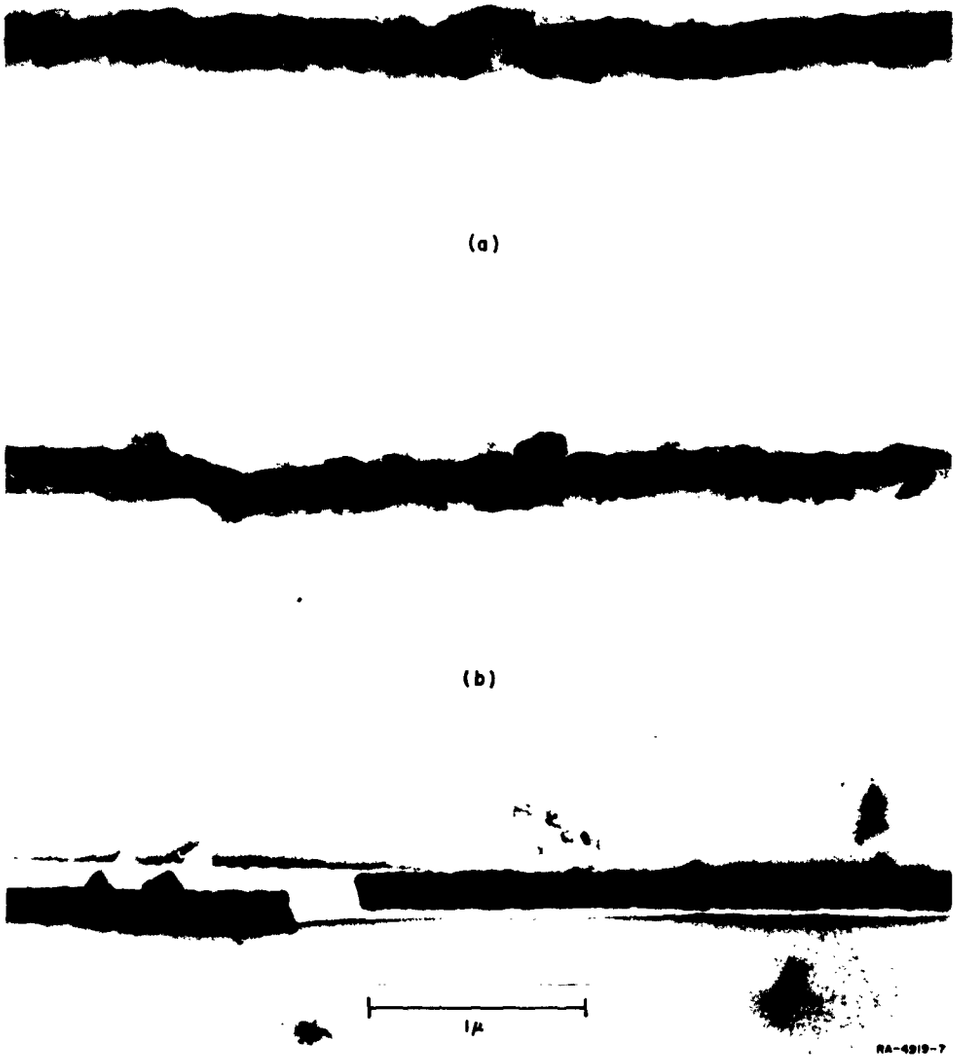

FIG. 11 ELECTRON MICROSCOPE CROSS SECTIONS OF ALUMINUM FILMS (a) AND (b) 2500 Å FILM DEPOSITED ON 150°C SUBSTRATE (c) 1500 Å FILM DEPOSITED AT ROOM TEMPERATURE

FIG. 12 ELECTRON MICROSCOPE CROSS SECTION OF FILM CAPACITOR

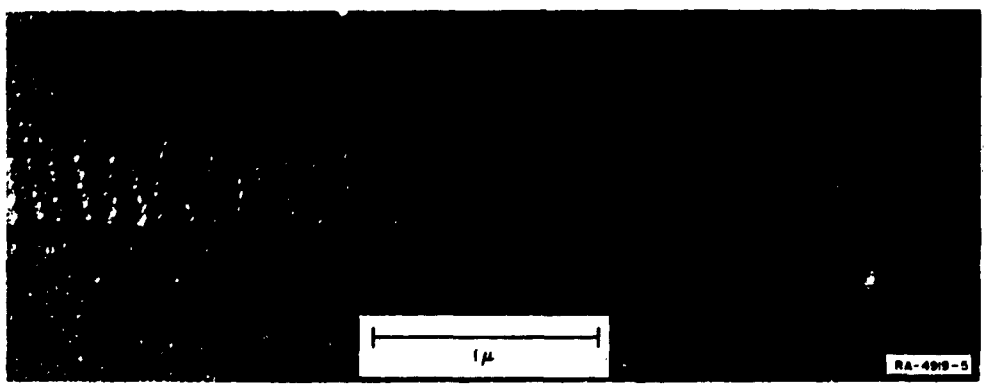

FIG. 13 SURFACE REPLICA OF FACE OF EPOXY MOUNTING BLOCK CONTAINING CAPACITOR

electrode was 1500 Å, and the second was 2000 Å (thickness monitor). The SiO thickness was judged from its interference color to be 3500 Å. The aluminum crystal structure is similar to that already seen in the aluminum cross sections. The difference in thickness of the two aluminum layers is apparent, although thickness values measured from the micrograph are both about 30% lower than the monitor value. The reason for this is not known. Measured SiO thickness checks well with the value estimated from its interference color.

Vacuum-deposited SiO is known to be amorphous therefore, no sign of crystalline structure would be expected. The rectangular chunk form which appears in the figure is interpreted as hard, glassy chips of SiO cut in a regular pattern by the diamond knife. The chips are featureless except for variations in grey shade within a chip, probably due to thickness variations. Some overlapping of chips produced denser patches of grey.

To confirm the interpretation that the SiO was chipped from the surface of the epoxy block during sectioning, a replica of the block surface was made, after sectioning. Normally, a knife cut would leave the surface of a block smooth, therefore, a chipped-out pattern should show up by replica. The micrograph in Fig. 13 shows the surface features expected for the proposed manner of cutting.

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Signal Corps. Contract DA 36-039-AMC-02204(E). Technical Requirements No. SCL-7600B. Unclassified Report.

Edge Effect. By means of electron microscope study techniques, important properties of aluminum electrode edges were determined. It was established that (1) the surface of the film at its edge is smoother than in the planar area, (2) aluminum crystal size becomes smaller as the edge becomes thinner, (3) edge slope of practical electrode thicknesses and mask spacings is probably 5° or less, partly because diffusion of aluminum atoms on the substrate surface occurs. Through these findings, two candidate explanations for edge breakdown were ruled out: field

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show extreme variation: dissipation factor from 0.003 (slow films) to 0.075 (fast, thin films), and TCC from ≤ 40 ppm °C (slow films) to 5,700 ppm °C (fast, thin films).

It was concluded that low deposition rate and high residual gas pressure will favor the incorporation of oxygen into the film and will shift the oxygen silicon ratio from SiO toward SiO_2. This will confer SiO_2 electrical properties on the film resulting in reductions in dielectric constant, dissipation factor, leakage, and TCC.

Life tests of SiO capacitors at 85 and 125°C are in progress; the former for periods between 336 and 472 days (for 1 300 Å and 10 000 Å capacitors) and the latter for 76 days. No pattern of dielectric failure is developing. There are only minor problems due to attachment of electrical leads.

Sputtered Dielectric Films. Reactive sputtering of metals to produce dielectric films offers an attractive route to the fabrication of materials

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