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The experimental procedure for evaporating silicon monoxide together with the methods for measuring the film thickness have been investigated. The effects of various process parameters on the rate of deposition, such as source temperature and source-substrate distance, have been studied. The uniformity of silicon monoxide films deposited by this particular vacuum system and evaporation parameters have been examined. The uniformity of the resultant films follows closely Knudsen's law.

Capacitors of 2,400 to 21,900 uuf/cm^2 with a silicon monoxide film thickness range of 2,457 to 21,567 Å have been deposited on Pyrex glass using evaporated aluminum films for conducting plates. Measurements of capacitors such as capacitance, dissipation factor, breakdown voltage, dielectric constant and leakage resistance have been investigated. Capacitor breakdown voltage in this range lies between 25 - 115 volts d-c,

depending upon the thickness of dielectric films. Dissipation factor, dielectric constant and leakage resistance of SiO films are very sensitive to deposition rate and somewhat sensitive to thickness. Possible causes of shorts in the capacitors are discussed.

VACUUM DEPOSITION OF SILICON MONOXIDE FOR CAPACITORS

by

JOSEPH PING KWAN LO

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APPROVED:

Redacted for privacy

Assistant Professor of Electrical and
Electronics Engineering

In Charge of Major

Redacted for privacy

Head of Department of Electrical and
Electronics Engineering

Redacted for privacy

Dean of Graduate School

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VACUUM DEPOSITION OF SILICON MONOXIDE
FOR CAPACITORS

I. INTRODUCTION

In recent years, the rapid progress in the field of microelectronics has led to the development of new fabrication techniques. Vacuum-deposited metal and dielectric films have received considerable attention by workers in the field of thin-film electronic circuits for making capacitors. This attention has been generated by the improved performance obtained from such films.

Silicon monoxide is by far the most widely used dielectric film in microcircuitry. Apart from its use as a dielectric in making capacitors, surface passivation and diffusion masking (16,p.341) are the most prominent applications for this amorphous film.

Although this material has been widely used in the fabrication of thin-film, yet the existence of a true chemical compound SiO is still a question. A literature search revealed no method of determining the percentages of Si, SiO, Si_2O_3 and SiO_2 in an evaporated thin-film sample. The dielectric film can range from SiO possibly to, or close to, SiO_2. However, it has been found that a <u>low deposition rate</u> will permit reaction of evaporated SiO with residual gas molecules (3, p.24). On condensation the compound probably disproportions according

to the following reactions:

With residual gas $SiO + \frac{1}{2}O_2 \rightarrow SiO_2$

or $2SiO + \frac{1}{2}O_2 \rightarrow Si_2O_3$

(that is, $SiO_{1.5}$)

and $SiO + H_2O \rightarrow SiO_2 + H_2$

Without residual gas $2SiO \rightarrow Si + SiO_2$.

Consequently, the composition of the condensed material depends on conditions of preparation which determine the optical and electrical properties of the thin-films.

There are several methods by which such oxide films can be obtained, but each possesses its own inherent difficulties and generally requires the use of a vacuum system as well as a high source temperature. Three methods of evaporating silicon monoxide are commonly used (4, p.4); a) boat source, b) radiation-heated source, and c) embedded filament source. All these sources suffer from several undesirable characteristics which would result in poor quality films with many pin-holes. To overcome this problem, several different evaporators have been designed with one basic design consideration; namely, elimination of a direct line of sight from the evaporant to the target (8, p.1). These newly designed evaporators have made a great improvement over the exposed designs and are commercially available. A multi-baffled box designed by the R. D. Mathis

Company is one of the several newly designed silicon monoxide sources which has been chosen to be used in this thesis.

A number of investigations has been reported concerning the evaporation of silicon monoxide material. However, there are difficulties involved in depositing silicon monoxide material suitable for making dielectric layers for thin-film capacitors with reliable and long term performance. The main problem seems to be that the properties of the SiO film depend on preparation conditions.

In order to understand the important factors that affect the performance of the thin-film capacitors, it is necessary to investigate the important variables involved and their effects on the properties of the SiO films. The purpose of this thesis is to investigate the technique of vacuum deposition of SiO material and to study the interrelationship between preparation conditions and dielectric properties. This will broaden the base of understanding of the material and, in addition, should aid in fabrication of the thin-film capacitors.

The thesis is divided mainly into two parts. The first part deals with the evaporation of SiO material under variable evaporating conditions. Apart from investigating how the source temperature and the

source-substrate distance affect the rate of evaporation at a relatively constant vacuum pressure, the uniformity of the deposited films have been studied also. The second part of this work is concerned with the fabrication of film capacitors. Capacitors with dielectric film thickness ranges from about 2500 Å to 20,000 Å have been deposited on Pyrex glass using evaporated aluminum films for the conducting plates. Measurements of the electrical properties of the silicon films have been made, and the measured capacitance values have been compared with the calculated values. The effects of the evaporation rate and source temperature on the capacitor breakdown voltage, dissipation factor and leakage resistance have been studied also.

II. SUBSTRATE PREPARATION

Substrate cleaning is essential in vacuum coating work. Good adherence to the substrate material can be achieved if the substrate surfaces are clean and free of moisture and oil contamination. There are numerous procedures for substrate cleaning. Solvent, detergent, and ultrasonic cleaning are commonly used. The 3" x 1" microscopic slides have been chosen to be used in the experiments. The following procedures have been used for substrate cleaning:

1. The selected substrates were immersed in a beaker containing detergent and water.
2. The beaker was then placed on the hot-plate and boiled for about 15 minutes.
3. After this, the substrates were taken out and rinsed under the water faucet for about two minutes.
4. The detergent bath of the 40-kc ultrasonic cleaner was filled with sufficient detergent and water; the substrates were then immersed in the detergent bath with ultrasonic agitation for ten minutes.
5. The substrates were then allowed to soak for about 20 minutes in the detergent bath, and finally treated again for approximately five minutes.
6. Again, the substrates were taken out one by one with a substrate holder, rinsed in deionized

water for one minute, and then in methanol for one-half minute.

7. The substrates were then immediately introduced into a dust-free bell jar and allowed to dry, still in a vertical position.

8. After drying, the substrates were then stored between two layers of filter paper and covered with a dust-free bell jar until used.

The effectiveness of this procedure is dependent on attention to detail. It is considered as essential to have the substrates dried in a dust-free area. A filtered air chamber would be most desirable, if it is available. It has been found that the substrates cleaned by the above procedure show a uniform surface finish, i.e., complete freedom from oily streaks and water marks, etc.

III. DEPOSITION TECHNIQUE

A. Experimental Apparatus

Figure 1 shows the experimental setup used in performing the experiments. The Mikros model VE-10 vacuum system, consisting of a Pyrex glass bell jar ten inches in diameter and 12 inches high and mounted on a stainless steel base plate, was used for making the films. The system was evacuated by an oil diffusion pump backed by a mechanical pump, and the bell jar could be evacuated to a pressure of about 7.5×10^{-5} torr in less than 15 minutes. Two independent low voltage power supplies for heating the source and the tungsten filament were used. It was therefore possible to control the temperature of two different sources separately. The baffled box source temperature was measured to within ± 10°C by means of a chromel-alumel thermocouple attached to the source under the radiation shields.

A baffled box SiO source, shown in Figure 2, designed to meet the necessary requirements of evaporation rate, input power, and prevention of particles of the bulk material from leaving the source before changing into gas phase, was used as a heater source. The 7/8" x 3/4" cross-section baffled box SiO source fabricated from tantalum was filled with 3.5 grams of SiO

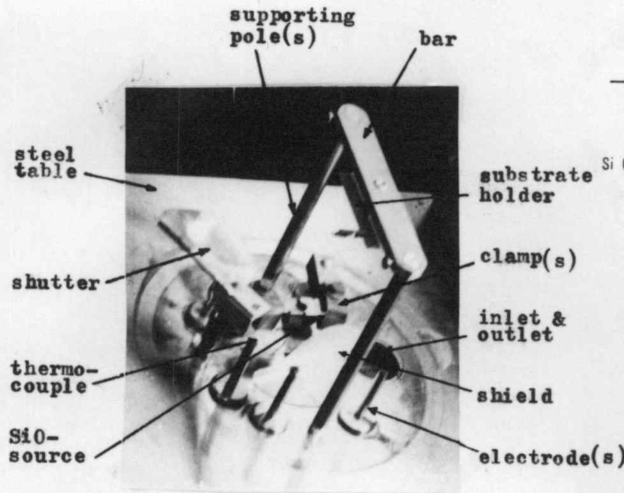


Figure 1. Experimental set up with bell jar removed.

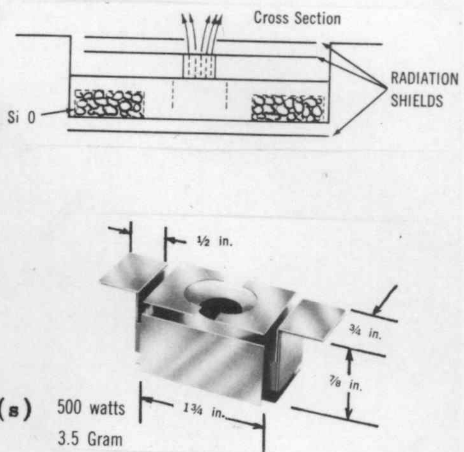
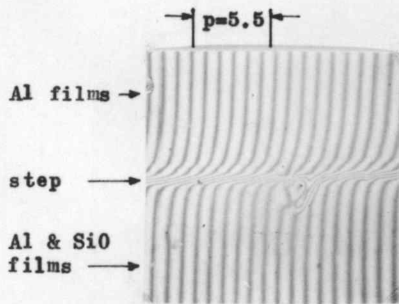
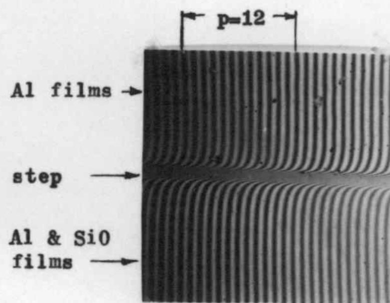


Figure 2. "Baffled box" SiO source with cross-section shown.



(a) Deposition time 5 min. source temperature 1000°C magnification 10X



(b) Deposition time 10 min. source temperature 1000°C magnification 10X

Figure 3. Comparison of fringe systems observed by two-beam interference method.

powder (SiO material originally in random lumps was ground into approximately 120 grit powder). A current of 200 amperes at five volts was required for heating the baffled box SiO source to about 1000°C. This temperature was necessary for evaporating at a rate of the order of 50 Å/sec. Aluminum was evaporated from a 0.75 mm diameter tungsten wire. A small piece of pure aluminum evaporant was loaded on the tungsten filament for each operation. A current of 60 amperes at 12 volts was available for heating the filament.

Substrate-source distance was adjusted by moving the bar of the substrate holder along the two supporting poles. The transistorized crystal oscillator of the deposition thickness meter was installed on the bar with the crystal wafer adjusted to approximately the same level as the substrate holder.

B. Experimental Procedure

The films were fabricated in the vacuum coating plant in which a pressure of about 7.5×10^{-5} torr was maintained throughout the evaporation process. The substrate was held on the substrate holder with two spring clips and maintained at room temperature prior to evaporation. The baffled box SiO source was filled with SiO powder, and a small piece of pure aluminum evaporant

was then placed on the tungsten filament. The bell jar was closed and evacuated to a pressure of about 7.5 x 10^{-5} torr in less than 15 minutes. A current of 25 amperes was used to heat the tungsten filament, and a film of aluminum was then deposited on the substrate surface. A piece of thick glass was placed on the substrate as a mask to give a step for thickness measurement. After the bell jar was evacuated to 7.5 x 10^{-5} torr again, the SiO source was heated by increasing the current gradually. At least one minute was allowed for the SiO source to warm up. After the required source temperature was reached, the shutter was removed from the SiO source by manual control. As soon as the evaporating time was reached, the shutter was shifted to the top of the SiO source again, and the current was turned off slowly. Sufficient time was allowed for the temperature inside the bell jar to cool down to room temperature before the work was removed.

IV. MEASUREMENT OF THE THICKNESS OF THE SiO FILMS

There are several methods by which the thickness of the deposited SiO film could be measured. The methods commonly used are (i) optical interference methods, (namely, wedge method, two-beam interference method with metallized or non-metallized sample, and multiple-beam interference method), (ii) the color reference method (comparing the color of the unknown with the colors of a set of standard films of different thickness), (iii) weight change method (weigh the sample before and after the deposition of SiO film in a microbalance).

In this experiment, the thickness of the SiO films was measured by the two-beam interference method with metallized samples and compared with the values determined by the vacuum deposition thickness meter. The measurements obtained from the vacuum deposition thickness meter were used to provide a rough check on the thickness of the deposited SiO films rather than to take as standard value for the measurements. The measurements obtained from the two-beam interference method were more accurate and reliable than those values measured from the vacuum deposition thickness meter.

A. Two-Beam Interference Method With Metallized Sample

The sample with a uniform wedge-shaped SiO film step fabricated by the previous deposition technique was metallized by depositing a thin film of aluminum on the surface with a vacuum evaporator. The metallized sample was then examined with a Unitron metallurgical microscope equipped with a Watson interference objective. The fringe system shown in Figure 3 (page 8) was obtained with monochromatic light (λ = 5460 was used in all the calculations of this experiment), and examined in reflection. The displacement of the fringes on going from the aluminum base to the SiO film corresponds to a step up. The film thickness was calculated by (1, p.1206)

$$d = p\,\frac{\lambda}{2}$$

where d = the thickness of the SiO film

λ = the wavelength of the monochromatic light

p = the fringe displacement.

An accuracy of measurement within ± 0.1 fringes was obtained by this method. Some difficulty was at first experienced in measuring films several half-wavelengths thick. It was necessary to make an oblique step by shadowing the edge of the masking plate glass slightly, otherwise at a sharp step it was difficult to follow the fringe system and find the order of interference. It

was found that instead of using a thick glass plate, a 1.5 mm diameter copper wire was used to mask a portion of the work surface. An oblique step was obtained satisfactorily by using this technique.

B. Vacuum Deposition Thickness Meter

The vacuum deposition meter was used to measure the thickness of the silicon monoxide films and then calibrated with the measurements of thickness obtained from the two-beam interference method. Figure 4 (Table I) shows the calibration curve of film thickness versus thickness monitor frequency. The curve is a particular characteristic of the vacuum system used in this work and to a large extent is dependent on the evaporation parameters. It has been found that the values of silicon monoxide film thickness measured by the deposition thickness meter are not consistent. The difference in reading from one evaporation to another may be as high as 0.5 - 1 kc, because the crystal oscillator of the deposition meter is fairly sensitive to temperature. Placing the thickness detector at a distance further away from the source reduced the temperature effect to a large extent. It is essential to maintain the thickness detector at a relatively low temperature before any accurate measurements of thickness can be obtained.

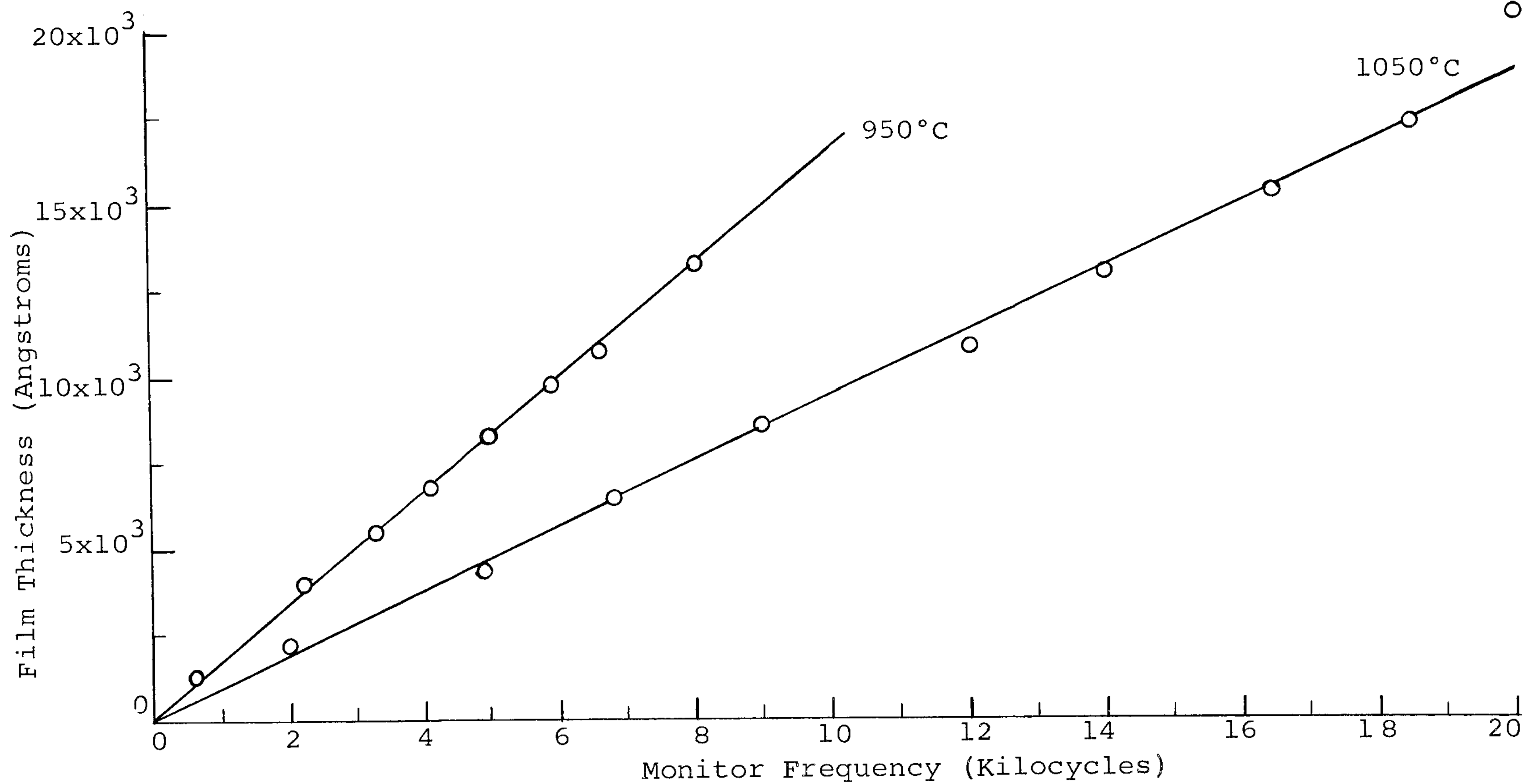


Figure 4. Calibration curve of film thickness versus monitor frequency for various source temperatures at a source-substrate distance of 5¼ inches and bell jar pressure of $7.5x10^{-5}$ torr.

V. THE DEPOSITION RATE OF SiO

A. The Effect of Source Temperature On Evaporation Rate

The thickness variation as a function of evaporation time for different source temperatures is shown in Figure 5. These curves are plotted for source temperatures 950°, 1050°, and 1150°C. It is noted that the thickness of the SiO films varies linearly with the evaporation time.

Figure 6 shows the curve of deposition rate versus source temperatures for a source to substrate distance of 5¼ inches with a vacuum evaporating pressure of about 7.5×10^{-5} torr. The curve indicates that the deposition rate increases linearly with source temperatures from about 1100°C to 1250°C. The experimental results agree fairly well with the findings of a number of investigators (9, p.319) that deposition rates are dependent to a large extent on source temperatures.

B. The Effect of Source-Substrate Distance On Evaporation Rate

The variation of evaporation rate as a function of source to substrate distance for a source temperature of 1050°C is shown in Figure 7 (Table IV). It is noted that the deposition rate is rather high for source-substrate distance less than four inches, but the variation of evaporation rate is quite small for source to substrate distance larger than four inches.

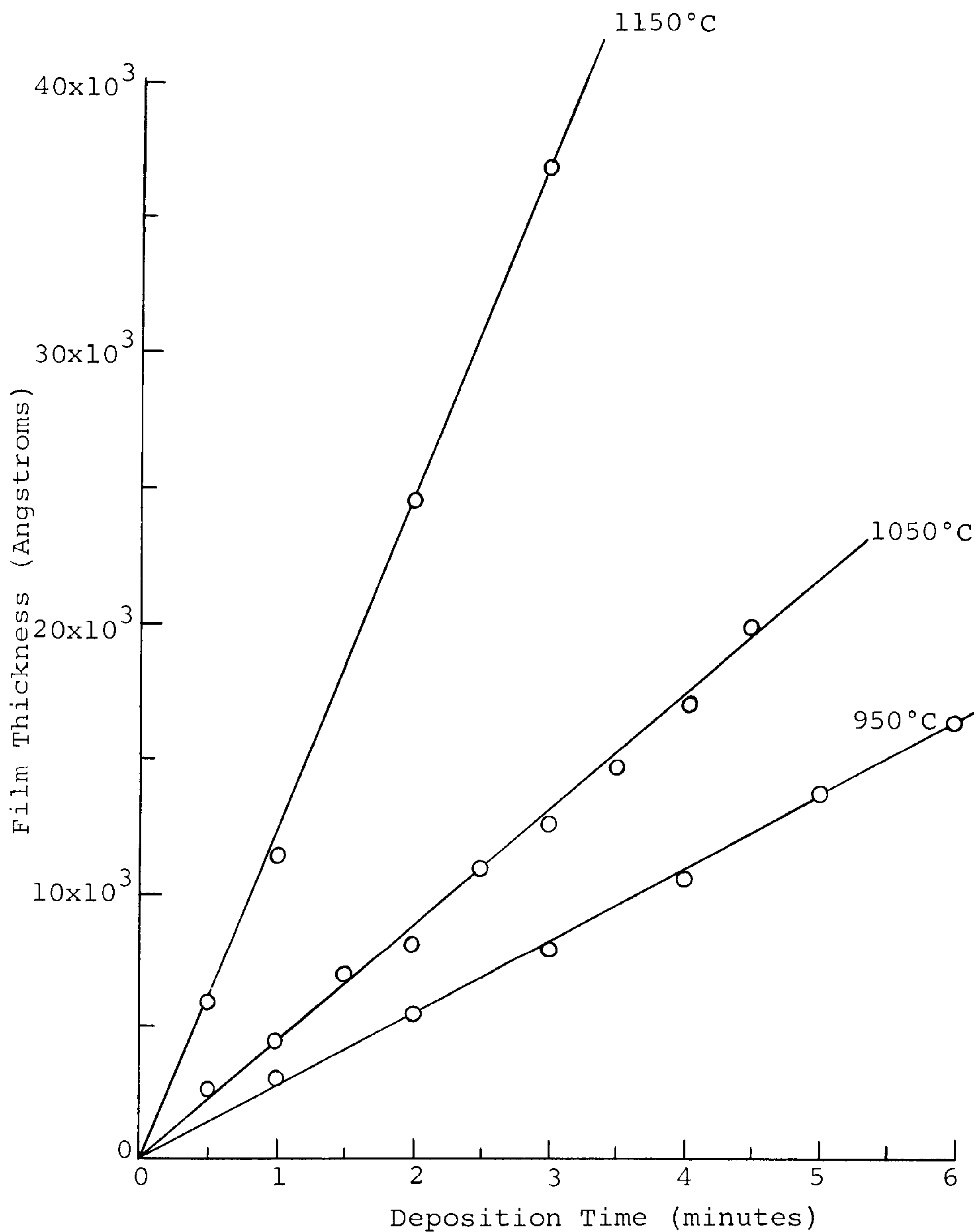


Figure 5. Film thickness versus deposition time for various source temperatures of a source-substrate distance of 5¼ inches and at bell jar pressure of 7.5×10^{-5} torr.

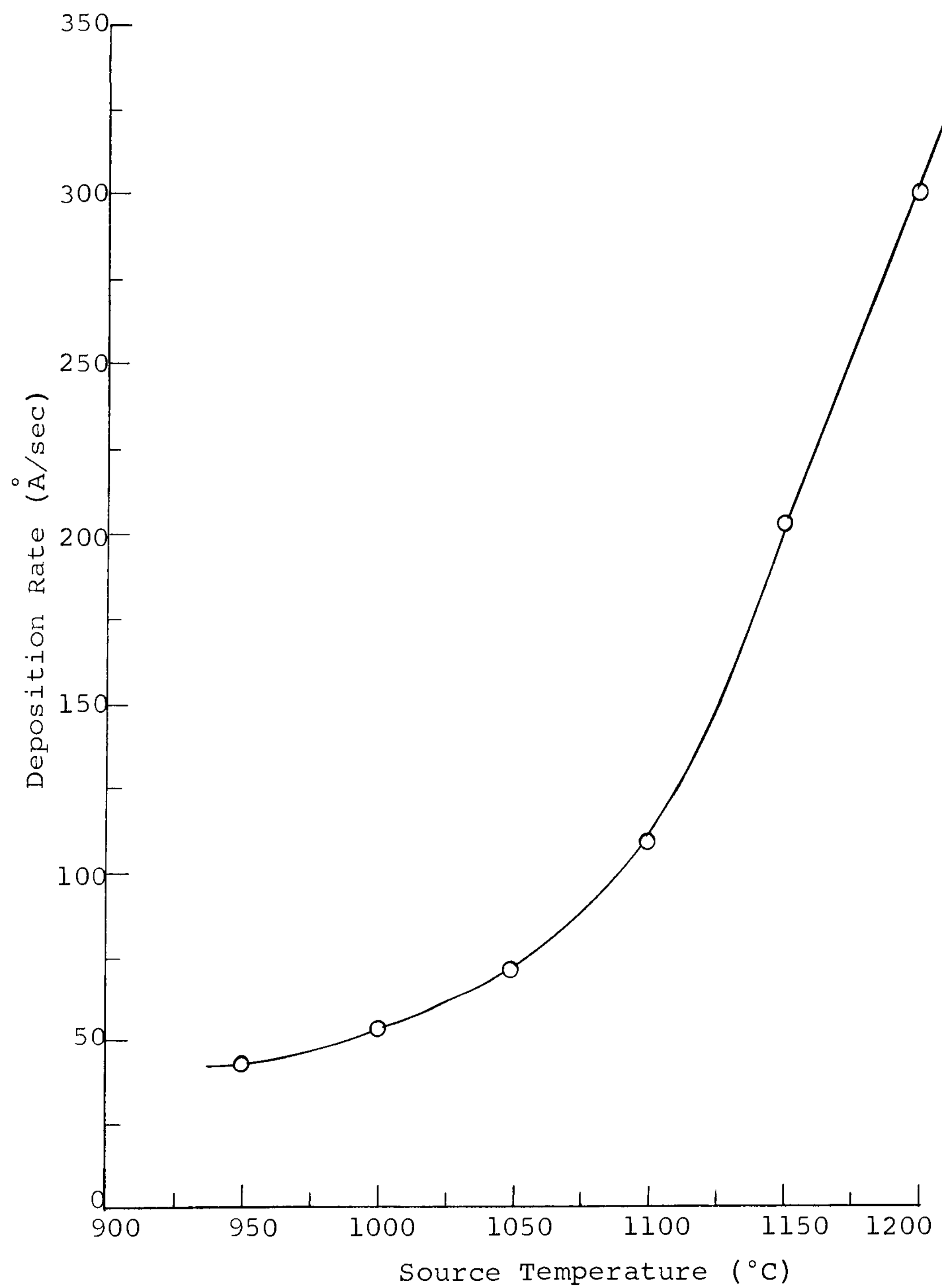


Figure 6. Deposition rate versus source temperature at a source-substrate distance of 5¼ inches and at bell jar pressure of 7.5×10^{-5} torr.

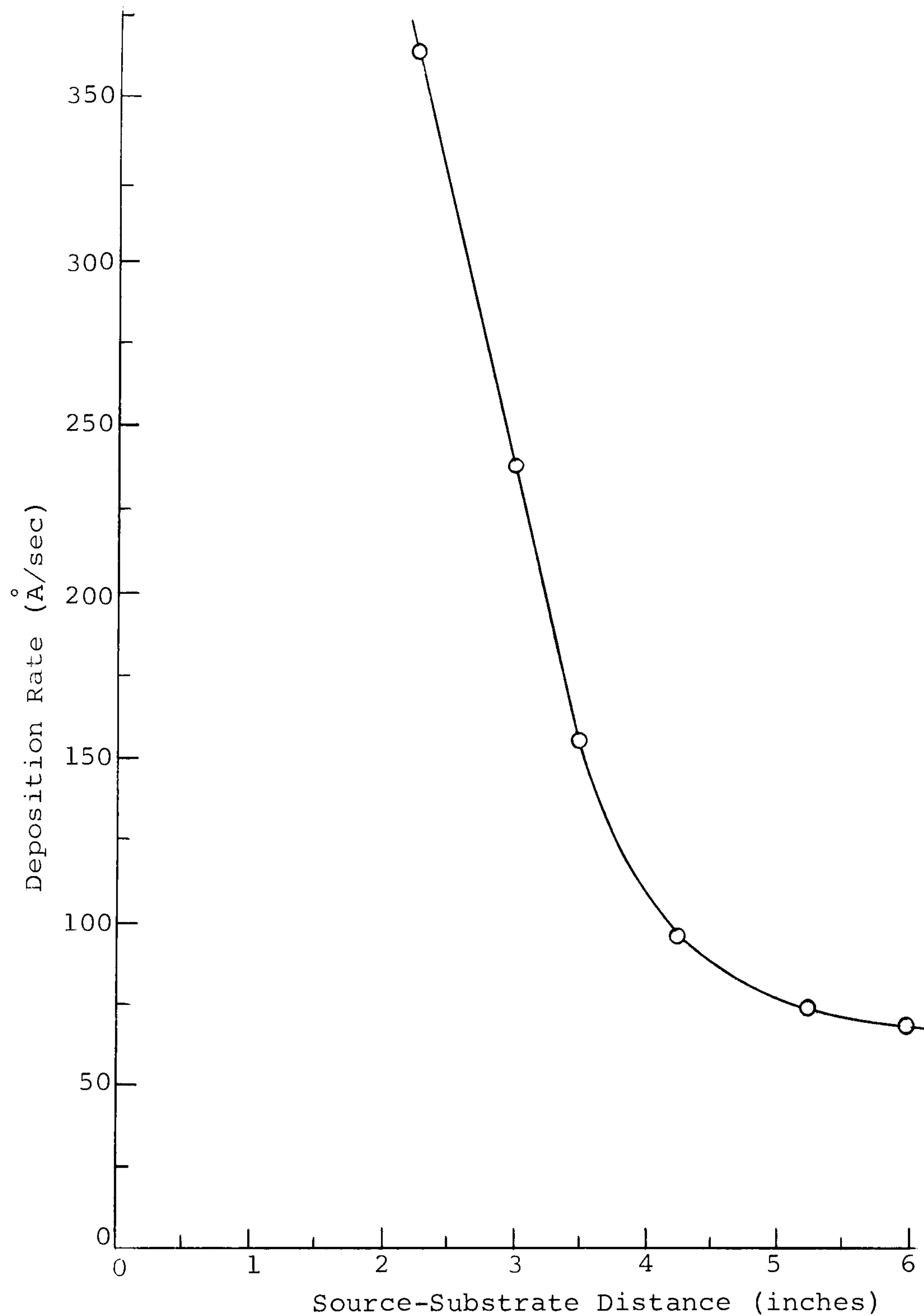


Figure 7. Deposition rate versus source-substrate distance with source temperature at 1050°C and bell jar pressure at 7.5×10^{-5} torr.

VI. THE UNIFORMITY OF THE DEPOSITED SiO FILMS

The uniformity of SiO films is an important factor in making capacitors with high performance. It is therefore considered as essential to investigate the thickness distribution of SiO films.

A. The Technique of Measuring the Uniformity of SiO Films

In order to obtain data for studying the thickness distribution of SiO films, two ultrasonic detergent cleaned substrates were placed end to end on the substrate holder over the baffled box SiO source. Copper wires of about ½ mm diameter were used to mask the substrates at 1 cm intervals. Following the procedure described previously, a thin film of SiO was deposited on the substrate surfaces. The thickness of the SiO film at 1 cm intervals was then measured by the two-beam interference method.

B. Comparison of the Measured Values of the SiO Film Thickness Distribution With the Calculated Values

Figure 8 (Table V) shows the thickness variation of the SiO film as a function of distance from target center directly over the source at a distance of 5¼ inches. The measured thickness distribution curve is

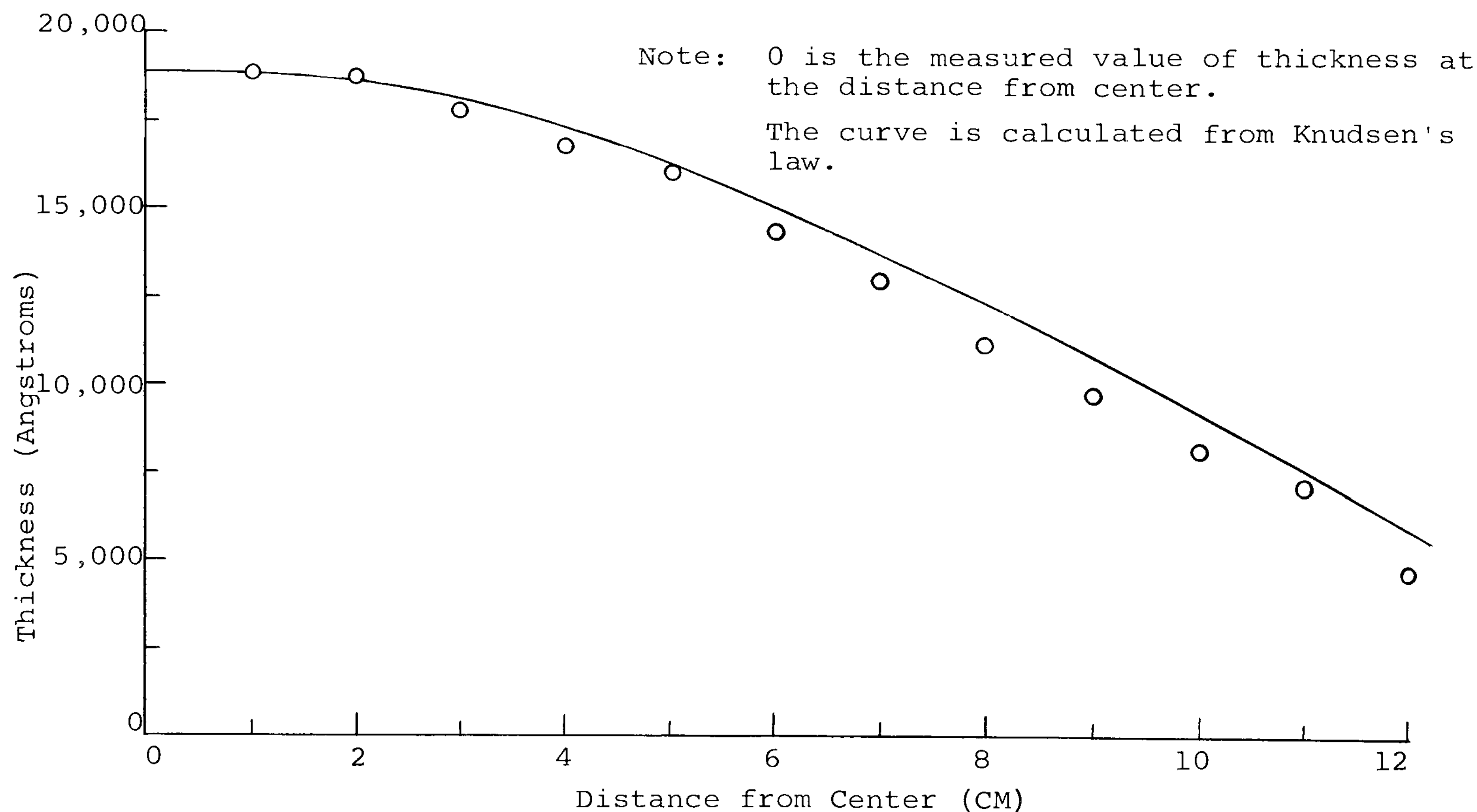


Figure 8. Measured and calculated thickness distribution of SiO film deposited at a source-substrate distance of 5¼ inches with source temperature at 1050°C and bell jar pressure at 7.5×10^{-5} torr.

compared with the calculated curve. The calculated thickness distribution curve is based on Knudsen's law (6, p.146) and the relationship:

$$\frac{t}{t_o} = \frac{1}{(1 + (x/h)^2)^{3/2}} .$$

Where t_o = Thickness in cm at a point directly above the source at distance $\underline{h}$ in cm

t = Thickness at a point, a distance from the zero point of x cm.

It is noted that the measured thickness distribution curve follows closely the calculated curve for distances from the center of 0 - 8 cm. However, the calculated curve and the measured curve do not agree well for distances from the center larger than 8 cm.

VII. THIN-FILM CAPACITORS

In general, thin-film capacitors are incorporated into circuits with low power dissipation, so it is not necessary to be capable of handling high power. However, it is desirable to design a capacitor with sufficiently high capacitance and insulation resistance values together with relatively high breakdown voltage. Capacitor breakdown voltage usually depends on film thickness and also the quality of the deposited film. Uniform dielectric film with few pinholes is one of the most important factors to yield good thin-film capacitors with high breakdown voltages. It is obvious that the quality of film capacitors fabricated by evaporation techniques depends to a large extent on the evaporation parameters, the materials selected, and the degree of care exercised in the fabrication.

A. Variables Determining the Value of Capacitance

The capacitance of a configuration is obtained from the relationship (13, p.107)

$$C = \frac{0.0885\ K\ (N-1)A}{t}$$

where C = capacitance in picofarads

K = dielectric constant of the material

N = the number of plates

A = the area of the plates in square centimeters
t = the thickness of dielectric material in centimeters.

In microminiature circuits, the dimensions of the circuit limit the area of the capacitor. Due to the complexities involved in fabrication, capacitors fabricated with more than two plates are undesirable. Obviously, the remaining variables which can influence the value of a capacitor are the nature of the dielectric material and its thickness. The variation of dielectric constant for a particular dielectric material is relatively small. For instance, the dielectric constant of silicon monoxide lies in the region betwen five and six, depending on evaporating conditions. Consequently, the thickness of the dielectric remains as the most effective variable for determining the value of a capacitor.

B. Capacitor Fabrication

In general, at least two methods can be used in making capacitors by vacuum evaporation techniques. In one method the dielectric film is deposited directly on a thin metal foil followed by a top metal electrode; in the other method a metal/dielectric/metal multilayer is deposited on a ceramic or glass base. The second method is commonly used in laboratory investigation and has been adopted throughout this work.

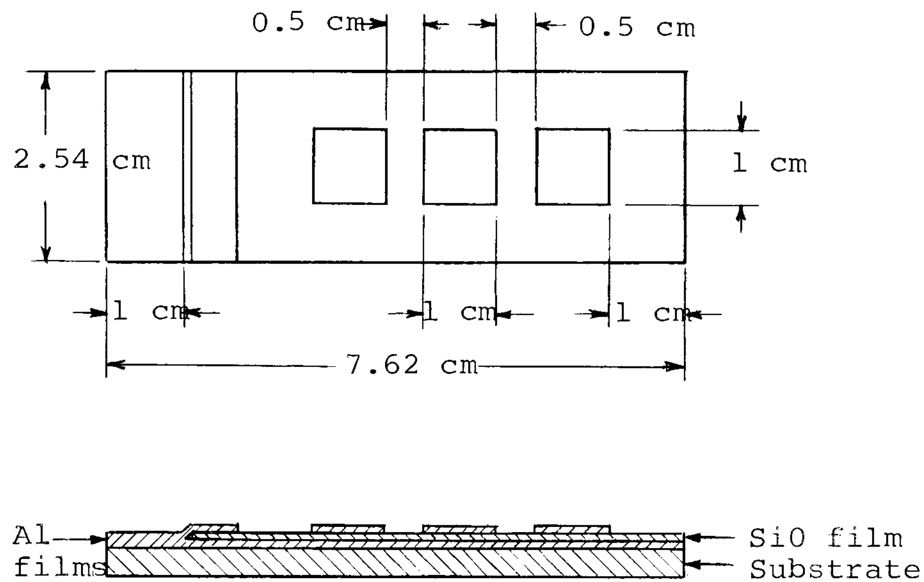
Thin-film capacitors were made with multi-layers of aluminum / silicon oxide / aluminum deposited on 3" x 1" microscopic slides. The substrates were carefully selected; those showing high number of defects under high-intensity, low angle lighting were discarded. The substrate was then ultrasonically cleaned according to the procedure described previously and placed under the substrate holder, and the vacuum system was pumped down to less than 10×10^{-5} torr. The aluminum metal was melted and evaporated on a tungsten wire. With the substrate at room temperature, the aluminum source was heated and the metal deposited in about one minute. After the deposition of aluminum film, a piece of round-edged thick glass was then placed on the substrate. Approximately 1 cm from one end, the substrate was suitably masked so as to give the required step for dielectric thickness measurement.

Following the experimental procedure described previously, the SiO source temperature was then raised slowly to 1050°C, and sufficient time was allowed for the source to warm up. The evaporation taking place at a pressure of about 7.5×10^{-5} torr and a deposition rate of about 70 Å/sec was used. Raising the substrate temperature by a radiation heater was eliminated. Since the evaporation was carried out at a source-substrate

distance of 5¼ inches, during the warm up period, the radiation of heat from the SiO source was sufficient to raise the substrate temperature to 100-150°C. The evaporation time for the desired dielectric thickness was estimated from the curve of SiO film thickness versus evaporation time shown in Figure 5. The calibration curve of SiO film thickness versus frequency for the thickness monitor shown in Figure 4 was also used as a rough check of the oxide film thickness while the evaporation was in process. The thinner capacitors required a proportionally shorter time. After the deposition of SiO film, sufficient time was allowed for the temperature inside the bell jar to cool down to about room temperature.

If a mask changer had been available, the evaporation of capacitors would be simpler. The fabrication of the entire device could be achieved during a single pump-down. However, in this work the substrate was masked with a brass mask containing three 1 cm square holes spaced about 0.5 cm apart. Experimental results shown in Figure 8 (Table V) have indicated that SiO films prepared by this particular vacuum system and evaporation parameters had a comparatively uniform area up to a few square centimeters. The mask was placed carefully on the substrate surface within the uniform area so that

the variation in film thickness for the three capacitors would not be appreciable. A thin film of aluminum was then deposited on the SiO film through the 1 cm square holes, and at the same time the wedge-shape SiO film step was metallized for the dielectric thickness measurement. The completed capacitors together with the metallized SiO film step are shown in Figure 9.



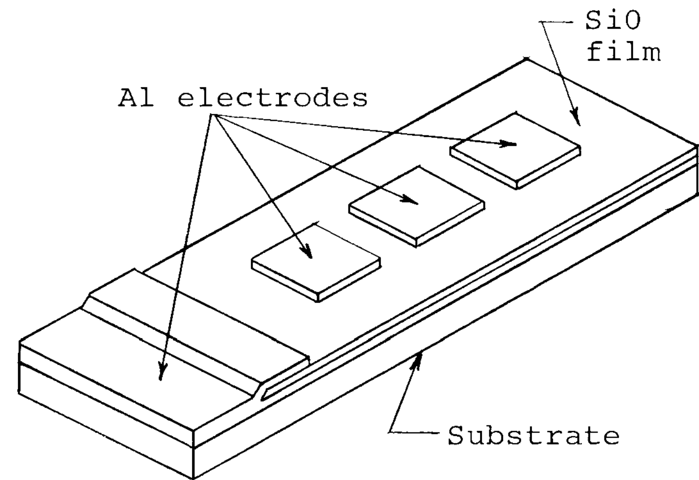


Figure 9. Vacuum deposited parallel plate capacitors and oxide film step for thickness measurement with dimensions shown (not to scale).

VIII. CAPACITOR MEASUREMENTS

The completed capacitors were tested by using flexible spring contacts held in a micromanipulator to contact the aluminum terminal areas. Care was taken not to apply excessive spring pressure on the top aluminum electrode, so as to prevent causing a short in the capacitors. Through these contacts the capacitance and dissipation factor of each of the three capacitors were measured on a model 250-DA ESI impedance bridge, using the internal 1000 cycle testing frequency. The capacitor breakdown voltages were checked with a Tektronix 575 curve tracer. The dielectric constant values of the evaporated SiO films were then estimated by calculation. The measured and calculated results are shown in Figures 10, 11, and 12 (Tables VI, VII).

A. The Measured and Calculated Values of Capacitance

The accuracy of the measured values of capacitance depends to a large extent on the skill in operating the impedance bridge. Inspection of Figure 10 (Table VI) indicates that the measured values of capacitance follow closely the calculated values, and the deviation between the measured and the calculated curves is small. It is noted also that the change in capacitance values

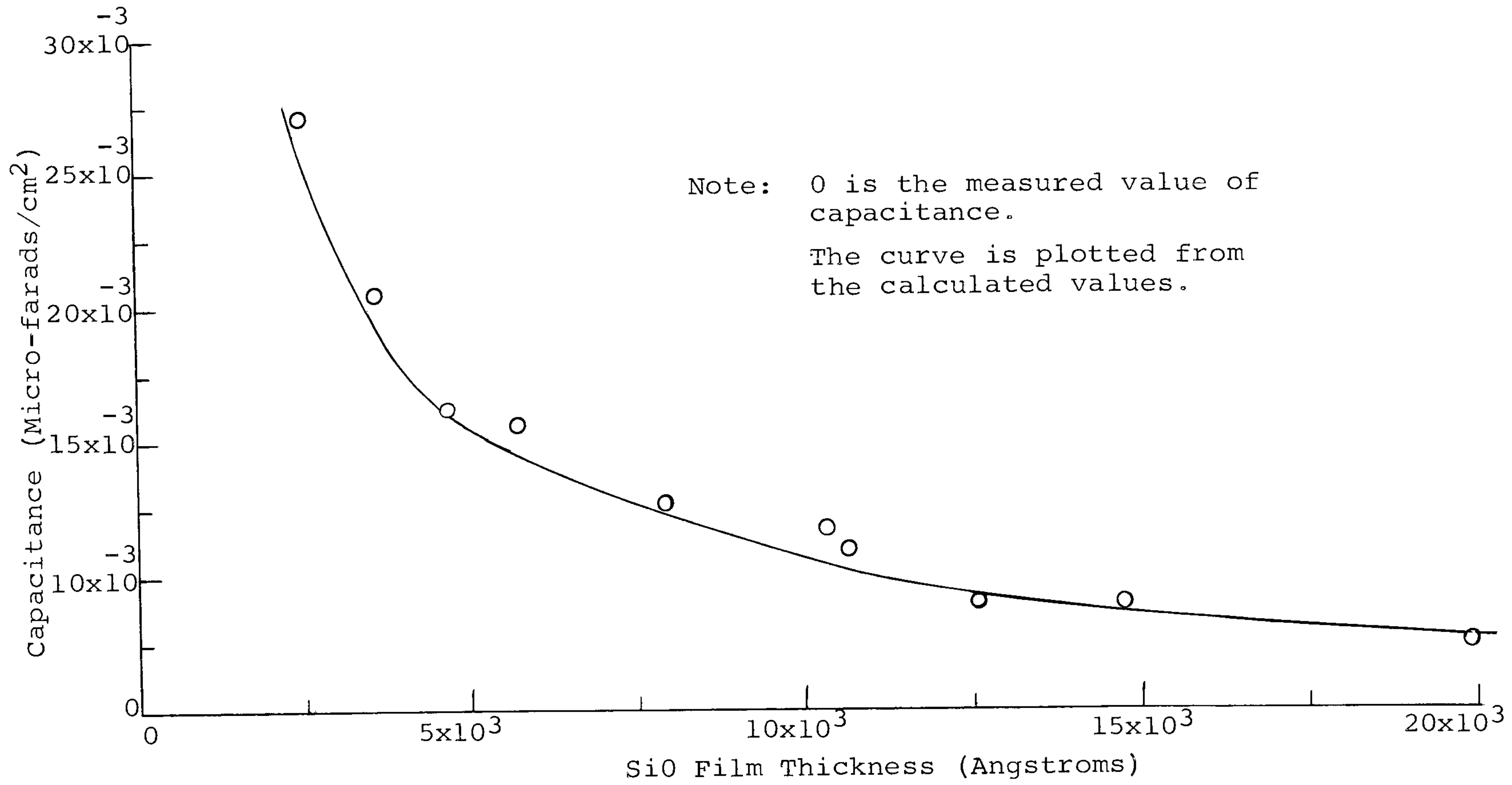


Figure 10. The measured and calculated capacitance versus SiO film thickness.

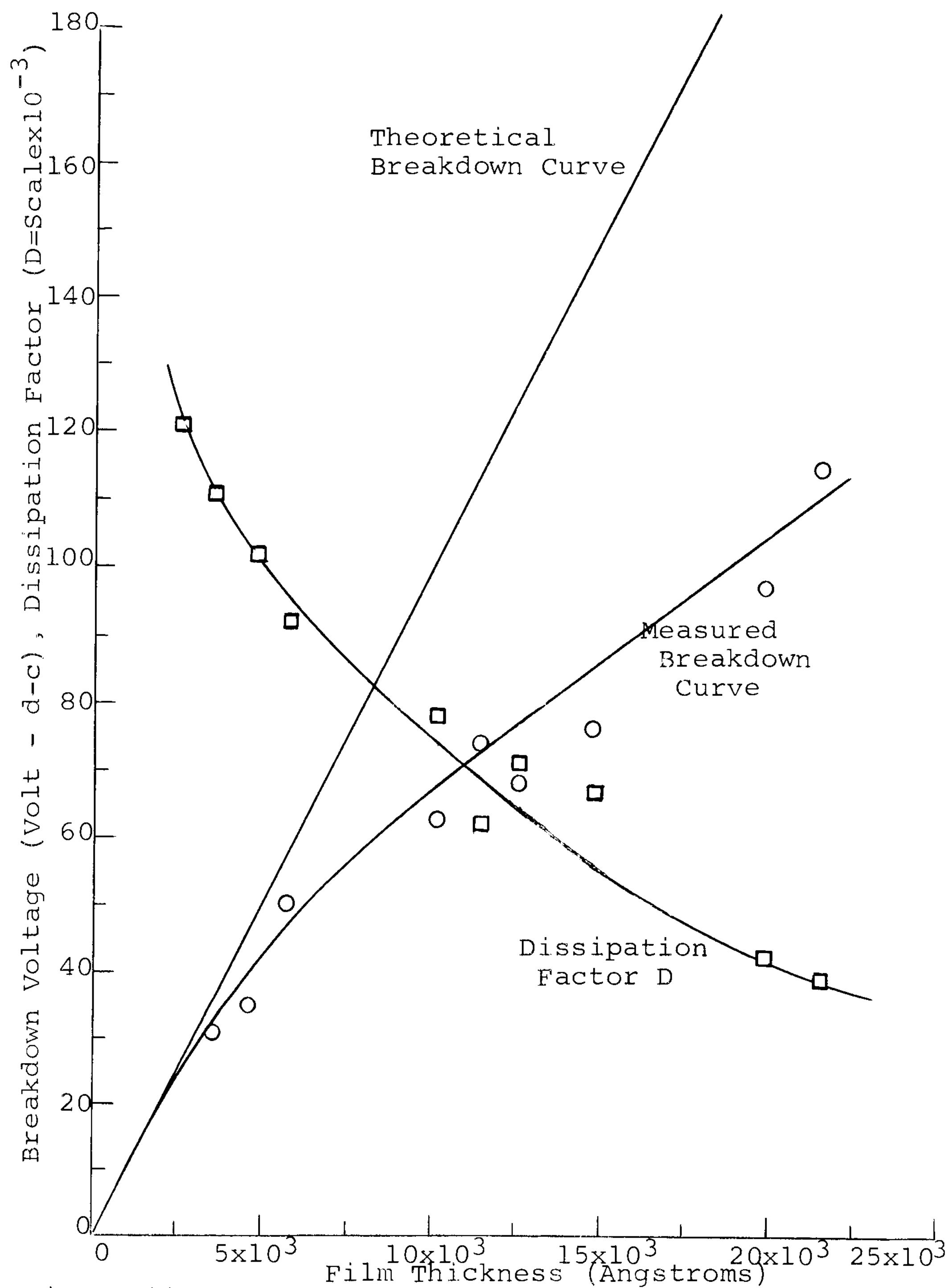


Figure 11. Breakdown voltage and dissipation factor of the SiO capacitors; plotted against film thickness.

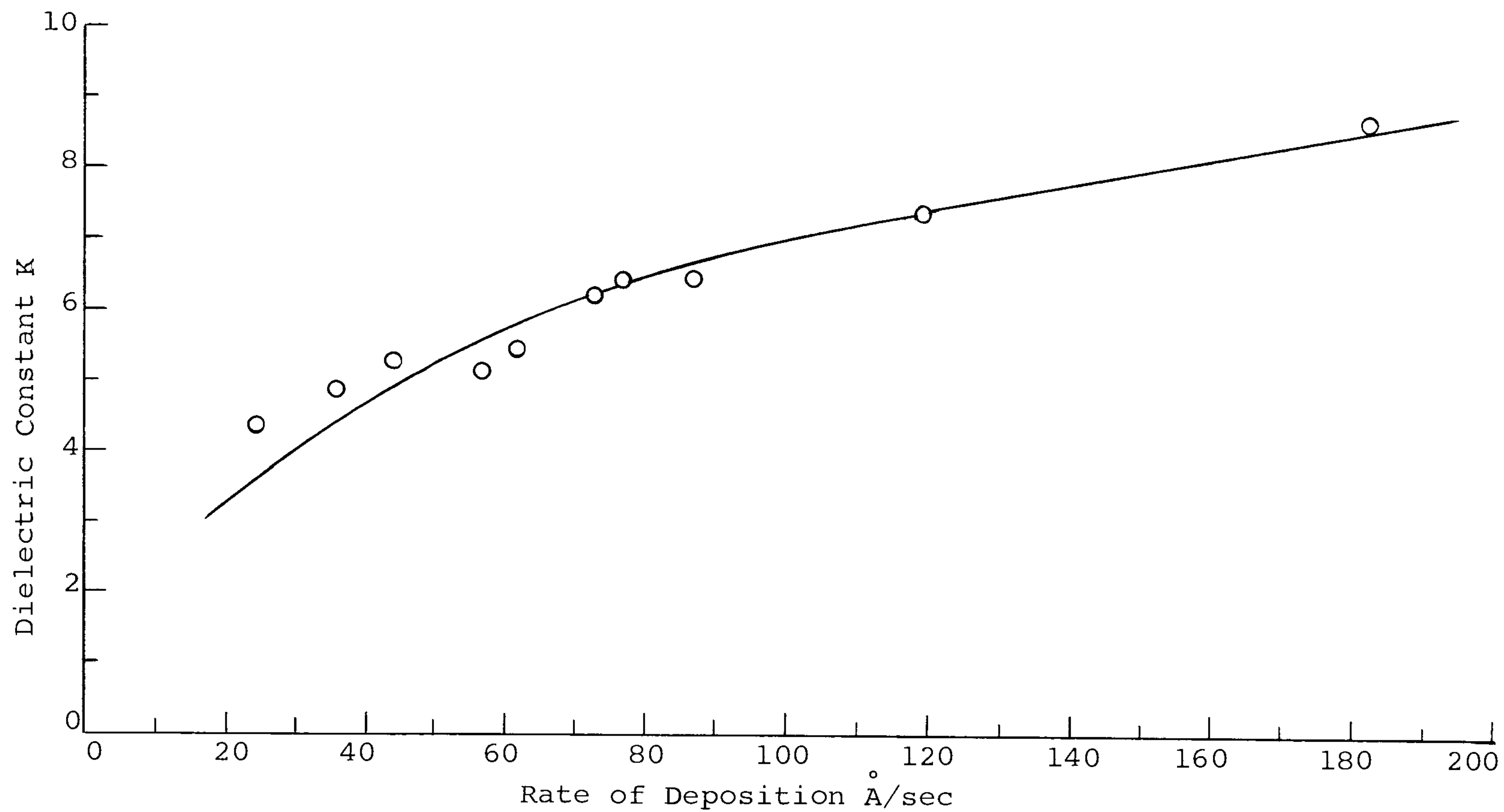


Figure 12. The dielectric constant of the vacuum deposited silicon oxide films; plotted against rate of deposition.

corresponding to a small change in SiO film thickness is comparatively large for the oxide film thicknesses less than 5×10^3 Å, and rather small for the thickness ranges from 10×10^3 Å and up.

B. Dissipation Factor

Dissipation factor values measured from the ESI impedance bridge are tabulated in Table VI. It is noted that dissipation factor is sensitive to thickness, higher for the thin films than the thick ones. With the exception of sample four, the dissipation factor is especially high, (D = 0.14). It is probably due to a deposition rate of higher than 70 Å/sec being used in the evaporation, since the dissipation factor is comparatively higher for a fast deposition rate than a slow one (3, p.19).

C. Breakdown Voltage

The capacitor breakdown voltages were measured with a Tektronix 575 curve tracer using spring contacts to contact the capacitor terminal areas. Breakdown voltage is dependent on film thickness. The measured values of breakdown voltage range from 25 to 115 volts d-c, as shown in Table VI. Figure 11 shows the breakdown voltage versus film thickness. Experiments have

indicated that most of the capacitors can withstand at least about 150 volts d-c after the breakdown occurs. But further increase in voltage would cause shorting of the capacitors.

D. Dielectric Constant

No attempt has been made to measure the dielectric constant, but rather the values of the dielectric constant have been calculated from the basic relationship for capacitance. The calculated values of dielectric constant are in range 4.33 - 8.73 as shown in Figure 12 (Table VII). These values of dielectric constant are expected for the high deposition rate of 24 to 182 Å/sec being used in the evaporation, and confirm the general tendency toward a higher value of dielectric constant with increasing rate of deposition. The values of dielectric constant also depend on the temperature of the source, the evaporation rate, and the pressure and composition of the residual gas in the vacuum.

E. Leakage Resistance

The leakage resistance of silicon monoxide films has been studied extensively by a number of investigators. Therefore, no detailed investigation was carried out. The leakage resistance of a few of the capacitors

with film thicknesses of 2500 and 10,000 Å has been measured by using a sensitive voltmeter together with a multitapped battery and a 100 kilohm series resistance. The results are tabulated below for comparison:

Measuring Voltage d-c	Dielectric Thickness	Leakage Resistance in Megohms	
		Medium Deposition Rate 25 Å/sec	Fast Deposition Rate 70 Å/sec
3 V	2,500 A	55	15
9 V	10,000 A	15,000	850

Leakage resistance of silicon monoxide films has been found to be sensitive to deposition rate and somewhat sensitive to thickness. It is noted that the fast deposited film of 2500 Å is fairly leaky, 15 megohms at three volts. The faster film for the thickness of 10,000 Å seems better. The results confirm the findings of a number of investigators that the slower film has a higher leakage resistance than the faster ones (3, p.19).

IX. FAULTY CAPACITORS

Although it is possible to prepare capacitors with thinner dielectric films, the number of shorted films increases rapidly as the thickness decreases. Experimental observations have shown that capacitors fabricated with the SiO film thickness less than 2000 Å are mostly shorted. It has been found also that capacitors prepared at a source temperature higher than 1300°C, and hence a deposition rate of much higher than 70 Å/sec are unreliable and with a large percentage of shorts. In general, faults in thin-film capacitors could be caused by the following parameters:

(i) The diffusion of aluminium around the edge of the plate (12, p.278).

(ii) A weak point in the dielectric at the sharp step in the bottom electrode.

(iii) Pinholes in the films due to lattice defects or imperfections (15, p.462).

(iv) Ruptures in the films due to the strain effect (10, p.946; 11, p.301).

Possibilities of Causing Shorts

The causes of (i) and (ii) are less likely to occur in the particular kind of thin-film capacitors shown in Figure 9. However, whenever two thin layers are formed on top of one another, a stress is inevitably set up in

one of the two films. When the stresses are great enough, one or the other of the two films may rupture and relax the stress. If the dielectric film ruptures, a short appears. The strain effect is usually smaller for thin films than for thick ones. The strain effect could be reduced by annealing the film to remove the stresses. This is usually achieved by heating the substrate during deposition, since the films have been prepared at a comparatively short source-substrate distance (5¼ inches). The radiation of heat from the source would be enough to maintain the temperature of the substrate at a relatively high value and hence reduce the strain effect to a minimum. However, the annealing method is not always successful for thick films if the difference between the temperature coefficients of expansion of the film and base is too large (12, p.278). This could be the reason why capacitors with silicon monoxide films prepared at a high source temperature have a large percentage of shorts. Another reason could be due to the ejection of small particles from the source as observed at source temperature higher than 1300°C. This would result in poor quality of films with many pinholes.

Shorts occurring in the dielectric films of thickness less than 2000 Å increase rapidly as the thickness

of films decreases, which could be due to lattice defects or imperfections. It has been shown by a number of investigators (13, p.109) that the initial few layers of any thin films less than 100 Å formed by any one of the available techniques are discontinuous in thickness and appear to nucleate at specific sites on the surface. The film buildup takes place by addition of atoms or molecules to these nucleating centers. Finally, the nucleation sites overlap and a continuous film is formed. But it might happen that a few small holes which have not been bridged by overlap of material from the nucleating sites still remain in the film. As a result of these pinholes, a short appears. This phenomenon usually exists in very thin films. But there is no optimum thickness below which the film is discontinuous; this thickness is dependent to a large extent on the processing parameters, the dielectric material and the substrate used.

X. DISCUSSION

The experimental results confirm the findings of a number of investigators that the composition (5, p.353) and electrical properties (12, p.274) of evaporated silicon monoxide films can be altered appreciably by changing the evaporation rate, the total pressure in the system, or source-substrate distance. Possible explanations have been advanced in terms of a reaction of the silicon monoxide with the residual gas in the system (14, p.15) and decomposition in the solid state after deposition of the film (2, p.351). Literature search has indicated that the chemical composition of the film produced by vacuum evaporation of SiO is usually a composite of Si, SiO, Si_2O_3. The predominance of one component over the others is a function of source temperature and residual gas present during evaporation, and there is no method to determine the exact composition of each component.

In general, the partial pressures of the residual gases differ from one system to another, and the temperature of the molecular beam which is related to source construction and geometry may also vary considerably. The curves shown in this work are characteristic of a particular vacuum system depending on residual gases, source-to-substrate distance and source temperature, etc.

The resultant SiO films deposited in this work are coherent and exhibit good adherence characteristics as tested by the scotch tape technique. This is attributed to the standards developed for the selection and cleaning of substrates and to the procedures and techniques for depositing silicon monoxide material.

Figure 5 (Table III) shows the curve of evaporation rate versus source temperature. It is noted that the deposition rate (300 Å/sec) at a source temperature of 1200°C is much higher than the deposition rate (40 Å/sec) at a source temperature of 950°C. However, under conditions of high evaporation rates, ejection of small particles has been noted to occur. This would result in poor quality films with many pinholes and must be eliminated. It has been found that the source temperature is best maintained at 1050°C for the particular evaporation system used in this experiment.

Figure 7 (Table IV) shows the plot of deposition rate versus source-substrate distance at a source temperature of 1050°C. The curve indicates that the evaporation rate at a source-substrate distance of three inches is about 240 Å/sec which is much higher than the evaporation rate (70 Å/sec) at a source-substrate distance of $5\frac{1}{4}$ inches. This very nearly follows the inverse square law.

The breakdown voltage in any film is, of course, dependent on film thickness. It is important that dielectric film should be uniform. The thickness variation of SiO film as a function of distance from target center directly over the source is shown in Figure 8 (Table V). In general, the measured thickness distribution curve agrees quite well with the calculated curve. It has been found that the curves follow Knudsen's law as expected. If the source-substrate distance is sufficiently large, a uniform SiO film could be deposited on the substrate surfaces over a large area.

The influence of SiO deposition rate on its dielectric properties is fairly well known, but the film thickness as a relative parameter is not as well known. Measurements of the capacitors fabricated with different thicknesses of films have been made to obtain quantitative details regarding these interrelationships. Aluminum has been chosen for electrode material because of its small grain size which results in a relatively smooth surface. All electrical measurements have been taken from devices that have been fabricated with aluminum electrodes. The measured values of capacitance agree extremely well with the calculated curves. Figure 10 (Table VI) shows the plot of capacitance versus film thickness. It is noted that after a critical thickness

(15×10^3 Å) is reached, the variation in capacitance is very small for a large increase in thickness.

The breakdown voltage and dissipation factor of the capacitors are plotted against film thickness as shown in Figure 11 (Table VI). It is noted that the dissipation factor measured at room temperature (300°K) decreases with increasing film thickness. The measured breakdown voltage range of 25 to 115 volts for the thickness of films (range 2,457 to 21,567 Å) is compared with the theoretical breakdown voltage curve, calculated by taking the dielectric breakdown strength of 10 v/1000 Å. Published information on the dielectric breakdown strength of silicon monoxide ranges from 5 v/1000 Å to 20 v/1000 Å or even higher and is dependent to a large extent on the evaporation parameters. The dielectric breakdown strength is relatively low for a fast deposited film. It is noted that the measured breakdown curve follows closely the calculated one for film thickness less than 5000 Å. The ratio in breakdown voltage between the calculated and measured values is about two times as the film thickness increases to about 20,000 Å. This could be due to the low quality of films caused by the increase in strain effect as the thickness of films increases.

The dielectric constant of the vacuum deposited

silicon oxide films is plotted against rate of deposition as shown in Figure 12 (Table VII). The dielectric constant is range 4.33-8.73 for a relatively high deposition rate range 24 to 182 Å/sec used in the evaporation. This again is as expected and is in agreement with the results obtained by a number of investigators. The dielectric constant lies between that of Si(11.6) and SiO_2(3.8). It is expected that the composition of the deposited film would be in some intermediate oxidation state Si_xO_y. Slow deposited films have composition close to SiO_2 with low dielectric constant of above 3.8, whereas fast deposited films should have a relatively high dielectric constant. But in any case the dielectric constant should not exceed 11.6 (17, p.274).

Leakage resistance of SiO film has been found to be sensitive to deposition rate and somewhat to thickness. It is obvious that silicon monoxide films may be made which have high dielectric breakdown strength, low leakage, and low dissipation factor, but this requires careful control of evaporation rate and residual gas pressure. However, the dielectric constant of SiO is too low to achieve high values of capacitance in small areas. This and difficulties of controlling the evaporation parameters have limited the uses of silicon monoxide to a large extent (7).

XI. SUMMARY AND CONCLUSION

The vacuum deposition of silicon oxide films has been studied. The resultant silicon oxide films are amorphous, coherent, and exhibit good adherence characteristics. The distribution of oxide film thickness deposited on a substrate from an evaporation source follows Knudsen's law. It has been found that the variation in film thickness on substrates a few cm sq. from the center of the source is not appreciable. The silicon monoxide film deposition rates have been shown to be a strong function of the source feed rate which again depend on the source temperature.

Capacitors have been made from vacuum-deposited films ranging from 2,457 - 21,567 Å that have specific capacitances in a range of about 2,400 - 21,900 uuf/cm^2. It has been found that capacitors with oxide film thicknesses less than 2,000 Å deposited at a rate of about 70 Å/sec are low quality with a large percentage of shorts.

Experimental results indicate that the dielectric constant, breakdown voltage, dissipation factor and leakage resistance are dependent on fabrication parameters. The breakdown voltage and dissipation factor are found to be proportional to film thickness. It is also noted that the dissipation factor and dielectric

constant are sensitive to deposition rate. The dissipation factor for the specific range of capacitors which have breakdown voltages between 25 - 115 volts d-c is in the order of 0.038 - 0.14. The dielectric constants of the films are in the range of 5.63 - 6.92 for a deposition rate of about 70 Å/sec. The leakage resistance is rather sensitive to the deposition rate and somewhat sensitive to the thickness.

The quality of SiO capacitors fabricated by vacuum evaporation is dependent largely on the evaporation parameters and the degree of care exercised in fabrication. Extreme difficulty is to be expected in the fabrication of defect-free films. The greater number of imperfections in the dielectric films, the lower the breakdown voltage which may be expected. The capacitance is limited by the thickness of the film which can be reliably fabricated "short-free." The low values of dielectric constants in the SiO films make the material unsuitable for use in fabricating high values of capacitance. Reliable thin-film capacitors using silicon monoxide as a dielectric can be fabricated by vacuum evaporation, provided the preparation conditions are understood and controlled.

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APPENDIX

Table I. Calibration Curve of Oxide Film Thickness Versus Thickness Monitor Frequency.

Source-substrate distance = $5\frac{1}{4}$ inches.
Vacuum pressure = 7.5×10^{-5} torr.

Sample No.	Deposition Time (min)	Source Temp.950°C		Source Temp.1050°C	
		Thickness (Å)	Freq. (KC)	Thickness (Å)	Freq. (KC)
1	0.5	1,250	0.6	2,250	2.0
2	1.0	2,750	1.5	4,375	4.9
3	1.5	4,000	2.2	6,500	6.8
4	2.0	5,500	3.3	8,625	9.0
5	2.5	6,750	4.1	10,750	12.0
6	3.0	8,250	5.0	13,000	14.0
7	3.5	9,750	5.9	15,250	16.5
8	4.0	10,750	6.6	17,250	18.5
9	4.5	12,250	8.1	19,500	20.0

Table II. Oxide Film Thickness Versus Evaporation Time.

Substrate-source distance = 5¼ inches.
Vacuum pressure = 7.5 x 10^{-5} torr.

Sample No.	Source Temp. (°C)	Deposition Time (min)	Fringe Displacement (No. Fringes)	Oxide Film Thickness (Å)
1	950	1	1.1	3,003
2	"	2	2.0	5,460
3	"	3	2.9	7,917
4	"	4	3.9	10,547
5	"	5	5.9	13,923
6	"	6	6.1	16,653
7	1,150	0.5	2.1	5,733
8	"	1	4.2	11,466
9	"	2	9	24,570
10	"	3	13.5	36,855
11	"	4	18	49,140

Table III. Deposition Rate Versus Source Temperature.

Source-substrate distance = 5¼ inches.
Pressure = 7.5 x 10^{-5} torr.

Sample No.	Source Temp. (°C)	Deposition Time (min)	Fringe Displacement (No. Fringes)	Oxide Film Thick. (Å)	Evap. Rate (Å/sec)
1	950	3	2.9	7,917	43.95
2	1,000	2	2.3	6,279	52.33
3	1,050	2.5	3.9	10,647	70.98
4	1,100	2	4.8	13,104	109.20
5	1,150	2	9.0	24,570	204.75
6	1,200	1	6.6	18,018	300.30
7	1,250	1	9.4	25,762	429.30

Table IV. Deposition Rate Versus Source-Substrate Distance.

Source temperature = 1,050°C.
Vacuum pressure = 7.5 x 10^{-5} torr.

Sample No.	Source to Substrate Distance (inches)	Deposition Time (min)	Fringe Displacement (No. Fringes)	Oxide Film Thick. (Å)	Deposition Rate (Å/sec)
1	2¼	2	16	43,680	364.00
2	3	2	10.5	28,665	238.80
3	3½	2	6.8	18,564	154.70
4	4¼	2	4.3	11,466	95.55
5	5¼	2	3.3	9,009	75.08
6	6	2	3	8,190	68.25

Table V. Measurement of the Uniformity of SiO Film.

Source-substrate distance $h = 5\frac{1}{4}$ inches. $= 13.34$ cm Source temp. $= 1{,}050°C$

Vacuum pressure $= 7.5 \times 10^{-5}$ torr. Deposition time $= 4\frac{1}{2}$ min.

Distance from Center Above Source (χ) (cm)	Fringe Displacement (No. Fringes)	Measured Oxide Film Thickness (Å)	χ/h $\frac{\chi}{13.34}$	$(\frac{\chi}{h})^2$	$1+(\frac{\chi}{h})^2$	$\left[1+(\frac{\chi}{h})^2\right]^{3/2}$	Calculated Oxide Film Thickness (Å) $t=\frac{1}{\left[1+(\frac{\chi}{h})^2\right]^{3/2}}t_o$
0	6.9	18,837	0	0	1	1	18,837
1	6.9	18,837	0.075	0.0056	1.0056	1.005	18,837
2	6.9	18,837	0.15	0.0225	1.0225	1.03	18,600
3	6.8	17,764	0.23	0.053	1.053	1.078	17,750
4	6.2	16,653	0.30	0.090	1.09	1.136	16,840
5	5.7	16,107	0.38	0.145	1.145	1.175	16,250
6	5.2	14,190	0.45	0.201	1.201	1.315	14,520
7	4.9	13,104	0.53	0.282	1.282	1.45	13,109
8	4.1	11,193	0.60	0.36	1.36	1.585	11,205
9	3.5	9,828	0.68	0.463	1.463	1.765	10,820
10	3	8,190	0.75	0.565	1.565	1.956	9,770
11	2.6	7,098	0.83	0.708	1.708	2.24	8,502
12	2.0	5,460	0.90	0.81	1.81	2.34	8,050

Table VI. Capacitor Measurements.*

Substrate-source distance = 5¼ inches.
Source temperature = 1,050°C.
Vacuum pressure = 7.5 x 10^{-5} torr.

Sample No.	Thickness (Å)	Measured			Calculated		
		Capacitance $\mu f/cm^2$	Dissipation Factor D	Breakdown Voltage (volts) d-c	Capacitance $\mu f/cm^2$	Dielectric Constant K	Breakdown Voltage (volts) d-c
1	2,457	0.0219	0.12	25	0.0216	6.07	25
2	3,549	0.0154	0.11	30	0.0150	6.25	35
3	4,641	0.0114	0.10	34	0.0115	5.97	46
4	5,733	0.0111	0.14	50	0.0093	6.92	57
5	10,101	0.0058	0.077	62	0.0053	6.62	101
6	11,466	0.0055	0.061	74	0.0046	6.56	114
7	12,558	0.0041	0.070	68	0.0042	5.83	125
8	14,742	0.0037	0.066	76	0.0036	6.15	147
9	19,929	0.0025	0.041	95	0.0027	5.63	199
10	21,567	0.0024	0.038	115	0.0025	5.84	215

* Each value is the average of the three capacitors on the substrate.

Table VII. Dielectric Constant Versus Rate of Deposition.*

Source-substrate distance = 5¼ inches.
Vacuum pressure = 7.5 x 10^{-5} torr.

Sample No.	Rate of Deposition (Å/sec)	Thickness (Å)	Capacitance (1KC/S) μF/cm²	Dissipation Factor D	Dielectric Constant K
1	24.0	10,100	0.0038	0.055	4.33
2	36.4	5,460	0.0079	0.064	4.88
3	43.9	10,370	0.0045	0.061	5.27
4	56.9	10,200	0.0025	0.072	5.07
5	61.4	5,460	0.0095	0.093	5.86
6	72.3	15,000	0.0037	0.066	6.26
7	76.5	11,460	0.0053	0.061	6.86
8	86.5	10,380	0.0058	0.071	6.81
9	119.9	5,730	0.0114	0.105	7.38
10	182.2	11,200	0.0069	0.079	8.73

* Each value is the average of the three capacitors on the substrate.

Sample Calculations

1. The calculated value of capacitance (Sample No. 1, Table VI) was estimated from the capacitance relationship

$$C = \frac{0.0885\ K\ (N - 1)\ A}{t} \qquad (13,\ p.107)$$

where C = capacitance in picofarads
K = dielectric constant of SiO (use K = 6)
N = number of plates
A = area of plates in sq. cm
t = thickness of SiO film in cm

$$C = \frac{0.0885 \times 6 \times (2 - 1) \times 1}{2457 \times 10^{-8}}$$

$$= 21.6 \times 10^{3}\ \text{pf} = 0.0216\ \text{uf}$$

2. The dielectric constant of the oxide film (Sample No. 1, Table VI) was estimated from the measured values of capacitance and oxide film thickness by using the following relationship

$$K = \frac{Ct}{0.0885\ (N - 1)\ A}$$

$$= \frac{0.0219 \times 10^{6} \times 2457 \times 10^{-8}}{0.0885 \times (2 - 1) \times 1} = 6.07$$

3. The theoretical breakdown voltage (Sample No. 1, Table VI) was estimated from the simple relationship

$$V_{br} = St$$

where V_{br} = dielectric breakdown voltage in volts
S = dielectric breakdown strength of the oxide film in V/Å (use S = 10 v/1000 Å)
t = thickness of oxide film in Å

$$V_{br} = 10 \times 10^{-3} \times 2457 = 24.57 \cong 25\ \text{volts}$$