SILICON OXIDE FILMS GROWN AND DEPOSITED IN A MICROWAVE DISCHARGE

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Prepared under Contract No. NAS8-11931 for
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SUMMARY

The growth and deposition of silicon dioxide in a microwave discharge was investigated. The oxide growth can be characterized by a rate limiting diffusion process modified by sputtering effects produced by the discharge. Analysis of the growth behavior leads to the conclusion that a limiting oxide thickness is obtained at infinite time. The growth process provides a technique for rapidly oxidizing silicon at temperatures estimated to be 500°C or lower. At these low temperatures growth rates corresponding to steam oxidation rates at 1100°C can be obtained.

Etch rate, infrared spectra, breakdown strength, and resistivity measurements indicate that the high quality oxides produced by this process have properties which are for the most part indistinguishable from those of thermal grown oxides. MOS capacitance measurements indicate the oxides are quite stable under temperature-bias stressing. These measurements also show that the small shifts observed in the C-V characteristics are not due to the motion of mobile ions in the oxide.

The deposition technique provides a process for rapidly depositing silicon dioxide to any desired thickness at a constant deposition rate. Etch rate, infrared spectra, breakdown strength, and resistivity measurements show that in these properties the deposited oxides are indistinguishable from those of thermal oxides.

MOS field effect transistors fabricated from both microwave grown and deposited oxides on p-type silicon behaved as depletion mode transistors. The devices could also be operated in the enhancement mode. In general the characteristics of these devices were very similar to that of commercially available MOS field effect transistors made using thermally grown oxides.

INTRODUCTION

Silicon dioxide films are used for a variety of purposes in the fabrication of silicon devices. Very high quality oxides are produced by thermal oxidation of silicon substrates. The flaw seeking processes that occur during oxide growth probably assist in achieving this high quality. However, in order to produce films thicker than 1000 A in reasonably short periods of time, the oxidation must be performed at high temperatures. The high temperatures involved in this process are undesirable for a number of reasons, e.g., redistribution of prior diffusion fronts may occur, dislocation densities tend to increase, and lifetime may suffer.

Electrical discharges have been used to produce oxide films at low temperatures. Oxidation in a dc discharge[1] does not appear to offer much promise of achieving the moderately thick films required in many device applications. Recently it has been shown that in the denser plasma produced in a microwave discharge, films thicker than 1000 A can be rapidly produced.[2] The purpose of this investigation was to determine the potentialities of the microwave discharge technique as a process for producing oxides for various device applications and, in particular, for critical device applications such as metal-oxide-silicon field effect transistors. The growth behavior and the properties of the oxides obtained by this technique were investigated.

Deposition techniques, e.g. sputtering, offer another method of producing silicon oxide films and are of interest for a number of

reasons. They can be used to deposit silicon oxide on substrates other than silicon. Thick films can be obtained more rapidly since the deposition rate is usually independent of thickness. In thermal oxidation the growth rate is essentially inversely proportional to the thickness. None of the substrate is consumed by a deposition process. In oxide growth, silicon is consumed, and with a doped substrate impurities are introduced into the oxide. While the introduction of a small amount of impurities would not be expected to produce large changes in the oxide properties, it is not known at present how significant this effect may be in critical devices applications.

With the dc reactive sputtering techniques it has been necessary to employ rather low deposition rates in order to obtain silicon dioxide with the desired stochiometry. The denser plasma produced by a microwave discharge has been shown[3] to be capable of depositing silicon oxide films at very high rates. Based on these promising preliminary results, this technique was used to deposit silicon oxide and the properties of these oxides investigated.

OXIDE GROWTH APPARATUS

The apparatus used to grow silicon oxide on a silicon substrate in a microwave discharge is shown in Figure 1. The quartz discharge tube, except when otherwise specifically mentioned, had an 11 mm bore. A tapered matching waveguide section was used to couple power to the discharge tube from a 2.4 kMc/sec microwave generator with a power output variable between 500 and 1000 watts.

It has been previously shown that in dc discharges[1] and microwave discharges[2] the oxidation rate is enhanced if a positive dc potential is applied to the sample. Two electrodes were inserted in the discharge tube solely for the purpose of enhancing the rate of oxidation. The lower electrode acts both as the anode and the sample pedestal. The upper electrode in this system serves to complete the dc circuit; being cathodic it can also behave like a sputtering target. To prevent sputtered material from reaching the sample, the spacing between the electrodes were made large. At a pressure of 100 μ, the 20 cm spacing used between the two electrodes in this apparatus corresponds to a distance of about 200 mean free paths. Thus, material sputtered off the cathode should be scattered to the walls before reaching the sample.

The electrodes are a potential source of contamination. To minimize the problems from this source, silicon rods (9mm in diameter) were used as the electrodes. Impurities driven from the walls of the discharge tube due to bombardment of the walls by energetic species in the discharge, serve as another potential source of contamination. To

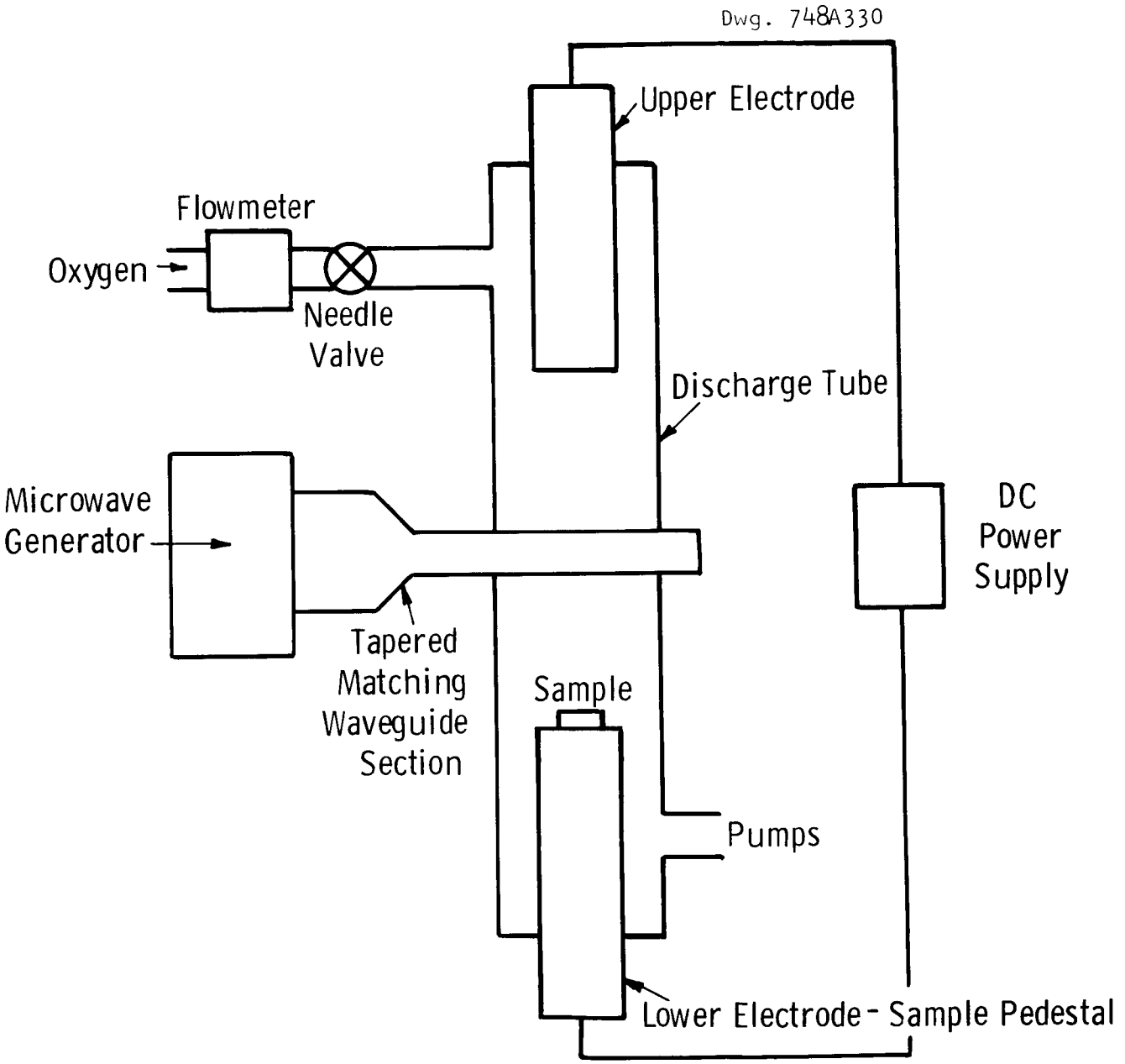

Fig. 1 Microwave discharge system for oxide growth.

minimize contamination from this source the apparatus was operated as a dynamic flow system with oxygen being metered into the system through a needle valve.

In the dynamic system both the flow rate and pressure influence the discharge characteristics. Pressure measurements in this system were made at the outlet end of the discharge tube. Under conditions of constant outlet pressure, the pressure in the main body of the discharge tube increases with flow rate. The pressure in the main body of the discharge tube can be estimated from the appearance of the discharge. Under conditions of constant flow rate, outlet pressure and microwave input power, the reproducibility achieved in overall system performance was the same under dynamic and static conditions.

EXPERIMENTAL CONSIDERATIONS

In a typical experiment a 6 x 6 mm square silicon wafer was placed on the sample pedestal and the system evacuated to the 10^{-6} to 10^{-7} torr range. Oxygen was metered into the system at 50 cc/min and the outlet pressure adjusted to 150 μ Hg. With the microwave generator adjusted to deliver about 600 watts, the electrodeless microwave discharge produced a pale red oxygen plasma in the discharge tube. Under these conditions the volume of the plasma was sufficient to immerse both silicon rods (and the sample) in the plasma. Oxide growth was observed on the sample and on both silicon rods.

At higher pressures the plasma became a deeper red; at lower pressures it gradually changed over to a bluish-white. At pressures below about 10 μ it was impossible to maintain a discharge in the tube. The volume occupied by the discharge increased as the pressure was reduced.

With other conditions constant, increasing the microwave input power increased the volume occupied by the discharge without significantly changing the appearance of the discharge. This result suggested that variation in the microwave power input did not produce significant changes in the plasma density, but only in its total volume.

The most significant effects produced by changes in the flow rate were ones that could be attributed to the accompanying changes in the pressure of the discharge. Sufficient experimental data is not available to predict the effects of flow rate under conditions in which the discharge pressure is held constant.

The oxygen plasma produced by the microwave discharge contains about equal concentrations of negative and positive excited species in addition to excited neutral species. In addition to electrons and positive ions the oxygen plasma contains a variety of negative ions, e.g., O^-, O_2^-, O_3^-. However, the relative populations of these various species and their variations with plasma conditions have not been investigated in sufficient detail to be used as a basis for analyzing the oxidation behavior.

Changes in the appearance of the plasma with pressure provides a useful way of estimating the pressure of the discharge. Most of the lines and bands of the oxygen spectra occurring in the visible region are due to atomic oxygen transitions or transitions in the first negative system ($^4\Sigma_g \rightarrow {}^4\pi_u$) of O_2^+ ions. The observed color changes in the plasma appear to be due to variations in the intensity of various bands of this first negative system of O_2^+ with pressure.

The walls of a discharge tube act as both a recombination surface and a perturbing influence on the plasma. Because the electron velocity is considerably higher than the positive ion velocity, more electrons than positive ions will strike an uncharged surface. The surface will eventually assume a negative potential such that equal numbers of electrons and positive ions reach it. Thus, the walls of a discharge tube are at a negative potential with respect to plasma. As a result of this negative potential the walls are covered by a positive ion space charge sheath.

The silicon rods in the discharge tube are essentially large Langmuir probes. An insulated probe behaves in a manner similar to the tube walls and also assumes a negative potential (its insulated potential) with respect to the plasma. When an ideal probe is made sufficiently negative with respect to its insulated potential, the current to it will be limited by the random positive ion current density in the plasma and further increases in the negative potential will only effect the thickness of the positive ion space charge sheath. When made positive with respect to its insulated potential (but still negative with respect to the plasma), the electron current to the probe exceeds the positive ion current. When the probe potential is made equal to the plasma potential a large net electron current will flow, equal to the difference between the large random electron current and the small random positive ion current. At this potential the space charge sheath disappears.*

The silicon rods in the discharge tube form a double probe system. The net probe current which can flow in an ideal double probe system will be limited (as long as the applied potential is not high enough to produce secondary ionization) by the random positive ion current. With increasing applied potential, the anode tends to approach plasma potential, but always remains at a potential somewhat negative with respect to the plasma. Under these conditions, the space charge sheath surrounding the anode remains positive, and the positive ion current to

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* A more detailed discussion of probe theory can be found in standard texts on gas discharges, e.g., J. D. Cobine, "Gaseous Conductors" (Dover Publications, Inc., New York, 1958).

the anode is of about the same magnitude as the positive ion current to the cathode. The applied potential distributes itself with most of its potential dropped across the space charge sheath adjacent to the cathode. The magnitude of the electron current flowing to the anode is, under these conditions, approximately twice that of the positive ion current flowing to this electrode.

The perturbing influences of a probe on a plasma are readily observable in the experimental apparatus. When the silicon rods are immersed in the plasma, a white glow fills the region surrounding them. The additional perturbing influence of an external applied dc potential manifests itself by an increase in intensity and volume of the region occupied by this white glow. Similar perturbations can be produced by other means and will be discussed later.

When a dc potential of between 200 and 400 volts is applied between the silicon rods, violent random sparking is occasionally observed at the cathode. This sparking is only observed if an oxide has been allowed to build up on the cathode. It has been suggested[2] that sparking is due to electrical breakdown which occurs when the positive surface charge on the oxide becomes large enough to produce a field across the oxide which exceeds the breakdown strength of the oxide. Sparking can be prevented if the cathode is clean, i.e., has no visible oxide in it, and the external potential is applied when the oxidation is started. Under these conditions heavy positive ion bombardment on the end surface of the cathode prevents any appreciable oxide build-up. Some

oxide formation is observed on the sides of the cathode, but apparently the rate of positive surface charge accumulation on the sides is not sufficient to produce a field exceeding the breakdown strength of the oxide. When large applied potentials are used, more stable operation is achieved by using a constant current source.

The temperature of the sample being oxidized can only be estimated rather crudely. Pyrometric observation shows that the sample temperature must be less than 700°C. Conversely the sample temperature must be greater than the measured temperature of the lower end of the sample pedestal (150°C). Other temperature measurements show that with 600 watts microwave power, a flow rate of 50 cc/min, and a pressure of 150 μ, the outside walls of the discharge tube reach a temperature of 450°C near the tapered matching waveguide section and 400°C near the upper end of sample pedestal. Because of the cooling provided by the silicon support it would be expected that the sample temperature would be equal to or less than the wall temperature. However, we must consider the thermal contact between the sample and the sample pedestal. The following indicates that it is quite poor. The growth rate on top of the sample pedestal is significantly lower than on the sample. When a thin piece of glass is interposed between the sample and sample pedestal, only a slight increase in growth rate on the sample is observed. Application of a large rf potential to the sample pedestal heats the sample to incandescence (about 1000°C) but not the sample pedestal (less than 700°C). Hence, it seems reasonable to assume the sample is not significantly cooled by the silicon support and its temperature should be approximately equal to the wall temperature of the tube in its vicinity.

OXIDE GROWTH BEHAVIOR

As long as the sample is immersed in the plasma, variations in the microwave power level do not significantly influence the growth rate except for effects that might be attributed to small changes in the plasma density and temperature of sample.

Figure 2 illustrates the results of growth rate studies with a microwave power of 600 watts, an oxygen flow rate of 50 cc/min, and a pressure of 150 μ. The rate of oxide growth when no external voltage is applied to the silicon rods is shown by the curve A. The enhancement in the oxide growth rate obtained using externally applied voltages (V_{dc}) is illustrated by the two remaining curves in this figure. Curve B shows the oxide growth behavior when a potential of V_{dc} = 50 volts is applied between the silicon rods. The oxide growth behavior when a constant current source adjusted to deliver 100 ma is connected to the silicon rods (potential across rods approximately 300 v) is shown by curve C.

The perturbing effects in the plasma produced by the application of an externally applied voltage (as manifested by the white glow region surrounding the sample) can be produced by other means. For example, a split non-magnetic metal ring clamped around the outside of the discharge tube so that it encircles the top surface of the sample pedestal produces an increase in the intensity and volume of the white glow region. An enhanced oxide growth rate is also obtained. Figure 3 illustrates the growth behavior using the ring. Curve A represents the growth behavior both without an externally applied voltage and with an external dc potential of 50 volts. Comparison of this curve with curve C

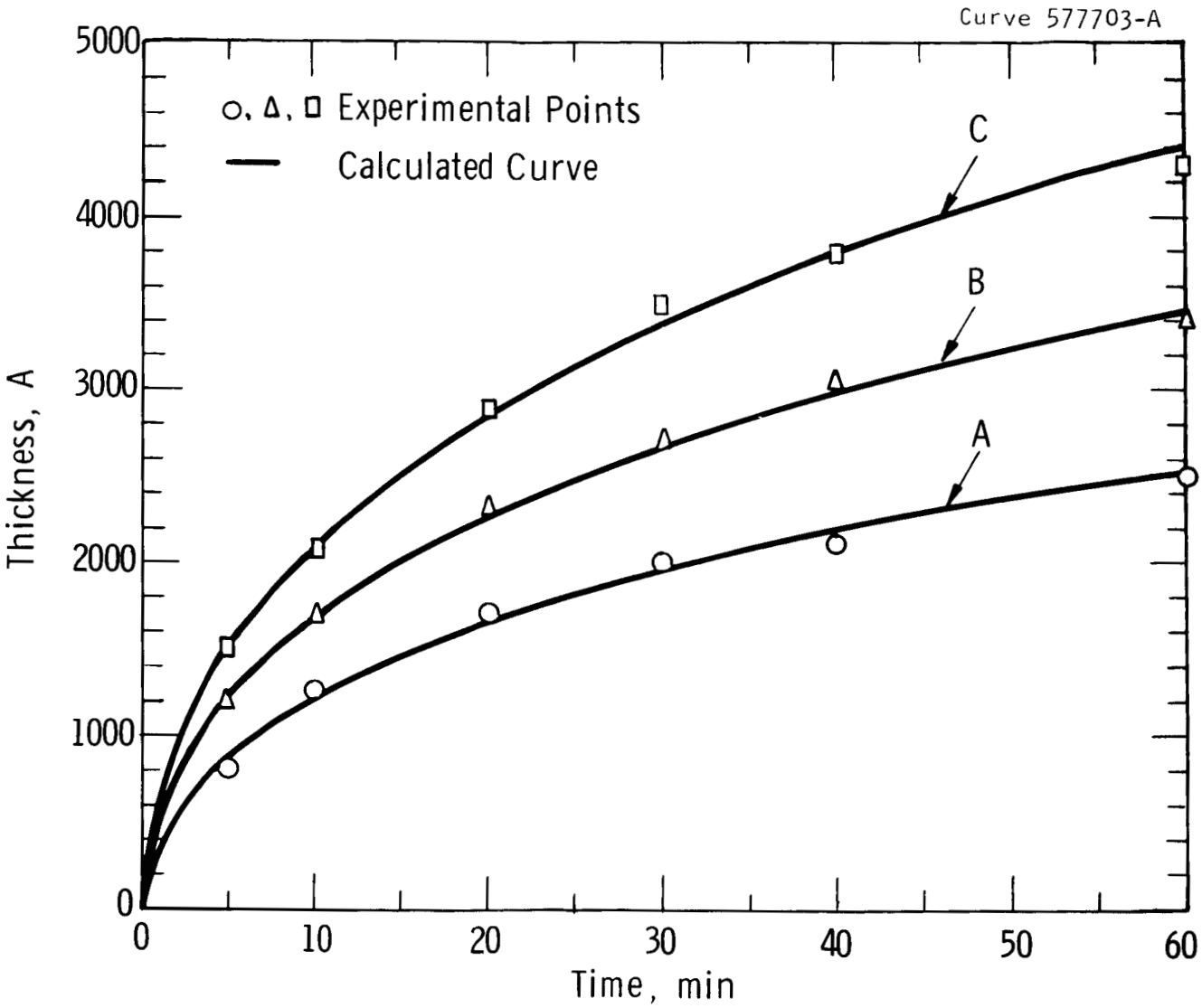


Fig. 2 Oxide growth in a microwave discharge. Microwave input power: 600 watts; oxygen flow rate: 50 cc/min; pressure: 150 μ. Circles: no externally applied potential. Triangles: 50 v externally applied potential; sample pedestal positive. Squares: 100 ma externally applied current; external potential approximately 300 v; sample pedestal positive. Solid curve: calculated using Eq. (2) and the constants in Table I.

of Figure 2 indicates that a higher growth rate can be achieved at V_{dc} = 0 using the ring that can be obtained at V_{dc} = 300v without the ring. Curve B in Figure 3 shows the oxide growth rate obtained using the ring when a constant current source set to 100 ma is connected to the silicon rods ($V_{dc} \sim$ 300v). A film approximately 6000 A thick was grown in 60 minutes under these conditions. About 300 minutes at 1300°C, or about 1000 minutes at 1100°C would be required to thermally grow an oxide of this thickness in dry oxygen at 1 atm pressure. Even in steam at 1 atm pressure, a temperature of 1100°C would be required to thermally grow an oxide of this thickness in 60 minutes.

To further study the growth behavior in the microwave discharge, oxidations were also carried out on silicon wafers that had been previously thermally oxidized. A rather interesting result was obtained on samples which had a thick thermal oxide of about 10,000 A. Instead of growing thicker these oxides became thinner. Typically a 10,000 A oxide might lose 400 A in an hour. These results suggest that in addition to growth in the discharge, bombardment by energetic species in the discharge simultaneously sputters-off oxide. We will return to this sputtering effect again in our analysis of the growth behavior.

Oxides were grown on low (0.1 Ω-cm) and high resistivity (50 Ω-cm) n- and p-type silicon. No significant differences in the growth behavior were observed as a function of resistivity or type.

The effect of pressure on the oxide growth rate was investigated under static conditions using a microwave power of 600 watts and without applying an external voltage. At pressures below about 40 μ no

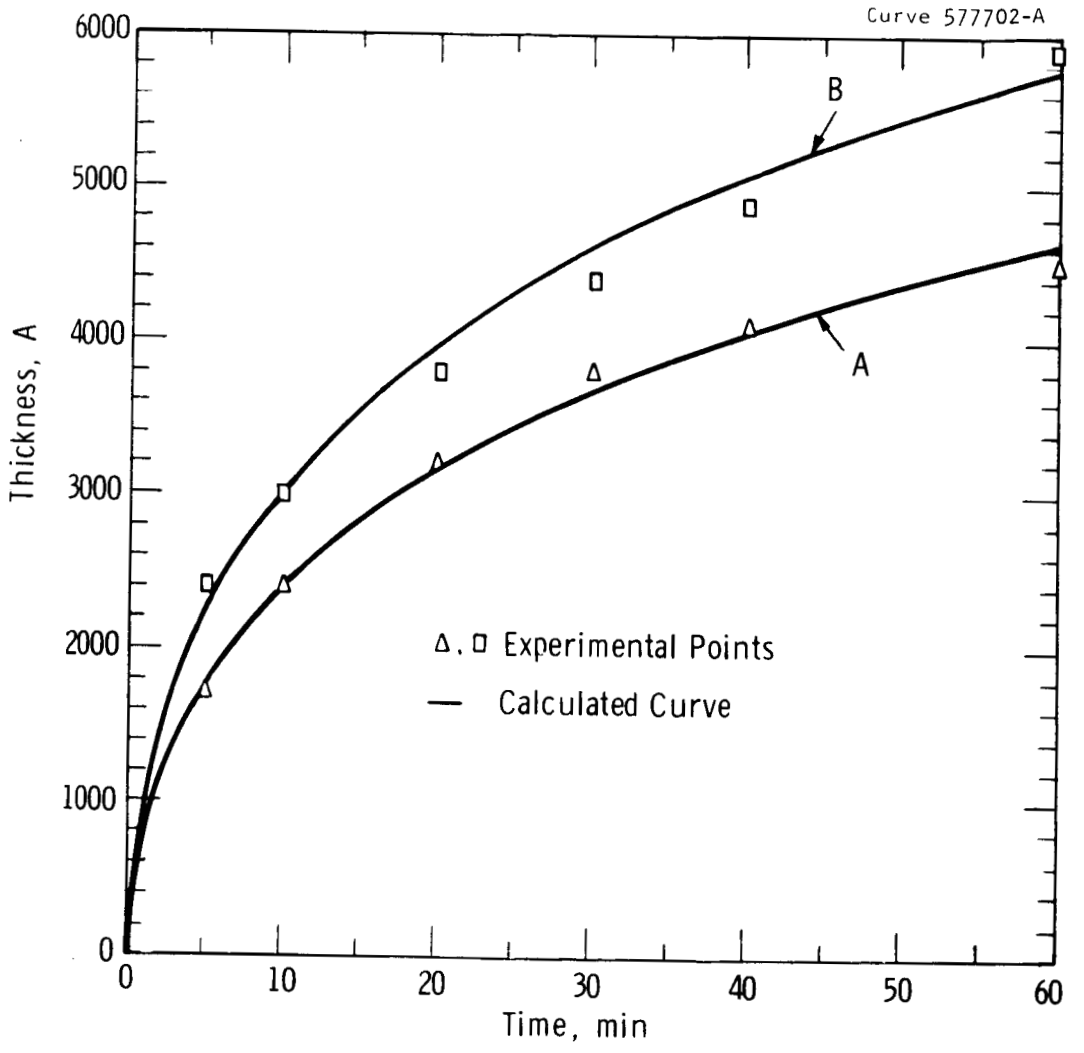


Fig. 3 Oxide growth in a microwave discharge using an external ring. Microwave input power: 600 watts; oxygen flow rate: 50 cc/min; pressure: 150 μ. Triangles: 50 v externally applied potential; sample pedestal positive. Squares: 100 ma externally applied current; external potential approximately 300 v; sample pedestal positive. Solid curve: calculated using Eq. (2) and the constants in Table I.

significant growth was observed. A broad maximum in growth rate occurred in the range from about 150 to 700 μ. At pressures above this the growth rate falls off. The significant changes in the appearance of the discharge make it relatively simple to adjust conditions in the flow system so that the pressure in the discharge tube is within the region corresponding to the broad maximum in the growth rate. The results shown in Figures 2 and 3 correspond to operation in this region.

OXIDE UNIFORMITY

While it has been possible to grow on occasion oxides of rather uniform thickness, e.g., an oxide 2000 A thick up to the very edge of sample where the thickness is about 1800 A, it has not been possible to do this reproducibly. More typically only the central region covering 50-75% of the sample area was uniform on samples comparable in size to sample pedestal. The edges of such samples were usually about 1000 A thinner than the central region. On some occasions oxides with a valley type of pattern were obtained in which the oxide in the region surrounding the thicker uniform central portion was also slightly thinner than the oxide at the sample edges.

For samples comparable in size to sample pedestal the contour lines of oxide thickness follow the shape of the specimen. This was not true of samples of very small size, i.e., about 1 mm square. For example, if a number of these small samples were placed at random sites on the sample pedestal and simultaneously oxidized, a variety of growth patterns were observed. Some of the small samples were very uniform throughout. Others had two regions of uniformity, but of different thickness, with a sharp line of demarcation between them. Still others had very non-uniform patterns bearing no relationship to the shape of the specimen.

This aspect of the oxidation growth behavior was also investigated in a discharge tube of somewhat different design than the one shown in Figure 1. In this discharge tube the central section also

had an 11 mm bore (6 cm long), but the two end sections had a 27 mm bore. Oxidation studies were made using electrodes of the same size as those used in the first tube (9 mm dia) and with large electrodes (25 mm dia). Large silicon wafers (25 mm dia) and smaller wafers were oxidized. The results were not encouraging. Growth rates were significantly lower in this tube even at a microwave power of 1000 watts. The lower plasma density in the large bore tube may account for this. The use of a ring gave no significant enhancement in the growth rate with this tube. Uniform oxide thickness was not obtained.

The oxidation process in a microwave discharge is not well enough understood to explain the various growth patterns observed. Perturbations in the plasma distribution and configuration that occur adjacent to the sample surface may be responsible. If these perturbations are not uniform, differences in the thickness of space charge sheath, the density of space charge in the sheath, and differences in the recombination rate of species at the sample surface may result. Inhomogeneities of this sort would be expected to become more pronounced as the sample edges are approached. Experimentally these edge effects are manifested by a more intense white glow at the edges of the sample. The most uniform oxides were obtained when this white glow was most intense (using 300 v bias) and most uniform across the sample surface. However when we have on occasion observed what appeared to be non-uniformities in the intensity of this white glow over the sample surface, we were unable to correlate these non-uniformities with the resulting growth pattern.

ANALYSIS OF GROWTH BEHAVIOR

In many of the earlier investigations of the thermal oxidation of silicon the experimental data was analyzed using a parabolic rate law. More recently attempts have been made to analyze the data based on a linear-parabolic rate expression.[4] A rate expression of this form was originally suggested on the basis of a model in which the oxidation rate would be limited by a boundary reaction at the beginning and become diffusion limited at later stages.[5]

While it appears that a satisfactory analysis of the steam and wet thermal oxidation of silicon can be made using the linear-parabolic rate expression, certain difficulties arise when this rate law is used to analyze the dry thermal oxidation of silicon. In particular this analysis leads to the conclusion that an oxide about 200A thick is present before the oxidation is started. This unrealistically large initial thickness has been interpreted as implying an initial rapid oxidation process.[4] While this conclusion appears to be supported by measurements made at the early stages of oxidation of silicon at 700°C, it also indicates that a different and probably more complicated rate expression than linear-parabolic form is required to fit both the initial and later stages of the oxidation process.

These results suggest that a complicated rate expression will also be required for a detailed analysis of the oxidation behavior in a microwave discharge. Such a detailed analysis will not be attempted here. Instead, we will assume that the growth behavior is essentially parabolic,

with the most significant deviations being due to the sputtering effect previously noted. If we further assume that the rate of removal by this sputtering process is constant, the simple parabolic growth expression is modified to the form

$$\frac{dx}{dt} = \frac{k_p}{2x} - s, \tag{1}$$

where x is the thickness, t the time, k_p the usual parabolic rate constant, and s the sputtering rate constant. When $(k_p/2x)-s = 0$, the growth rate becomes zero. This indicates that at infinite time the oxide asympotically approaches a limiting thickness given by $x_L = k_p/2s$. In comparison the simple parabolic expression, i.e., s = 0 in Eq. (1), implies an infinite thickness at infinite time.

Equation (1) can be integrated to yield the expression

$$t = \frac{-1}{s}(x-x_o) - \frac{k_p}{2s^2} \ln\left(\frac{k_p - 2sx}{k_p - 2sx_o}\right), \tag{2}$$

where x_o is the oxide thickness at t = 0. Somewhat better insight to the physical significance of Eq. (2) can be obtained by expanding the logarithmic term. For the case in which $x_o < x_L$, e.g., the oxidation of a bare silicon substrate, this expansion gives

$$t = \frac{1}{k_p}(x^2-x_o^2) + \frac{4}{3}\frac{s}{k_p^2}(x^3 - x_o^3) + \ldots \tag{3}$$

plus higher order terms. It is now easy to see that if s = 0, the equation reduces, as expected, to the simple parabolic rate expression.

When the experimental data shown in Figs. 2 and 3 is plotted on an x^2 versus t representation, the deviations from linearity are in the direction predicted by Eq. (3). This is shown in Fig. 4, where the data of Fig. 2 has been plotted in this x^2 versus t representation. A simple parabolic rate expression should yield a straight line. It can be seen that for small thicknesses, the data points do fall on a straight line. This is to be expected, since initially $k_p/2x$ will be much larger than s, cf., Eq. (1). As growth proceeds $k_p/2x$ decreases and the deviations from the straight line behavior should increase. This can be seen in Fig. 4.

The data shown in Figs. 2 and 3 have been fitted to Eq. (2) assuming $x_o = 0$. The rate constants obtained are shown in Table I. The solid curves, shown in Figs. 2 and 3 have been calculated using the constants in Table I. The fit is within the experimental accuracy of the data. While it is encouraging to be able to fit the data so well with this simple model, the constants listed in Table I must be interpreted with some caution. Other and significantly different values for the rate constants lead to fits only slightly poorer than those obtained with the values in Table I.

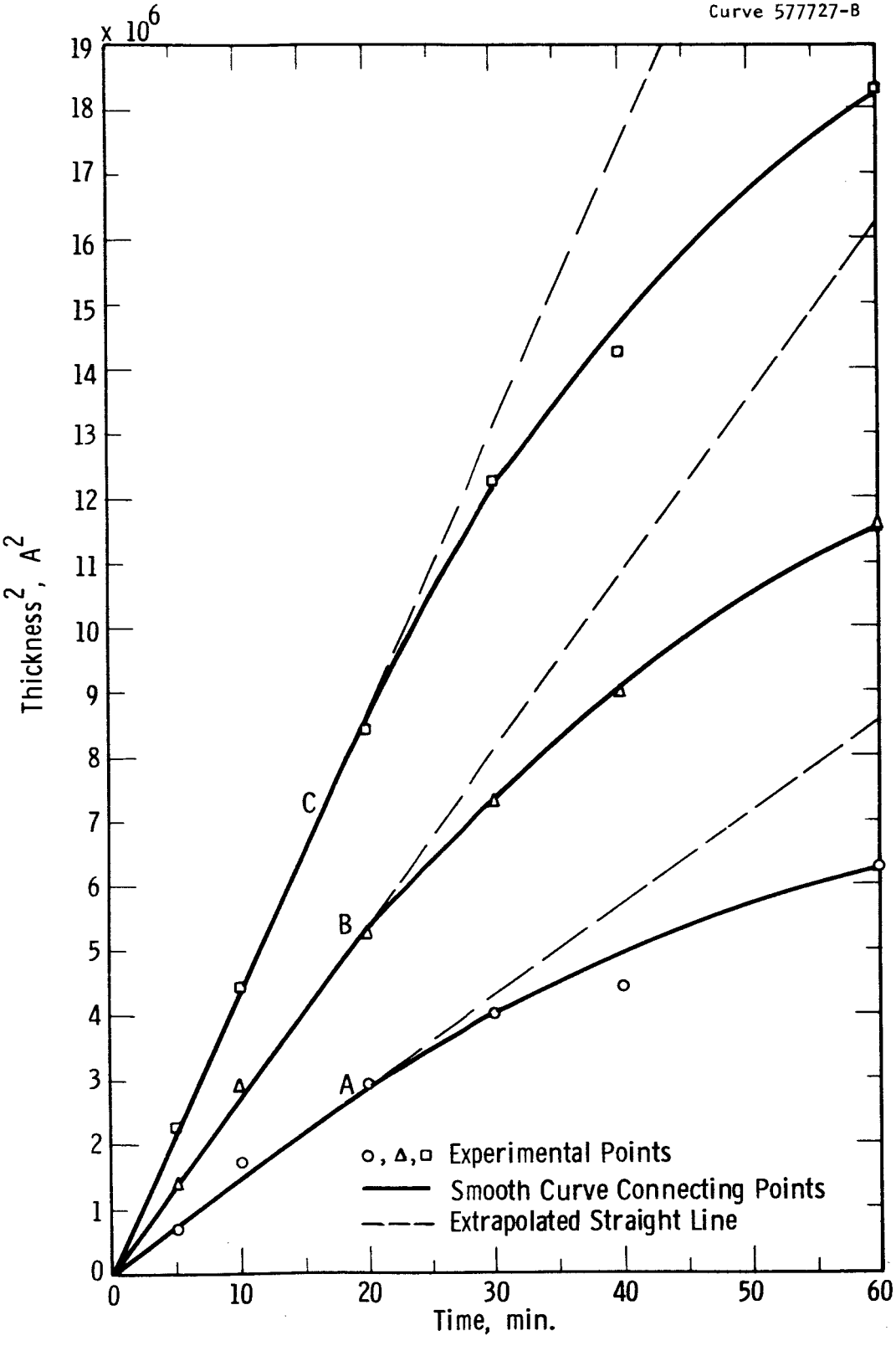


Fig. 4 A thickness squared versus time representation of the microwave oxide growth data of Fig. 2.

Table I. Analysis of Growth Behavior.

Oxidation Conditions	k_p (A^2/min)	s (A/min)	x_L (A)
without bias (Fig. 1, Curve A)	1.87×10^5	21.9	4300
50v bias (Fig.1, Curve B)	3.59×10^5	32.2	5600
300v bias (Fig. 1, Curve C)	5.46×10^5	34.7	7900
without bias-ring 50v bias-ring (Fig.2, Curve A)	7.70×10^5	60.3	6400
300v bias-ring (Fig.2, Curve B)	1.25×10^6	81.5	7700

OXIDATION MECHANISM

Despite the mass of data that has been accumulated on the thermal oxidation of silicon, the mechanism of oxidation is not completely understood. Oxidation in a microwave discharge is considerably more complex and, at present, we can only present a tentative description of the oxidation mechanism.

It has been previously suggested and appears to be generally accepted that, in the region of parabolic growth behavior, thermal oxidation of silicon proceeds by diffusion of an oxygen species. Analysis of the growth behavior in a microwave discharge indicates the oxidation is essentially a diffusion limited process and presumably an oxygen species is again the migratory particle.

In thermal oxidation the growth rate is determined by the mobility of the diffusing species and the concentration gradient of the diffusing species across the oxide film. Increasing either or both of these will result in a more rapid rate of oxidation. With increasing temperature the mobility of the diffusing species increases and the concentration gradient of the diffusing species may also increase. Relatively high temperatures(1000-1200^{o}C) are necessary to increase the mobility and concentration gradient sufficiently to achieve rapid thermal oxidation of silicon.

If it is assumed that the same migrating species is responsible for thermal growth and for growth in a microwave discharge, then the mobility of this species will be very low at the microwave oxidation

temperature. To account for the rapid oxide growth in the microwave discharge it would then be necessary for the concentration gradient to be very high. Energetic bombardment of the sample by various excited species in the plasma can provide the energy necessary to promote the formation of the migrating species. However, our present understanding does not allow us to state whether this process could enhance the concentration of the migrating species sufficiently to account for the rapid growth observed. An alternate possibility is that the energetic bombardment of the sample in the plasma promotes the formation of a different and more mobile oxygen species. This more mobile species would not normally be present in sufficient concentration to influence the thermal oxidation, but could account for the rapid oxidation in the microwave discharge.

It does appear that the rapid oxidation rate in the microwave discharge is not primarily due to the presence of negative oxygen ions in the plasma as has been previously suggested.[2] At least in the case where no voltage is applied to the electrode, the behavior of the electrodes will closely approximate the behavior of ideal probes. When insulated, the silicon electrodes assume a negative potential with respect to the plasma. Hence, only positive ions and energetic electrons from the tail of the Boltzman distribution will strike the electrodes (and sample). Very few, if any, negative ions will strike the electrodes, since practically all the negative ions are produced with only a few electron volts of thermal energy. For small applied potentials, ideal probe theory should still be valid and there will again be no significant negative ion flux to the electrodes. However, when the applied potential

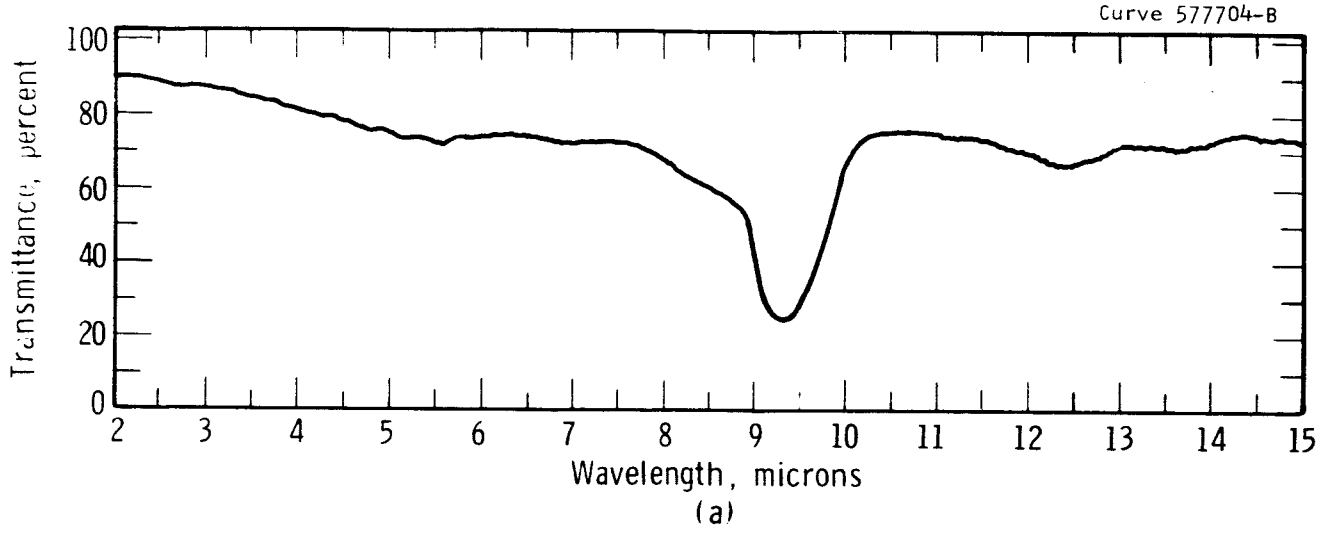
becomes large enough so that the drift current becomes comparable to the random electron and ion currents, ideal probe theory is no longer applicable. Under these conditions the perturbations produced by the probe are no longer confined to a thin space charge sheath surrounding the electrodes. Current in the double probe system is no longer limited by the random positive ion current and can, in fact, be considerably enhanced by ionization and secondary electron emission. Significant contributions to the anode current by negative ions can be expected under these circumstances. These conditions certainly prevail when the applied dc potential is about 300 volts and most probably even when the potential is about 50 volts. The large currents flowing to the anode impart additional energy to the sample. This can serve to further promote the formation of the mobile oxygen species, increasing the concentration gradient and, hence, the growth rate. At the cathode, any enhancement of the oxidation rate is more than counterbalanced by the effects of energetic positive ion bombardment, and a net loss of material by sputtering is obtained.

The influence of the negative oxygen ions flowing to the anode when a large external bias is applied to the electrodes may be two-fold. The mobile species may be one of the negative oxygen ions present in the plasma in sizable concentration. Those which strike the sample would then contribute directly to increasing the concentration gradient. In addition, this negative ion, plus the others present in the plasma can also impart energy to the sample promoting the formation of the mobile species.

OXIDE PROPERTIES

Thermally grown silicon dioxide films have been used so successfully in such a variety of device applications that they may serve as a standard to which silicon oxides produced by other techniques may be compared.

Earlier investigations have established that when oxides produced by other techniques have inferior qualities from the standpoint of device fabrication, there are also significant differences between various properties of these oxides and thermally grown oxides.[6] For example, the infrared absorption spectra of thermally grown silicon dioxide has an Si-O stretching vibrational band at 9.3 μ, a weaker Si-O stretching vibrational band at 12.4 μ, and an Si-O-Si bending vibrational band at 22 μ. The positions and half widths of these bands may be expected to be strongly influenced by the stoichiometry, defect structure, bond character, density, and porosity of the film. Figures 5 and 6 show the infrared spectra of silicon oxide films produced by four different techniques: microwave grown, thermally grown, anodically grown, and pyrolytically deposited. In Table II the position of one Si-O stretching band is tabulated for these various oxides. For both the anodic and pyrolytic oxides the position of this band is significantly different from the position of this band for the thermal oxide. The position of this band for the microwave grown oxide is indistinguishable from that of the thermally grown oxide.



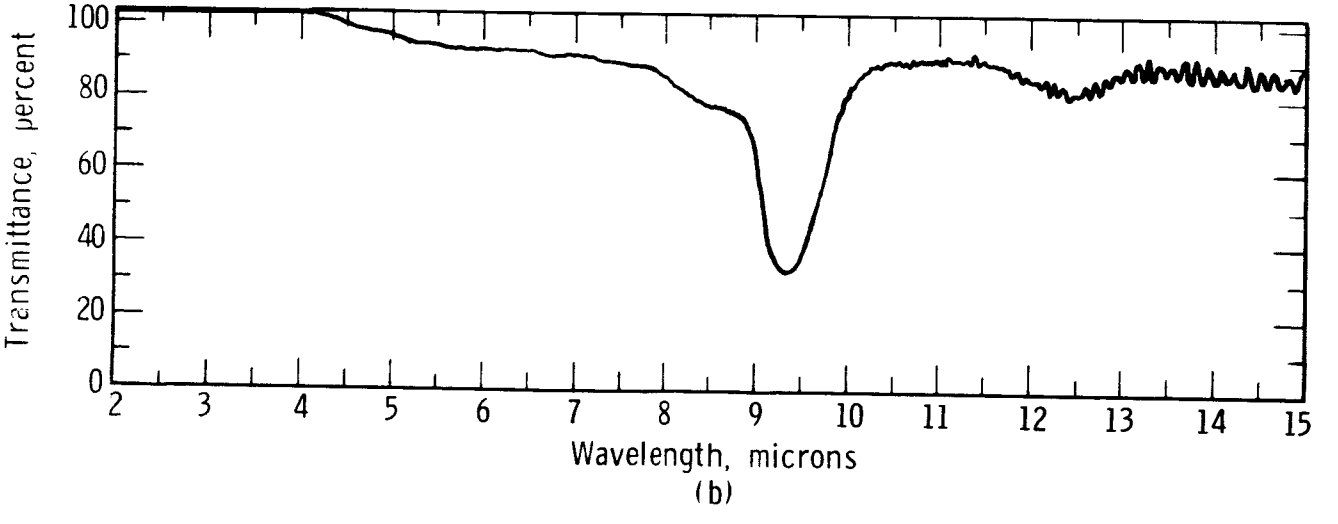
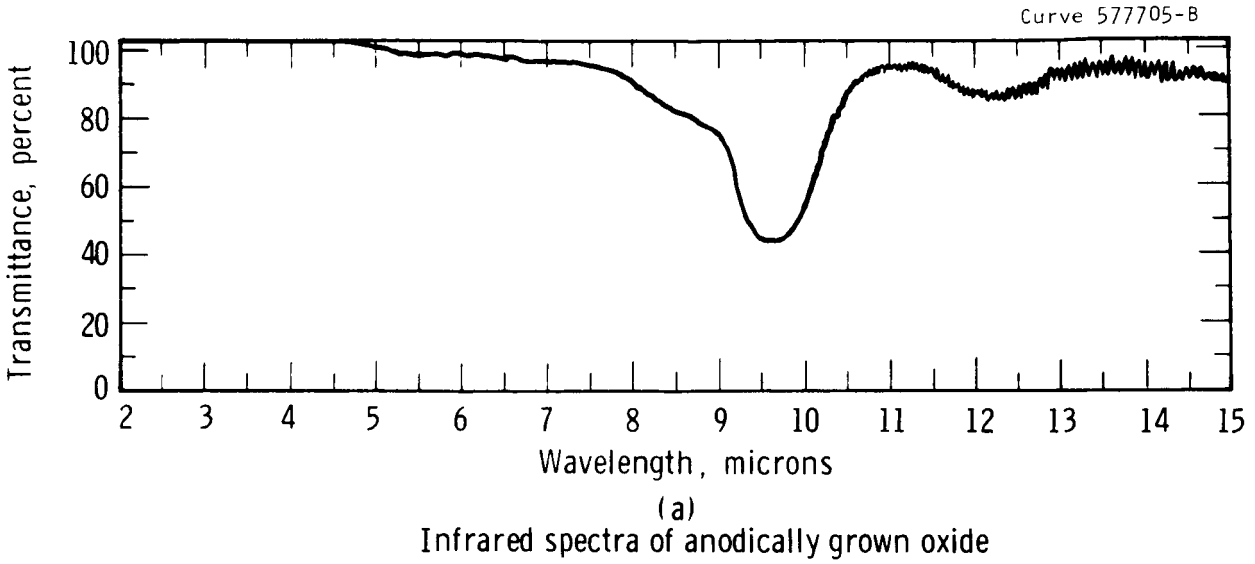


Fig. 5 Infrared spectra. (a) Microwave grown oxide about 3500 A thick. (b) Thermally grown oxide about 1000 A thick.



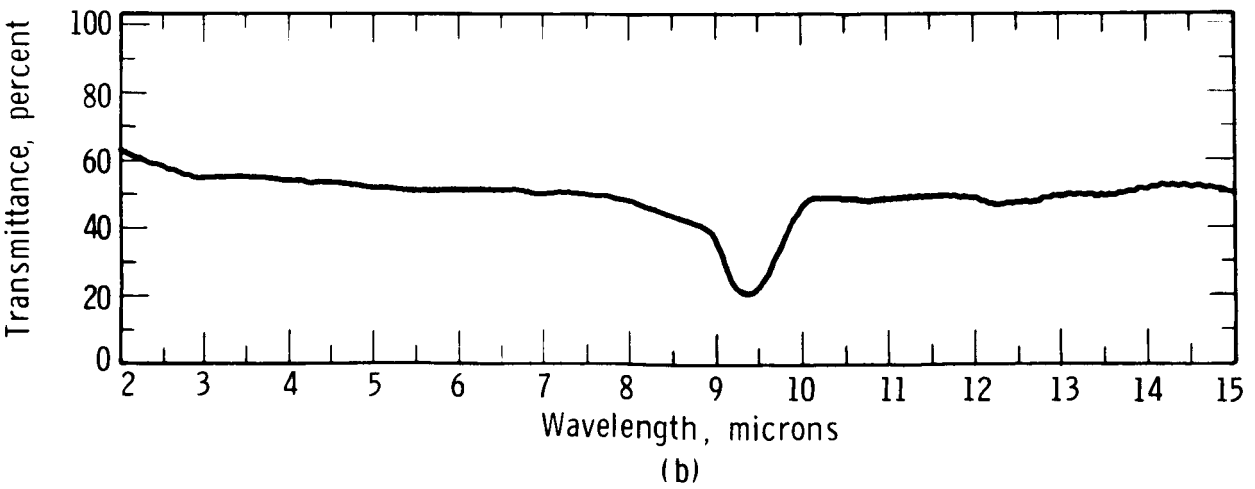


Fig. 6 Infrared spectra. (a) Anodically grown oxide about 1800 A thick. (b) Pyrolytically deposited oxide about 2600 A thick.

Table II also gives the results of our measurements of a number of other properties (etch rate, dielectric strength, resistivity) which can be used as measures of the quality of oxide films produced by various techniques. In these properties, the microwave oxides are again indistinguishable from those of thermal oxides.

Capacitance versus voltage (C-V) measurements were also made on MOS capacitors fabricated using oxides grown in the microwave discharge. Detailed analysis of C-V characteristics of the MOS capacitors is given in the literature.[7] In the measurements made in this investigation the small-signal high frequency (100 kc) capacitance of the MOS capacitor was studied as a function of the applied dc bias between the metal contact and silicon substrate (bias polarity being defined as the potential of the metal contact with respect to the silicon substrate). Variations in the bias voltage change the carrier concentration of the silicon layer at the oxide-silicon interface. As the bias is varied the change in carrier concentration from accumulation to depletion produces a change in the capacitance of the MOS structure from a value given by the oxide layer capacitance to a lower value given by the oxide capacitance in series with the depletion-layer capacitance. It is often convenient to use the flat band potential in describing the behavior of a MOS capacitor. At this potential the silicon conduction and valence bands are flat out to the oxide-silicon interface and the space charge in the silicon is zero. The dc bias which must be applied to the MOS capacitor to produce the flat band condition can be calculated, assuming the oxide capacitance, silicon doping, and the work function of the metal contact are known.

Table II. Some Properties of Silicon Oxides Produced by Various Techniques

	Etch Rate (p-etch)* (A/sec)	Breakdown Strength (v/cm)	Infrared Spectra Wavelength Si-O Stretching (μ)	Resistivity (Ω-cm)
microwave grown	2	$3\text{-}7 \times 10^6$	9.3	$0.1\text{-}5.0 \times 10^{16}$
thermally grown	2	$5\text{-}10 \times 10^6$	9.3	$0.1\text{-}5.0 \times 10^{16}$
anodically grown	30	$7\text{-}11 \times 10^6$	9.7	$0.1\text{-}1.0 \times 10^{16}$
pyrolytically deposited	10	4×10^6	9.35	$0.003\text{-}1 \times 10^{15}$

* p-etch: 15 parts HF, 10 parts HNO_3, and 300 parts H_2O.

Differences between the calculated value of the flat band potential and the value obtained from the measured C-V characteristics can be attributed to charges in surface states at the interface, and fixed or mobile space-charges in the oxide.

Figure 7 shows the C-V characteristics of an MOS capacitor fabricated using a microwave discharge oxide about 1800A thick grown on 50 Ω-cm n-type silicon. This MOS capacitor was fabricated by evaporating aluminum dots 0.2 mm in diameter on the oxide. The capacitor was then mounted on a header and a gold wire bonded to the metal dot. The curve labelled "Microwave: Original" shows the characteristics of the sample after fabrication was completed. The MOS capacitor was then subjected to temperature-bias stressing following the usual procedure of applying the desired bias to the structure, heating it to the desired temperature, allowing it to remain at this temperature for the desired time, cooling it to room temperature,and finally removing the bias. The C-V characteristics were then remeasured. The curve labelled "Microwave: 30 min, 150°C, 20v" shows the C-V characteristics remeasured after the MOS capacitor was kept at a 150°C for 30 min with a positive potential of 20v applied across the capacitor. For comparison the results obtained on a typical thermal oxide of about the same thickness are also shown. Figure 8 shows the results obtained on another MOS capacitor fabricated by the same procedure using a microwave discharge oxide about 1800A thick grown on 50 Ω-cm n-type silicon. This capacitor was subjected to temperature-bias stressing at 200°C, with both positive and negative bias voltages, as shown on the curve.

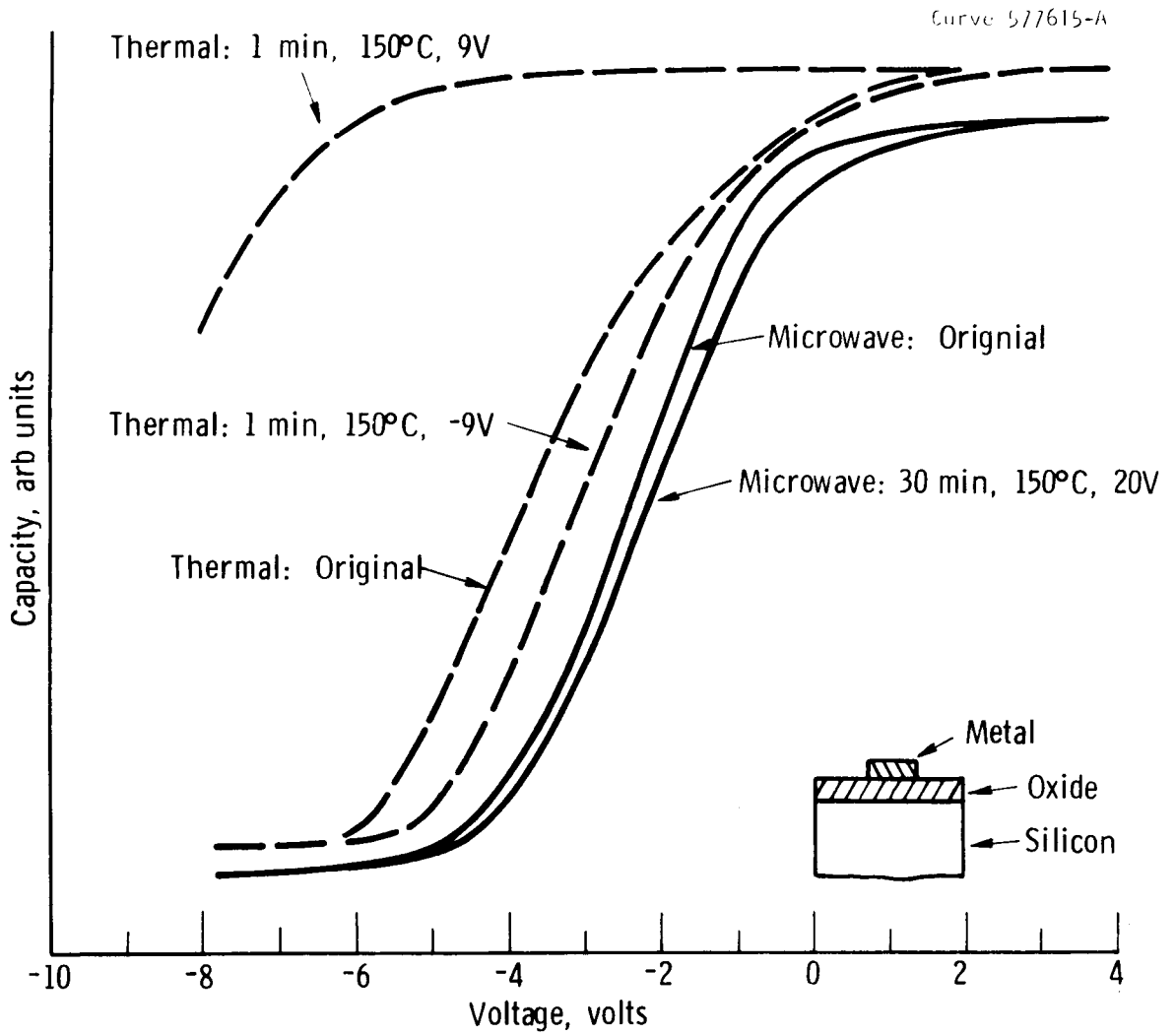


Fig. 7 Capacitance-voltage characteristics of MOS capacitors subjected to temperature-bias stressing.

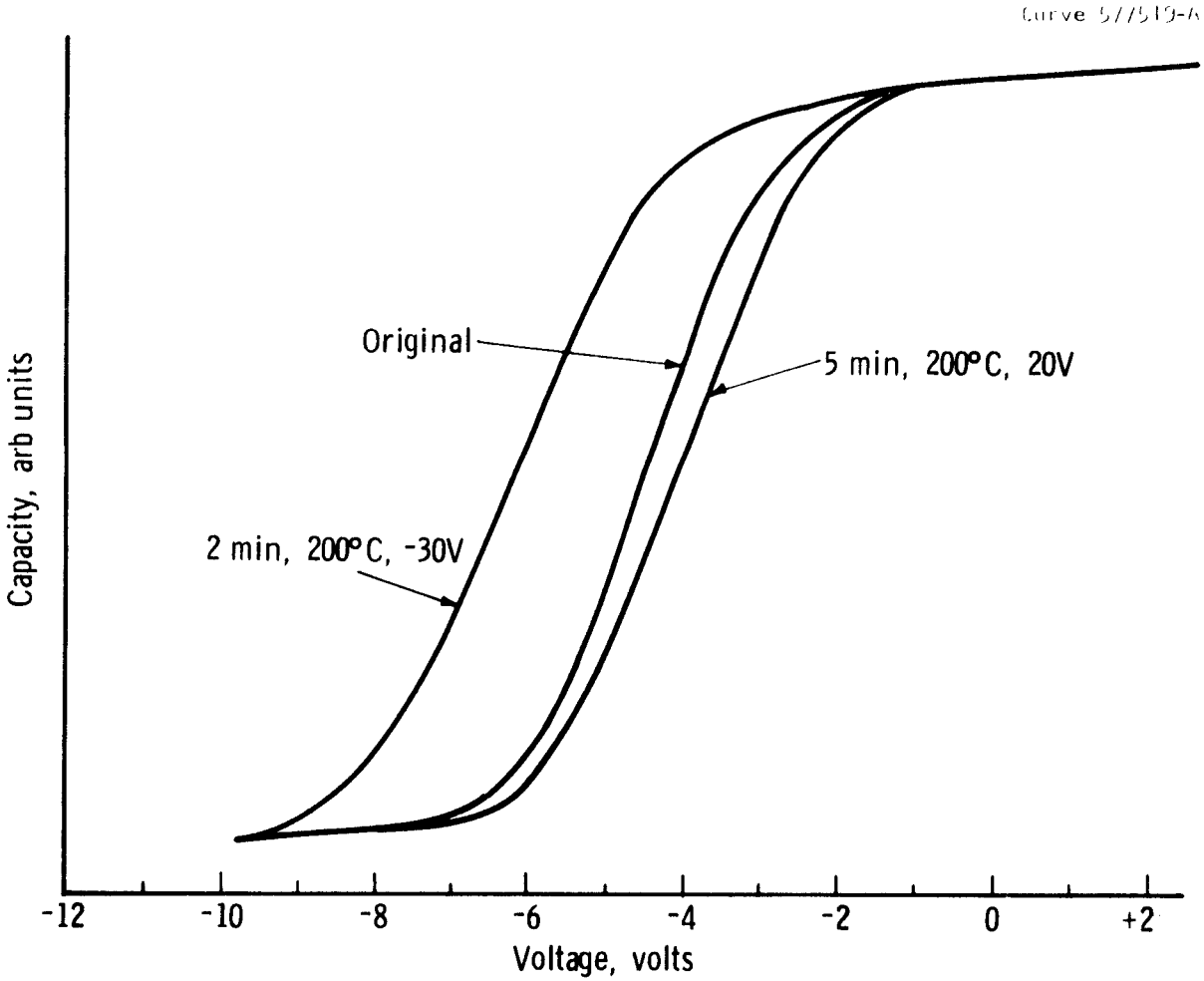


Fig. 8 Capacitance-voltage characteristics of MOS capacitors subjected to temperature-bias stressing.

First let us consider the behavior of MOS capacitors fabricated using the thermal oxide (see Fig. 7). The application of positive potential of 9v at 150°C for 1 min resulted in a large negative shift in the flat band potential. The application of a negative potential of 9v at 150°C for 1 min resulted in a smaller shift, but this time in the positive direction. These shifts have been attributed to the motion of ions in the oxide during the temperature-bias treatment. Since a larger shift is observed when the capacitor is subjected to positive bias during the temperature-bias treatment, it has been concluded that these shifts are due to the motion of positive ions.

The most significant feature exhibited by microwave grown MOS capacitors is that the flat band potential shifts in the negative direction with the application of a negative bias during temperature-bias treatment, and in the positive direction with the application of a positive bias. These results indicate that the motion of mobile ions in the oxide (either positive or negative) cannot be responsible for the observed shifts in the characteristics. In order for the C-V curves to shift in the same direction as the polarity of the applied stress voltage, charge extraction (or injection) must be occurring during the stress cycle. The most direct explanation is that surface states in the oxide-silicon interface region are being filled (or emptied) during the stress cycle and are unable to relax significantly at room temperature once the sample is cooled. Effects similar to this have been observed in wet chemical anodic oxides and in high temperature thermal oxides when grown in such a way as to avoid the presence of mobile positive ions, e.g., alkali ions. We conclude from these results that the plasma grown oxides are comparatively free of mobile ionic impurities.

MICROWAVE DISCHARGE DEPOSITION

In ordinary dc sputtering a dc glow discharge is produced in an inert gas, e.g., argon, by applying a large dc potential between an anode and cathode; energetic bombardment of the cathode by positive ions sputters material off the cathode. The sputtered material is deposited on a substrate placed in close proximity to the cathode. In dc reactive sputtering, the inert gas is replaced by a reactive gas, e.g., oxygen. The materials deposited in a reactive sputtering process are usually compounds of the cathode (sputtering target) and the reactive gas. In the ordinary sputtering process, the dc potential serves both to create the reactive plasma and to provide the energetic ions necessary for sputtering. By using a microwave generator, the reactive plasma density can be significantly increased. This allows stoichiometric deposition to be made at higher rates then would be possible with dc sputtering alone.

In the microwave discharge deposition technique a silicon rod serves as the sputtering target. During the sputtering process positive ion accumulation will occur on any oxide which has grown on this sputtering target. This positive ion accumulation can be large enough to cause dielectric breakdown of the oxide. Violent sparking and volatilization of silicon and its oxides then occur. In addition, positive ion accumulation on the oxide produces an electric field which tends to repel approaching positive ions, reducing the sputtering rate. This positive ion accumulation can be prevented if an rf potential is applied to the target instead of a dc potential. With an rf potential the polarity of the target is reversed every half cycle. During the positive half cycle, electrons and negative ions striking the target neutralize any positive

charge built up during the negative half cycle. For these reasons an rf accelerating potential was used on the sputtering target.

The apparatus for the microwave discharge deposition of silicon oxide is shown in Fig. 9. The essential difference between this apparatus and that used for oxide growth is in the spacing of the silicon rods. For deposition, a rod spacing of 1 cm was used, with the lower rod acting as the sample pedestal and the upper rod as the target. The output of an rf generator was connected to the target and capacitively coupled to one arm of the discharge tube. Using a 4 Mc rf generator and with an oxygen flow rate of 50 cc/min, a pressure of 200 μ, and a microwave power input of 800 volts, except for a short initial period with a higher rate of film formation, a constant deposition rate of 200 A/min was obtained. Oxide growth during the short initial period accounts for the more rapid initial increase in thickness. Under these conditions oxides about 13,000 A thick have been deposited with no indication that any limiting thickness exists. Reduction of the flow rate to 1 to 2 cc/min and the oxygen pressure to 30 μ had no significant effect on the deposition rate, but substantially reduced the oxide growth rate during the initial period.

Evaluation of the properties of these oxides is complicated by the fact that the application of the rf potential to the target results in both the target and the sample (but not the sample pedestal) being heated to incadescence. Pyrometric measurements indicate the target temperature is 1100°C and the substrate temperature 900°C. While lowering the substrate temperature would not be expected to effect the deposition rate, it might have a significant effect on the oxide properties.

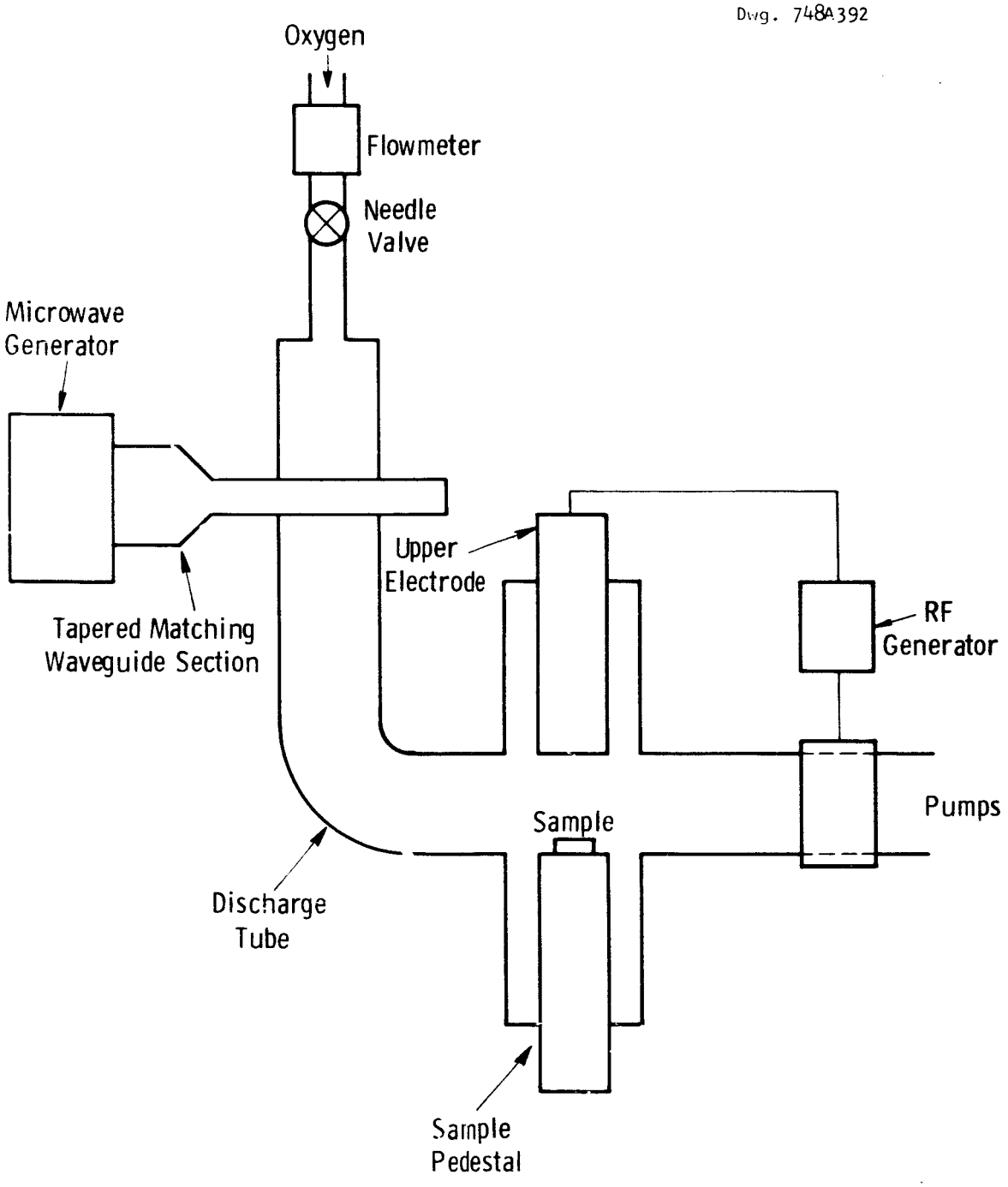


Fig. 9 Microwave discharge system for oxide deposition.

Etch rate measurements on these oxides in p-etch (15 parts HF, 10 parts HNO_3, and 300 parts H_2O) gave a rate of 2 A/sec. The infrared spectra of one of these oxides is shown in Fig. 10. The position of the Si-O stretching vibration is at 9.3 μ The oxides on some samples exhibited very low breakdown strengths (about 5×10^5 v/cm). Other samples deposited under similar conditions yielded breakdown strengths of the order 1×10^7 v/cm. The resistivities of the samples fell in the range of 0.5 to 5×10^{16} Ω-cm. Comparison of these results with those given in Table I, indicate that in these properties the microwave deposited oxides are indistinguishable from thermally grown and microwave grown oxides. The low breakdown strength observed on some of microwave deposited oxides may be due to the presence of pinholes.

The deposition technique yielded oxides reasonably uniform in film thickness. For example, on 6 mm square samples with oxide films about 2000 A thick, the oxide was about 200 to 500 thicker on one edge than on the remainder of the sample. Over the remaining 60 to 90% of the area of the sample there was no significant difference (less than 50 A) in the oxide thickness.

The C-V characteristics of MOS capacitors fabricated using the deposited microwave oxides have been studied on only a few samples. Figure 11 shows the results obtained on an MOS capacitor fabricated on an oxide 2300 A thick, deposited on 50 Ω-cm n-type silicon using an oxygen flow rate of 3 cc/min at a pressure of 35 μ, with a microwave input power of 1000 watts. Flat band potentials of between -20 and -25 volts were obtained on a number of MOS capacitors fabricated from this sample. Whether this large flat band potential is due to a high density of surface states or other causes is not yet clear.

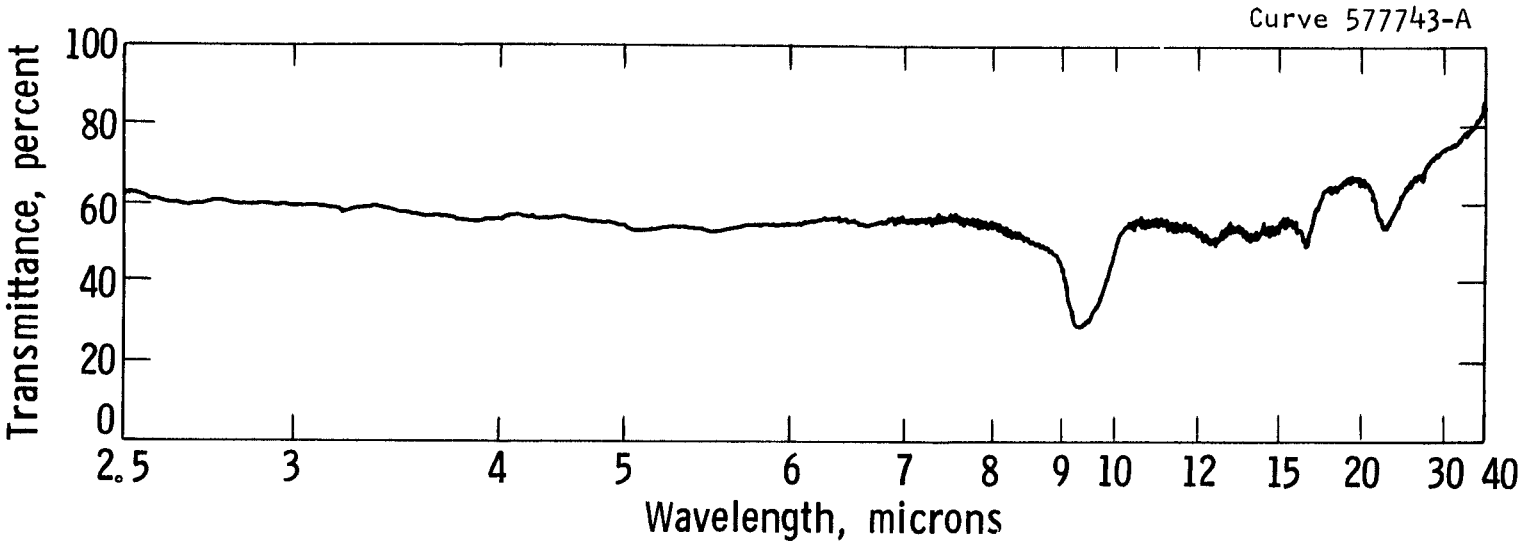


Fig. 10 Infrared spectra of microwave deposited oxide about 2300 A thick.

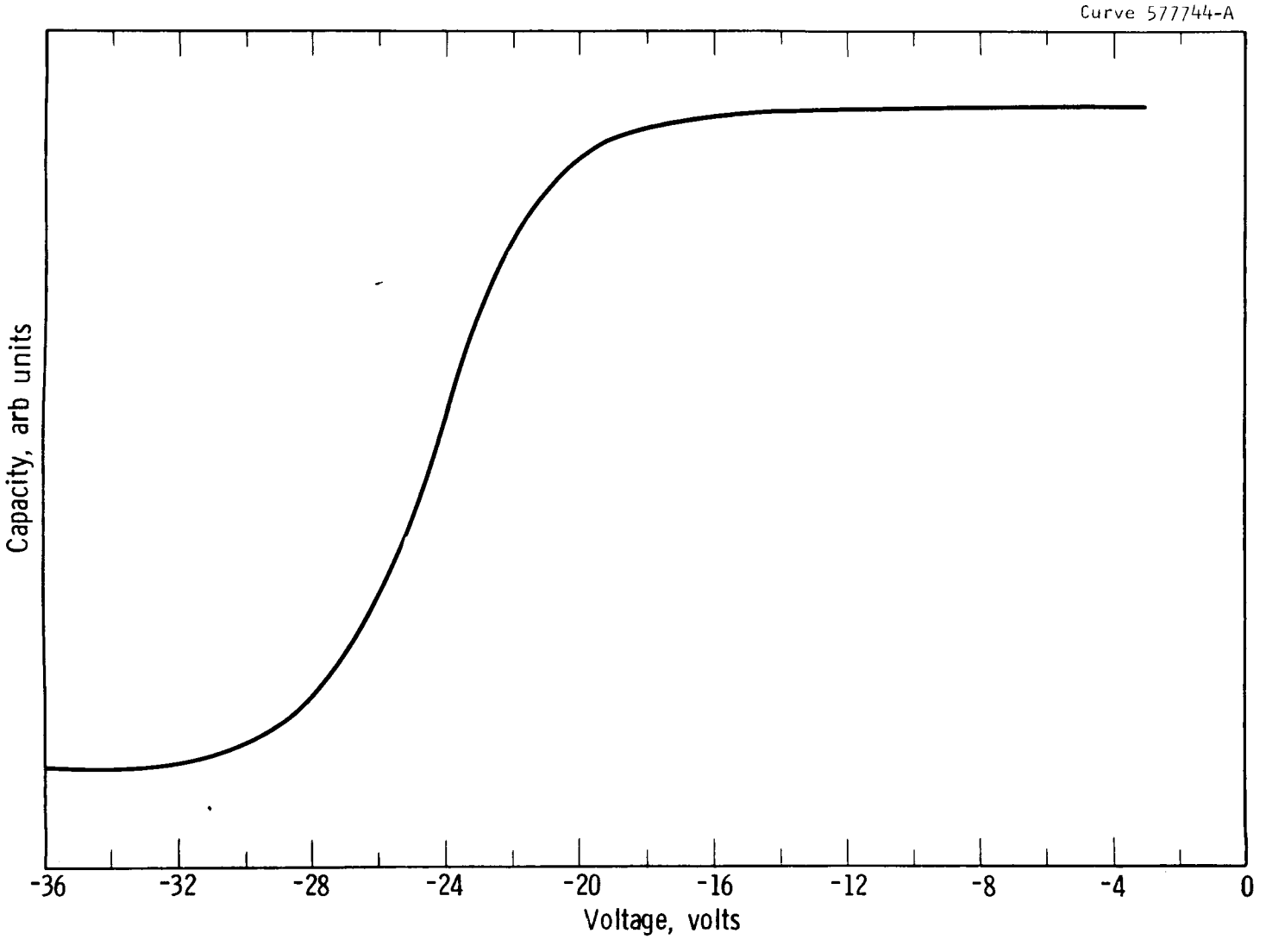


Fig. 11 Capacitance-voltage characteristics of an MOS capacitor fabricated from a microwave deposited oxide.

METAL-OXIDE-SILICON TRANSISTORS

MOS field effect transistors were fabricated* using both microwave grown and microwave deposited oxides. The devices were fabricated as follows: (a) A thermal oxide approximately 6000 A thick was grown on 15 ..-cm p-type silicon. (b) The oxide was masked with photoresist and windows opened where the source and drain regions were to be formed. (c) A phosphorous pre-deposition followed by a drive-in was performed. The source and drain regions after this step had junction depths of approximately 3 μ with sheet resistivities of 1 to 2 ohms per square. (d) The sample was etched to remove all remaining oxides. (e) A microwave oxide of between 1500 to 2000 A thickness was either grown or deposited on the sample. (f) The sample was masked with photoresist and contact windows opened in the source and drain regions. (g) An aluminum layer approximately 3000 A thick was evaporated onto the sample. (h) The sample was masked with photoresist and aluminum contact areas delineated. (i) The sample was diced and the individual devices mounted on headers. The devices were heated to 425°C for 45 seconds in this mounting operation. (j) Gold wires were bonded to the source, gate, and drain aluminum contact areas. A bonding temperature of 325°C was used.

Fig. 12 is a schematic drawing of the MOS transistor showing the dimensions of the device. Fig. 13 is a photomicrograph of the finished device prior to mounting on the header.

All devices after mounting on the headers behaved as depletion mode transistors. At zero bias an n-type channel was present

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* Pre-existing Westinghouse photoresist masks were utilized.

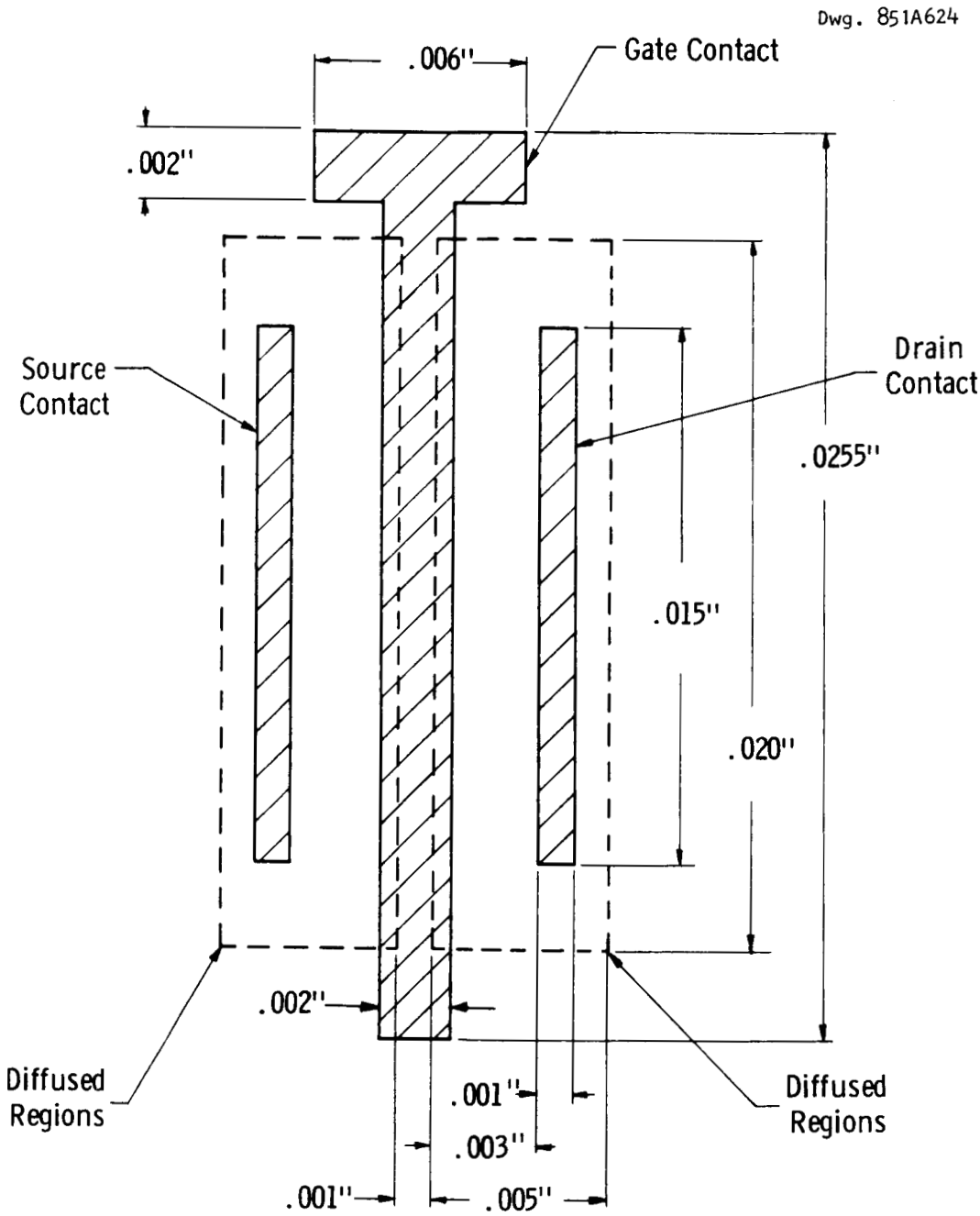


Fig. 12 Schematic drawing of MOS field effect transistor.

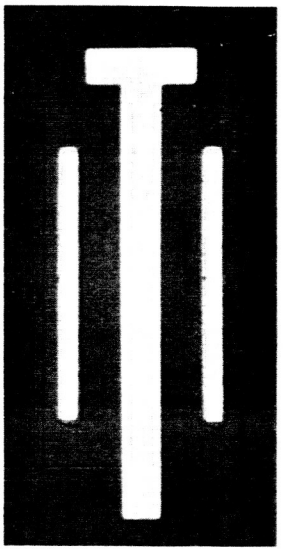


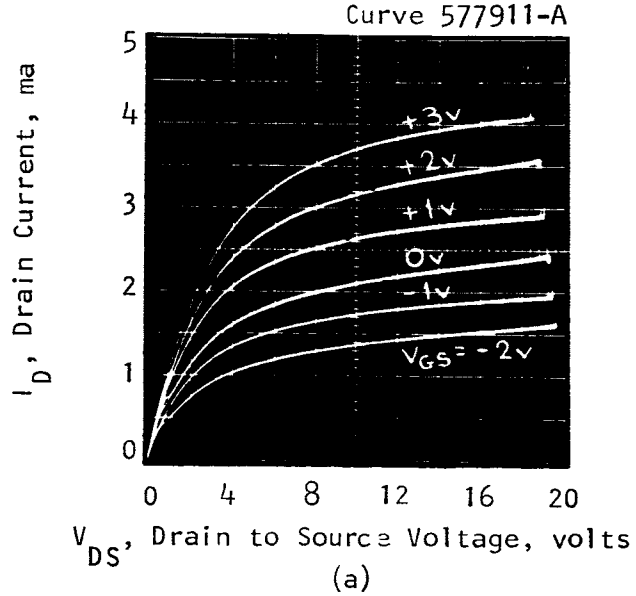
Fig. 13 Photomicrograph of MOS field effect transistor before mounting on header.

which could be depleted of electrons and the source to drain current reduced by application of negative gate bias. Fig. 14 shows the electrical characteristics of a device fabricated using a microwave grown oxide. Fig. 15 is the electrical characteristics of another MOS transistor fabricated using a microwave grown oxide. The devices could be also operated in the enhancement mode in which the source to drain current is increased by application of positive bias.

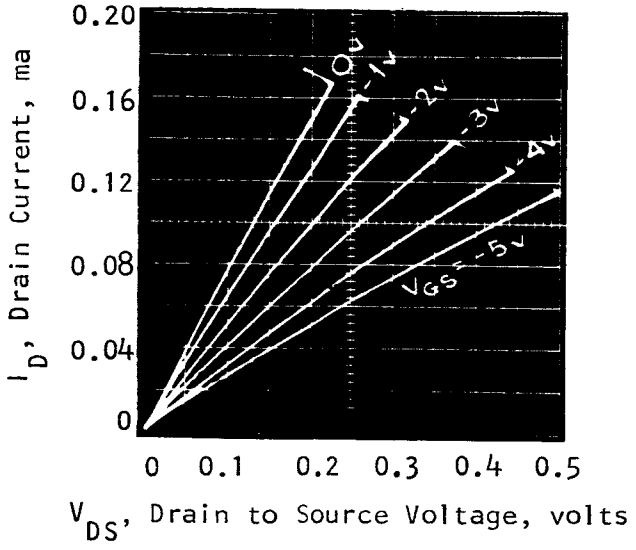
Figs. 16 and 17 show the electrical characteristics of the two devices fabricated using a microwave deposited oxide. A few devices from one silicon chip with a deposited microwave oxide did not behave as depletion mode transistors prior to mounting on headers. After mounting their behavior was similar to the other devices.

In general the characteristic of these devices are very similar to that of commercially available MOS field effect transistors. Fig. 18 illustrates the behavior of a device fabricated by the same procedure described above, except that a thermally grown oxide was used instead of a microwave oxide.

The number of devices made was too small to arrive at a statistically valid figure for the yield. It was observed, however, that a high proportion of the devices had leaky gates. This seemed particularly true of the devices fabricated using the microwave deposited oxide. The low breakdown strengths observed on the same microwave deposited oxides, which may be due to the presence of pinholes, may account for this behavior.



(a)



(b)

Fig. 14 Electrical characteristics of a microwave grown oxide MOS field effect transistor for various V_{GS}, gate to source voltage, in steps of 1 volt.

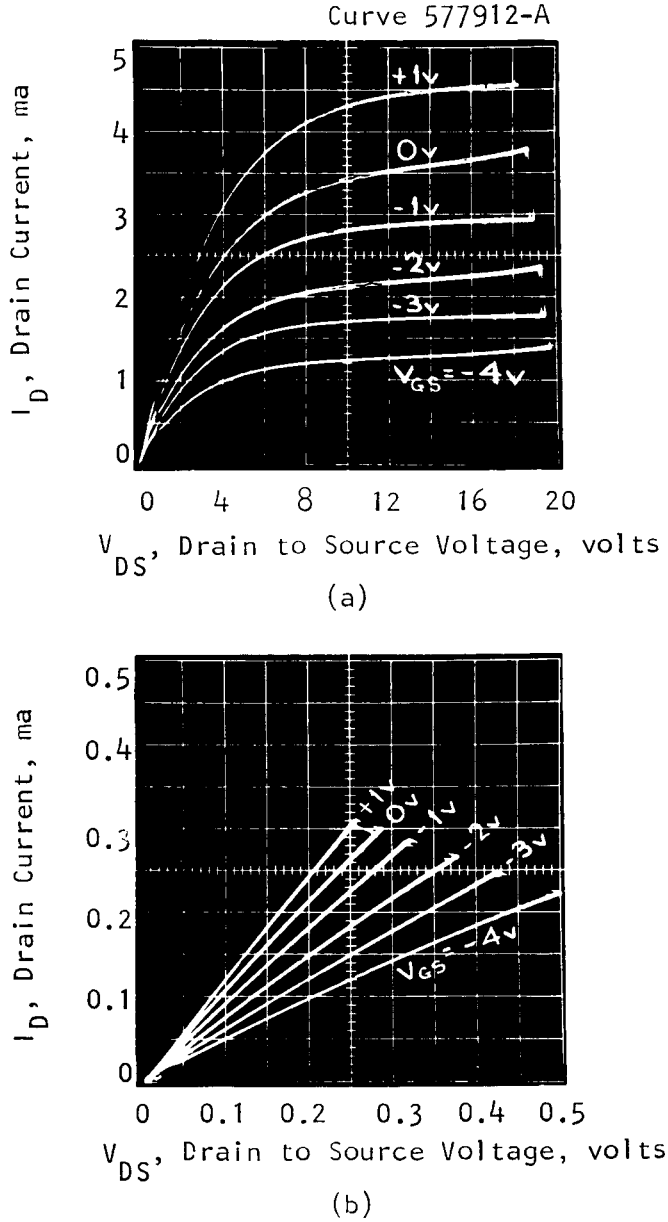
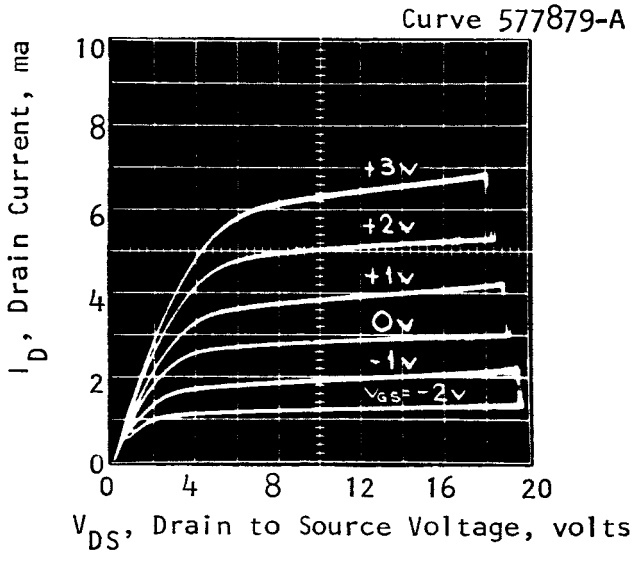
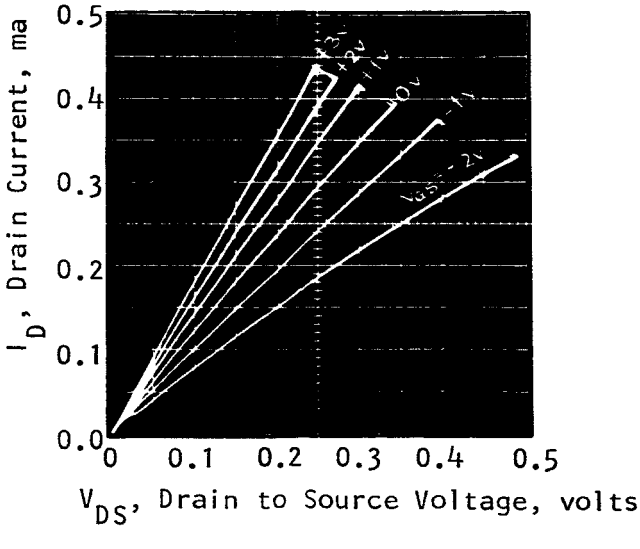


Fig. 15 Electrical characteristics of a microwave grown oxide MOS field effect transistor for various V_{GS}, gate to source voltage, in steps of 1 volt.

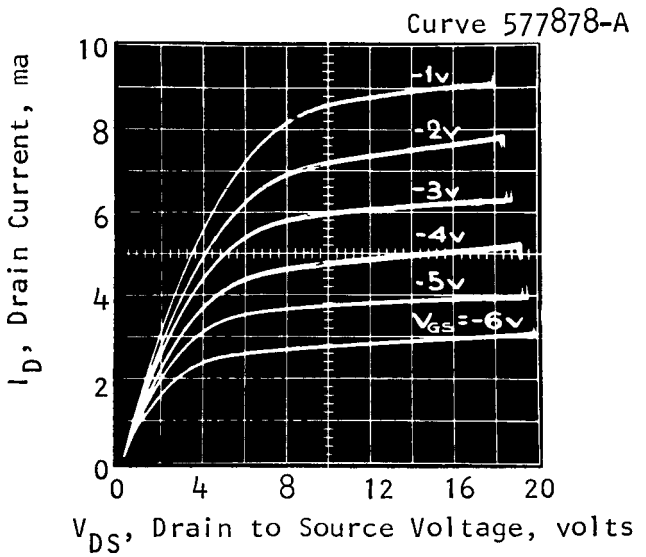


(a)

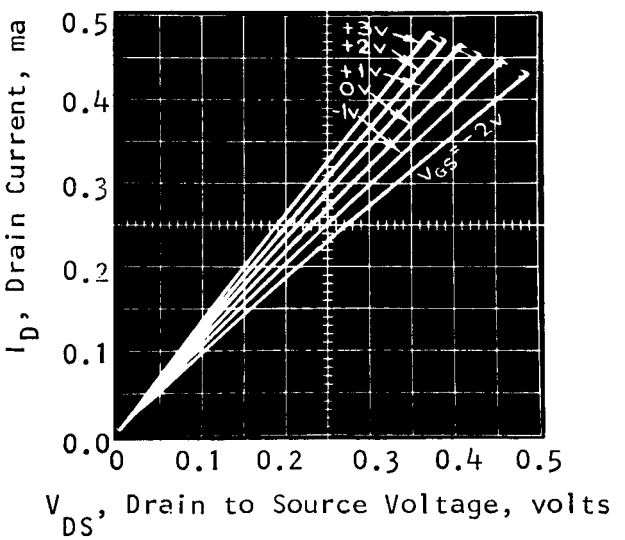


(b)

Fig. 16 Electrical characteristics of a microwave deposited oxide MOS field effect transistor for various V_{GS}, gate to source voltage, in steps of 1 volt.



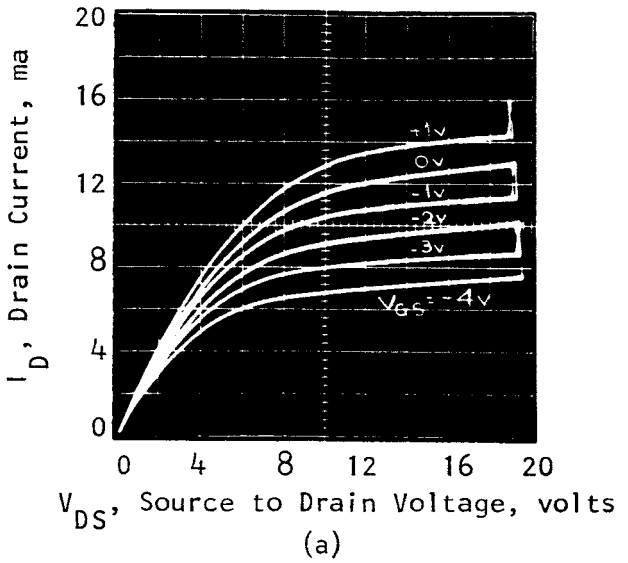
(a)



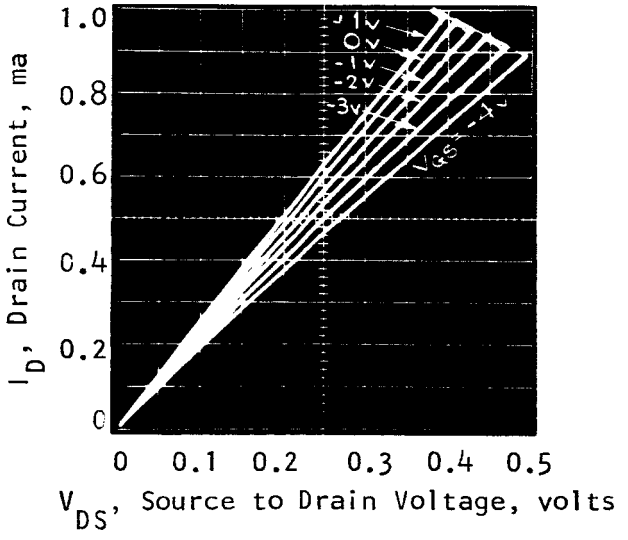
(b)

Fig. 17 Electrical characteristics of a microwave deposited oxide MOS field effect transistor for various V_{GS}, gate to source voltage, in steps of 1 volt.

Curve 577910-A



(a)



(b)

Fig. 18 Electrical characteristics of a thermally grown oxide MOS field effect transistor for various V_{GS}, gate to source voltage, in steps of 1 volt.

CONCLUSIONS

The microwave discharge growth technique provides a process for rapidly oxidizing silicon at temperatures estimated to be 500°C or lower. The growth rate can be enhanced both by the application of a dc potential to the sample and by external means which modify the plasma distribution and configuration. Rapid growth rates at these low temperatures corresponding to steam oxidation rates at 1100°C can be obtained.

Samples with thick (10,000 A) thermal oxides become thinner rather than thicker when placed in the microwave discharge. This effect is attributed to sputtering-off of the oxide by energetic species in the discharge. This and other results suggest that the oxide growth can be characterized by a rate limiting diffusion process modified by these sputtering effects. Observed growth rate data under a variety of conditions has been analyzed using a simple model assuming parabolic growth behavior modified by a constant rate of oxide removal due to sputtering. Very good fits with the observed data are obtained using this two parameter model.

Quite uniform oxides have been grown on occasion in the microwave discharge. However, in the experimental set-up used, the control of the plasma distribution and configuration was insufficient to enable uniform oxides to be grown consistently and reproducibly.

It appears reasonable to assume by analogy with the thermal oxidation process that the oxidation in the microwave discharge proceeds

by diffusion of an oxygen species. Negative oxygen ions which are present in an oxygen plasma can be extracted from the plasma by application of an external dc potential and may contribute to the enhanced rate of oxidation observed when a positive dc potential is applied to the sample. However, probe theory indicates that few, if any, of the negative ions will reach the sample if no dc potential is applied to the sample. Hence, the negative oxygen ions present in the plasma cannot account for the rapid oxidation rates observed when no external potential is applied to sample. Bombardment of the sample by electrons and positive ions can provide the energy necessary to promote the formation of the diffusing oxygen species. This energetic bombardment may create a sufficiently large concentration of the diffusing species to account for the rapid oxidation even at these low temperatures. The diffusing species produced by the discharge may be a different and more mobile oxygen species than the diffusing species in the thermal oxidation of silicon.

Various properties such as etch rate, infrared spectra, breakdown strength, and resistivity of microwave grown, thermally grown, anodically grown, and pyrolytically deposited oxide have been measured. While there were significant differences in the properties of the thermal oxides and the anodic or pyrolytic oxides, the microwave grown and thermally grown oxides were indistinguishable.

From capacitance-voltage measurements of MOS capacitors fabricated using microwave grown oxides it was found that these oxides

were quite stable under temperature-bias stressing. The measurements also showed that the observed small shifts under temperature-bias stressing were not due to the motion of mobile ions in the oxide.

The microwave discharge deposition technique provides a process for rapidly depositing silicon dioxide to any desired thickness. An essentially constant deposition rate, independent of oxide thickness, is obtained. Measurement of the oxide properties such as etch rate, infrared spectra, breakdown strength, and resistivity indicate no significant differences from the properties of thermal oxides. However, on a number of samples low breakdown strengths were observed. These may be due to the presence of pinholes in the oxide.

MOS field transistors were fabricated by conventional, masking, photoresist, and diffusion techniques on 15 Ω-cm p-type silicon. Devices fabricated using either the microwave grown or the microwave deposited oxides behaved as depletion mode transistors. The devices could also be operated in the enhancement mode. The electrical characteristics of these devices were very similar to those of commercially available devices made using thermally grown oxides.

June 16, 1966

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