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REACTIVE SPUTTERING OF TITANIUM OXIDES: TARGET OXIDATION PHENOMENA AND THIN FILM CHARACTERIZATION

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REACTIVE SPUTTERING OF TITANIUM OXIDES: TARGET
OXIDATION PHENOMENA AND THIN FILM CHARACTERIZATION

Kenneth George Geraghty
(M.S. thesis)

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REACTIVE SPUTTERING OF TITANIUM OXIDES:
TARGET OXIDATION PHENOMENA AND THIN FILM CHARACTERIZATION

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ABSTRACT

The reactive sputtering of titanium was studied in a 25 millitorr
Ar/O₂ rf plasma with oxygen mole fractions in the range 0 to 0.15,
bias voltages in the range of 1 to 2 kV and plasma power between 300
and 400 watts. Deposited titanium oxide films formed at various
plasma oxygen compositions were characterized for density, deposition
rate, electron diffraction characteristics and uv, visible and ir
absorbance. The deposition rates of the amorphous films varied from
1 to 10 Å/sec, with a sharp transition occurring at a critical mole
fraction of oxygen in the plasma, y* = 0.007. A similar trend was noted
for other film properties.

The effect of target oxidation on deposition parameters was
concurrently investigated, and transient and steady-state behavior of
the reactive sputter process were correlated with film properties.
y* was determined to be the critical oxygen mole fraction in the
plasma necessary for the initiation of target oxidation. At y < y*,
no oxide formed, and the sputtering rate reached a maximum at y = 0.002.
At y > y*, an oxide of finite thickness was formed, and the sputtering
rate was essentially constant.

Models for target oxidation based on a transient logarithmic growth
law and an exponential dependence of the overall sputtering rate on
oxide thickness are explored. From the model it is shown that a finite, steady-state target oxide thickness required that y exceed a critical value. The experimentally observed critical threshold for target oxidation is a consequence of the competing oxidation and sputter etching processes, and of the higher sputter yield of the metal as compared to that of the oxides. The application of titanium oxide films for protective coatings is discussed.
I. INTRODUCTION

A. Applications of Sputtered TiO$_x$ Films

The impetus for this study arose from an experimental project involving hot-pressing of garnets in graphite pressing dies. It was discovered that Fe$_2$O$_3$ powder reacted with the carbon of the die, under established reaction conditions (1200°C, 5000 psi), to form species of iron carbide in the resulting material.

Present-day technology employs a metallic sleeve as an interface between the graphite and the oxide powders. Normally, such a sleeve is fashioned out of molybdenum. An alternative to this approach is the deposition of a thin refractory coating on the die to act as a diffusion barrier between the oxide powder and the carbon.

To select the proper refractory, it was necessary to perform a thermodynamic analysis of the stability of the many available materials, with respect to the oxides and carbon, at the normal hot-pressing conditions. The free energy change associated with the reaction of oxide or carbon with each refractory was evaluated for two different reaction temperatures, and the results compiled in Table I. The variation of $\Delta G$ with pressure is negligible, and has not been included here.

These calculations indicate that TiO$_2$ and ZrO$_2$ are the most effective refractories for thin film diffusion barriers, because of their stability with respect to reduction by carbon even at elevated temperatures. Of the two, TiO$_2$ was selected for this study primarily for its additional utility in divergent fields. TiO$_2$ thin films have been sputter-deposited for microcircuit applications as resistors and
<table>
<thead>
<tr>
<th>Barrier Phase</th>
<th>Reaction</th>
<th>$\Delta G$ (kcal/mole)</th>
<th>Phase</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB₂</td>
<td>TiB₂+C+TiC+2B</td>
<td>21.366 20.168</td>
<td></td>
<td>stable</td>
</tr>
<tr>
<td>TiB₂</td>
<td>3TiB₂+2Fe₂O₃→3TiO₂+6B+4Fe</td>
<td>-89.078 -92.337</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>TiB₂</td>
<td>3TiB₂+5Fe₂O₃→3TiO₂+3B₂O₃+10Fe</td>
<td>-408.029 -414.579</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>ZrB₂+C+ZrC+2B</td>
<td>27.889 25.574</td>
<td></td>
<td>stable</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>3ZrB₂+2Fe₂O₃→3ZrO₂</td>
<td>-162.248 -165.885</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>3ZrB₂+5Fe₂O₃→3ZrO₂+3B₂O₃+10Fe</td>
<td>-481.199 -488.127</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>TiC</td>
<td>3TiC+4Fe₂O₃→3TiO₂+3CO₂+8Fe</td>
<td>-192.139 -262.299</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>ZrC</td>
<td>3ZrC+4Fe₂O₃→3ZrO₂+3CO₂+8Fe</td>
<td>-284.878 -352.065</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>TiN**</td>
<td>TiN+C→TiC+1/2N₂</td>
<td>-12.889 -1.634</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>TiN</td>
<td>3TiN+2Fe₂O₃→3TiO₂+3/2N₂+2Fe</td>
<td>-114.509 -147.939</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>BN</td>
<td>BN+Fe₂O₃→B₂O₃+N₂+2Fe</td>
<td>-36.985 -63.082</td>
<td></td>
<td>unstable</td>
</tr>
<tr>
<td>TiO₂</td>
<td>TiO₂+2C→TiC+CO₂</td>
<td>37.262 14.861</td>
<td></td>
<td>stable</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>ZrO₂+2C→ZrC+CO₂</td>
<td>68.984 44.383</td>
<td></td>
<td>stable</td>
</tr>
</tbody>
</table>

*Data obtained from JANAF Thermochemical Tables, 2nd edition, NSRDS-NBS 37, June 1971.

**Note the ZrN reduction reactions are very similar to the TiN reactions.
capacitors.\textsuperscript{1-3} The optical properties of TiO\textsubscript{2}, particularly its high refractive index, have proven invaluable to the optics industry for over 25 years. Much of the thin film research in this industry has been in the preparation of TiO\textsubscript{2} lens coatings.\textsuperscript{4,5}

Calculations of $\Delta G^o_f$ were performed for the most stable condensed phase of TiO\textsubscript{2}, the rutile phase. The dependence of the free energy of formation on temperature indicates that $\Delta G^o_f$ becomes positive (e.g., thermodynamically unfavorable) only above 2150°K.

Titanium dioxide in the rutile phase exhibits a high elastic modulus and the abrasion resistance necessary to withstand the elevated pressures involved in hot-pressing. Amorphous films, on the other hand, have a more open lattice and lower density, and hence are not as well suited for diffusion barriers. The establishment of rates and conditions for the deposition of TiO\textsubscript{2}, the Magneli phases Ti\textsubscript{n}O\textsubscript{2n-1}, n \geq 2, and TiO\textsubscript{2} by reactive sputtering thus became an objective of this study. An extensive treatment of the materials and techniques involved in graphite coating applications is provided by Samsonov and Epik.\textsuperscript{6}

B. Reactive Sputtering Processes

Bailey has reported that essentially all film physical properties of sputtered films are strongly dependent on deposition parameters such as time, deposit rate, argon pressure, cathode-anode distance and substrate temperature.\textsuperscript{7} During the course of the present investigation, it was found that the growth of an oxide layer on the Ti target surface significantly alters sputtering conditions. Forward power, bias voltage
and deposition rate were all found to be dependent on the oxidation state of the target. Accordingly, the scope of the research was expanded from the original aim, the study of reactive sputter deposition of TiO\textsubscript{x}, 0 \leq x \leq 2, to include an examination of target oxidation phenomena. Since target oxidation affects reactive sputtering rate processes, target oxidation transients are obviously significant when it is desired to deposit a material of specified stoichiometry.

As a result, the research involved two phases. In the first phase, titanium oxide films were deposited from an rf plasma containing variable percentages of oxygen in argon, and these films were characterized for density, deposition rate, spectroscopic properties and structure. In the second phase, the conditions under which target oxidation would occur were studied, including all changes in sputtering parameters associated with transients in the oxidation state of the target. Heat flows and temperatures in the system were also studied to provide data on reaction kinetics.

C. The Ti-O System

Attention devoted to target oxidation effects precluded a complete evaluation of the effectiveness of rutile as a coating material, primarily because of the difficulties involved in preparing rutile films by reactive sputtering. Nevertheless, there is a considerable literature on the condensed phases of the Ti-O system. Several investigators have determined the phase diagram of this system during the last 20 years.\textsuperscript{8,9,27}

The low temperature portion of the phase diagram for the Ti-O system after Roy and White\textsuperscript{27} is reproduced in Fig. 1. This diagram indicates that temperatures above 800°C are required to produce rutile
Fig. 1. Low temperature condensed phase diagram for the Ti-O system. Note the Magneli phases have the form \( \text{Ti}_n \text{O}_{2n-1} \) where \( n = 4, 5, 6, \ldots \infty \).
crystals. Below this temperature, anatase is the stable phase. Thus, in order to obtain rutile it is necessary to insure that the deposition temperature be maintained above 800°C, either by heat generated from the impacting atoms themselves or through external heating of the substrate.

The stability range of Ti$_3$O$_5$ and the Magneli phases with regard to temperature and oxygen fugacity were determined by Porter. These studies confirmed the existence of an indeterminate number of intermediate oxide phases between TiO and TiO$_2$. Of these, Ti$_2$O$_3$ and Ti$_3$O$_5$ are distinct phases, while the Magneli phases form a closely related series of shear-defect compounds with the homologous formula Ti$_{0.2n-1}$O$_{2n-1}$. Figure 2 summarizes the stability ranges of these phases as a function of the reciprocal temperature and oxygen fugacity. The figure shows that TiO$_{2-x}$ (anatase) is the stable oxide phase at an estimated target surface temperature of 400°C and an oxygen fugacity near unity. At the temperature of local hot spots on the target surface, 1750°C, reported by Carter and Colligon, TiO$_{2-x}$ (rutile) should be the stable oxide phase. For substrate temperatures below 800°C, TiO$_{2-x}$ (anatase) should be the phase deposited by reactive sputtering with Ar/O$_2$ over the entire range of easily controlled oxygen fugacity.

D. Properties of TiO$_n$ Phases

The optical properties of titanium oxides are summarized in Table II. Impurities tend to contribute significantly to many observed physical properties of these phases. As a consequence, the color of TiO$_2$ can vary from transparent to white, red, reddish brown, brownish black or yellow, depending on impurities and the method of preparation.
Fig. 2. Solubility of ranges of titanium oxides as a function of reciprocal temperature and oxygen fugacity.
Table II. Optical properties of titanium oxides.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>State</th>
<th>Color</th>
<th>Refractive Index</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO</td>
<td>Single Crystal</td>
<td>Golden Yellow</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Ti₂O₃</td>
<td>Polycrystal</td>
<td>Dark Violet</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Ti₃O₅</td>
<td>Polycrystal</td>
<td>Blue</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Polycrystal</td>
<td>Transparent, White, Red, Reddish Brown, Brownish Black, Yellow</td>
<td></td>
<td>35, 36</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Anatase</td>
<td></td>
<td>2.554</td>
<td>37</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Brookite</td>
<td></td>
<td>2.616</td>
<td>37</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Rutile</td>
<td></td>
<td>2.616</td>
<td>4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Rutile, 1000°C</td>
<td></td>
<td>2.5</td>
<td>16</td>
</tr>
</tbody>
</table>
The heating of compressed mixtures of TiO\textsubscript{2} and Ti to 1700°C in vacuo produces TiO with a golden yellow color. On the other hand, reduction of TiO\textsubscript{2} with magnesium produces TiO with a dark brown color.\textsuperscript{36}

The Magneli phases and TiO\textsubscript{2} are known to be insulators, while αTi and TiO are metallic phases. The width of the forbidden gap of TiO\textsubscript{2} was measured by Melik-Davtyan, et al. and found to be 4.87×10\textsuperscript{-19} joule or 3.04 eV, in the temperature range above 800°K.\textsuperscript{40} Smith gives a value of 4.8×10\textsuperscript{-19} joule or 3.0 eV for the band gap of TiO\textsubscript{2}.\textsuperscript{41} The activation energy for electronic conduction as reported by Vorob'ev\textsuperscript{38} is 1.10 eV, whereas Makovskii and Usachev\textsuperscript{39} report a value of 1.02 eV.
II. THEORY OF OXIDATION MECHANISMS

A. Theories of Target Oxidation

The sputtering process consists of accelerating positively-charged plasma ions into a target material under the influence of a bias electric field. The incident ions eject atoms of the target material from the target surface by initiating a chain-collision energy transfer process through the crystal lattice. The gaseous atoms can then be collected on a substrate placed in the system opposite the target surface.

While a dc bias voltage suffices for sputtering conducting materials, an rf field is required for dielectrics in order to remove the negative charge build-up at the target surface by highly mobile plasma electrons; rf power can also be used to sputter conducting materials. 29

The plasma gas for the sputtering process is normally an inert gas, typically argon. Introducing a reactive gas with the argon allows reactive sputtering, wherein the sputtered target atoms react with the active gas, and the products are collected on the substrate. The mechanism of this reaction is not clearly understood, as the precise time of reaction has not been determined. The reaction could occur at the target surface, in the plasma, on collision with the substrate, or by diffusion and surface reaction following deposition.

The subject of target oxidation has received even less attention than the reaction chemistry mechanism of reactive sputtering, perhaps because commercial applications are primarily concerned with the materials deposited during sputtering and not with the target condition. As long as desired film properties can be controlled, secondary processes are of little concern. A new impetus for work on target oxidation has arisen from recent
developments in the analogous field of plasma anodization and oxidation.¹⁹,²¹,²²

Plasma anodization is the process of growing an oxide film on a metallic substrate by immersing the substrate in an oxygen plasma and applying an electric field.²¹ Plasma oxidation is virtually the same technique lacking only the externally applied bias voltage.²¹ The current interest in these technologies stems from their application to the fabrication of oxide tunnel barriers for thin-film Josephson junction devices.

Since gaseous anodization offers certain advantages over liquid electrolysis in growing thin oxide layers, for example in the field of microminiaturization of electronic circuitry through thin-film technology, several investigators have examined the phenomenon.¹⁹-²¹,²⁴

The pioneering work of Miles and Smith offered the first indication of the potential uses of plasma anodization for both tunneling barriers and thin-film dielectrics.¹⁹ They offered a qualitative explanation of the oxidation process. They concluded that positive metal ions dissolve into the surface oxide layer under the influence of the electric field. The ions, under a combination of drift and diffusion, move to the oxide-plasma interface, and react chemically with gaseous oxygen, thereby initiating oxide growth. They further observed that for a constant bias potential, the oxide growth reaches a certain thickness and then ceases. Thickness control can be exercised by varying the applied field strength.

A few years after this work, several people began investigating the anodization technique for application to Josephson junction devices. Schroen looked at the physics of the oxidation process, and presented a molecular model for the reaction.²⁰ The initially neutral substrate is
raised to a negative potential by the mobile plasma electrons. This negative potential attracts $O_2^+$ positively-charged oxygen molecules to the target surface. These ions enter the target as $O_2$ neutrals, diffuse into the metal lattice, and react to form an oxide. The model is still tentative, as Schroen states, and lacks any quantifying formulae.

1. The Plasma Anodization Model

O'Hanlon reviewed plasma anodization, and presented a model very similar to Schroen's. He also emphasized that this model was not well-researched. O'Hanlon proposes two distinct mechanisms. One mechanism is that of Schroen, whereby $O_2^+$ ions dissociate upon impact, and diffuse into the target. According to this mechanism, the negative oxygen ions are generated at the oxide surface. A second possibility is that $O_2^+$ ions originating in the plasma are implanted directly into the oxide. This model is supported by Whitlock and Bounden\textsuperscript{[30]} and by Thompson\textsuperscript{[31]} who were unable to detect any measurable negative ion current density in the negative glow of an oxygen discharge.

Miles and Smith have studied oxide growth rates on aluminum by plasma anodization.\textsuperscript{[19]} An essential requirement for oxide growth by this method is the formation of a "priming oxide layer" by exposing the aluminum to an $O_2$ plasma for a period of 10 min before applying a bias potential. Without the priming period, no oxide was formed. The thin oxide layers ($<20\text{Å}$) formed after the priming period by plasma anodization without external bias potentials was shown by O'Hanlon\textsuperscript{[21]} to have a logarithmic dependence on time given by

$$x = x_0 + k \ln t, \ t > 1 \text{ min}$$

(1)
This law apparently holds only for times greater than 1 min, since this law does not extrapolate to zero thickness at \( t = 0 \).

Using the same data, however, one can show that a parabolic growth law is followed during the same time period

\[
x = k'\sqrt{t} \quad t > 0
\]

Thus, it appears that a diffusional mechanism could drive the plasma anodization process at zero bias.

The oxidation rate of Ti metal in pure \( O_2 \) at one atmosphere pressure has been measured by Kubaschewski and Hopkins.\(^{42}\) The oxidation time dependence could be described by the parabolic dependence of oxide thickness on time. The constant for this dependence is given for the temperature range between 550° and 850°C as

\[
K_p = 16 \exp(-188406.0 \times 10^3/RT)
\]

(3)

where \( K_p \) has the units \([\text{kg} \cdot \text{m}^{-4} \cdot \text{sec}^{-1}]\), \( R = 8.317 \times 10^3 \text{ joule kg}^{-1} \text{ mole}^{-1} \text{K}^{-1} \)

and \( T \) is in °K. Thus, at an assumed target temperature of 400°C, and for a TiO\(_2\) (anatase) target phase with a density of 3.84 gm/cm\(^3\), the oxide thickness \( x \) has the following dependence on time:

\[
x = 102.4 \ P_{O_2} t^{1/2} \quad (\mu\text{m})
\]

(4)

where \( P_{O_2} \) is the oxygen partial pressure in the plasma (on the order of \( 10^{-7} \text{ atm} \)). It can be anticipated that the oxidation rate in an oxygen containing plasma is partly diffusion controlled, in spite of the finite sputtering process.
2. Greiner's Model

The first quantitative analysis of the oxidation phenomena was advanced by Greiner, who investigated rf sputter etching in oxygen as an alternate procedure to anodization for forming tunneling barriers. The basis of Greiner's theory is the assumption that the sputtering and oxidation rates are independent and additive. In other words, the rate of change of oxide thickness is

$$\frac{dx}{dt} = R_{ox} - R_{sp}$$

where \(x\) = oxide thickness, \(R_{ox}\) is the oxidation rate, and \(R_{sp}\) is the sputter rate of the target phase.

In using this equation, Greiner invokes two assumptions. First, that the oxide thickness follows a logarithmic time dependence

$$x = x_0 + k \ln t,$$

and consequently

$$R_{ox} = Ke^{x/x_0},$$

and second, that the sputter etch rate, \(R_{sp}\), is constant. Miles and Smith have shown that the logarithmic law applies for plasma anodization of aluminum, but only after the growth of a thermal "primer" oxide layer.

Greiner independently verified the logarithmic law for transients in oxide thickness following abrupt changes in oxygen content in the plasma.

There is no evidence, however, to indicate that \(R_{sp}\) is constant, although this would seem likely for thick oxide films. A thick film in this sense would be one through which the impinging sputtering ions neither penetrate nor transfer a significant amount of energy to the metallic
substrate. For a thin oxide, the assumption that the sputtering rate is constant and independent of the target oxide thickness should not be true due to the dependence of the chain reaction mechanism of atom release during sputtering on lattice bond energy. Furthermore, while the oxide grown by plasma anodization is normally reported to be less than 25Å when no bias potential is applied, the implantation range of Ar ions at 2 keV is approximately 50Å, so a thick film in the sense defined above will not likely be formed.

Using Greiner's assumption, the total rate of change of oxide thickness becomes

\[
\frac{dx}{dt}_{\text{total}} = Ke \frac{-x/x_0}{-R_{sp}}
\]

which integrates to

\[
x = x_0 \ln \left[ \frac{K}{R_{sp}} - \left( \frac{K}{R_{sp}} - e^{x_1/x_0} \right) e^{-R_{sp}t/x_0} \right] x > x_0
\]

where \( x_1 \) is the oxide thickness at time \( t = 0 \). This equation has a transient time constant \( x_0 / R_{sp} \) and a steady state limit given by

\[
\lim_{t \to \infty} x = x_0 \ln \left( K / R_{sp} \right)
\]

The steady state limit can also be obtained by setting \( dx/dt = 0 \) in Eq. (7). Note that this theory predicts that a finite thickness of oxide is present on the target only if \( K > R_{sp} \), and that the time constant for transient oxidation is \( x_0 / R_{sp} \).
3. **Heller's Model**

In a more recent publication, Heller presented an analysis of the results of his work on reactively sputtering metals in oxidizing atmospheres. Heller found the existence of a critical oxygen partial pressure in the plasma, $P_0^*$, below which no oxidation of the target takes place. For $P_o < P_o^*$, the sputter rate exceeded the oxidation rate and no oxide layer formed on the target. For $P_o > P_o^*$, an oxide layer of finite thickness formed.

These experimental results are not inconsistent with Greiner's study in that Greiner never explored the range of $P_o^2$ value below which no oxide formed. The plasma oxygen mole fraction for the initiation of oxidation has been determined to be very small, but experimental difficulties prevent precise measurement of this mole fraction.

Heller has improved on Greiner's assumption concerning $R_{ox}$ and $R_{sp}$ by introducing the following oxidation equation. He defined

$$R_{ox} = \frac{A(P)}{\rho} e^{-x/x_0}$$

(10)

where the parameter $A(P)$ is a pressure-dependent function and $\rho$ is the density of the sputtered target phase. The target oxide density will vary with composition from 4.5 gm/cm$^3$ for Ti to 4.26 gm/cm$^3$ for TiO$_2$. Heller assumes that $R_{sp}$ is a monotonically decreasing function which yields the correct sputtering rates at $x = 0$ and $x \to \infty$, i.e.,

$$\left(\frac{dx}{dt}\right)_{sp} = R_{sp} = R_{sp,o} + (R_{sp,m} - R_{sp,o}) e^{-x/x_0}$$

(11)
where \( R_{sp,o} \) and \( R_{sp,m} \) are the sputtering rates of target oxide and metallic Ti, respectively. This assumption was tested in a second paper by Greiner who obtained sufficient data to determine the unknown parameters of his model.\(^23\) Thus for target oxidation of Pb he reports \( K = 3.4 \times 10^3 \text{ Å/min}, R_{sp} = 1.77 \text{ Å/min} \) and \( x = 9.2 \text{ Å} \) for rf sputter oxidation at \( 10^{-2} \) Torr, 360 volts and 24°C. He found that sputter oxidation is much faster than thermal oxidation and that in an oxygen plasma, \( O_2^+ \) ions produce sputtering while atomic oxygen in this plasma could be responsible for oxidation.

The target oxidation mechanism proposed by Greiner involves incorporation of atomic oxygen in the oxide during rf sputtering, followed by diffusion to the metal-oxide interface. He does not explain how the atomic oxygen is initially assimilated into the target. Presumably, the ions are neutralized and dissociate at the oxide surface. Alternatively, oxygen ions could be implanted directly into the oxide.\(^20\)

Notwithstanding the previous efforts to arrive at a quantitative analysis of the oxidation phenomenon, Leslie and Knorr have concluded, from their investigation of the plasma oxidation of tantalum, that the complex interrelation of system parameters and the present dearth of experimental work prohibit the formulation of any complete model.\(^24\)

B. An Alternate Model for Target Oxidation

1. Oxide Growth Equation

Greiner's initial assumption used to formulate his model based on the difference between sputtering and oxidation rates offers a convenient starting point for the present model. The assumption that \( R_{sp} = \text{constant} \) is not valid for oxide films because the sputtering rate
depends on oxide thickness. Thus, as the film grows, the sputtering 
rate decreases. As a first approximation, Heller's equation for the 
sputtering rate (Eq. (11)) is appropriate as it accounts for the effect 
of oxide thickness on the sputtering rate. Also, it is expected that the 
oxidation rate constant K in Eq. (6) should be proportional to the mole 
fraction of oxygen in the plasma, or K = γy, where γ is an effective 
solubility rate.

Using the logarithmic oxide growth law of Eq. (6) with the above 
modification, the expression for transient oxide thickness \( \frac{dx}{dt} \) becomes

\[
\frac{dx}{dt} = γy e^{-\frac{x}{x_o}} - R_{sp,o} - \left( R_{sp,m} - R_{sp,o} \right) e^{-\frac{x}{x_1}}.
\] (12)

This differential equation can be integrated to give the time dependence 
of transient oxide growth.

When the characteristic lengths \( x_o \) and \( x_1 \) are equal, Eq. (12) has 
the integral,

\[
x = x_o \ln \left( \frac{γy - ΔR_{sp}}{R_{sp,o}} - \left( \frac{γy - ΔR_{sp}}{R_{sp,o}} - e^{\frac{x_i}{x_o}} \right) e^{\frac{x}{x_o} t} \right)
\] (13)

where \( x_i \) is the initial oxide thickness at time \( t = 0 \), and
\( ΔR_{sp} = R_{sp,m} - R_{sp,o} \). The transient time constant for this equation is 
then \( x_o/R_{sp,o} \). In the limit of large time, the steady state oxide 
thickness becomes

\[
x = \begin{cases} 
0, & y < γ^{-1}ΔR_{sp} \\
 x_o \ln \left( \frac{γy - ΔR_{sp}}{R_{sp,o}} \right), & y > γ^{-1}ΔR_{sp}
\end{cases}
\] (14)
A consequence of this model is that no oxide is stable on the target when \( y < \gamma^{-1}\Delta R_{sp} \).

When the characteristic oxidation length exceeds that for sputter etching, or \( x_0 \gg x_1 \), the oxidation rate decreases slowly with increasing \( x \). The term \( e^{-x/x_1} \) is negligible for \( x \gg x_1 \). With these approximations, Eq. (12) becomes

\[
\frac{dx}{dt} = \gamma y e^{-x/x_0} - R_{sp,o}. \tag{14a}
\]

For the case where \( x \ll x_1 \), Eq. (12) can be written as

\[
\frac{dx}{dt} = \gamma y e^{-x/x_0} - R_{sp,m}. \tag{14b}
\]

Equations (14a) and (14b) differ only in the value of the constant term. Replacing both constants by \( R_{sp} \) and integrating yields

\[
x = x_0 \ln \left( \frac{\gamma y e^{-x/x_0}}{R_{sp}} - \left( \frac{\gamma y e^{-x/x_0}}{R_{sp}} - e^{x_1/x_0} \right) e^{-R_{sp} x_1 t} \right) \tag{15}
\]

where

\[
R_{sp} = \begin{cases} R_{sp,m}, & x < x_1, \ y > \gamma^{-1} R_{sp,m}, \ y \text{ increasing} \\
R_{sp,o}, & x > x_1, \ y > \gamma^{-1} R_{sp,m}, \ y \text{ increasing} \\
R_{sp,o}, & x > x_1, \ y > \gamma^{-1} R_{sp,o}, \ y \text{ decreasing} \end{cases}
\]

In this case, target oxide is metastable over the range of plasma oxygen mole fractions given approximately by
and a stable oxide thickness is only reached for $y < \gamma^{-1} R_{sp,m}$.

Thus, no oxide will form until $y$ exceeds $\gamma^{-1} R_{sp,m}$, at

which time oxidation will take place with the time constant $x_0/R_{sp}$, where

$R_{sp}$ decreases rapidly with oxidation from $R_{sp,m}$ to $R_{sp,o}$. Once the

oxide layer is formed, it should remain until $y$ falls below the value

$$y = \gamma^{-1} R_{sp,o}.$$

The steady state oxide thickness in the stable range of $y$ is then

$$x = x_0 \ln \frac{\gamma y}{R_{sp,o}}$$

The above models show that no target oxidation should take place

until the oxygen mole fraction in the plasma reaches a critical value,

$y^*$. Target oxidation then proceeds to a steady state value, either

increasing monatonically with $(y - y^*)$ if $x_0 = x_1$, or spontaneously

increasing to a finite value at $y \geq y^*$, if $x_0 \gg x_1$.

2. Estimates of Model Parameters

Equation (15) can be seen to relate oxide growth as a function of
time, requiring the constants $x_0$, $x_1$ and $\gamma$ to be specified. These

constants can be determined if oxide thickness is known, and a data regression

analysis applied. The oxide thickness has recently been measured in situ

using an ellipsometer and experiments designed to monitor $\left(\frac{dx}{dt}\right)$ for the

purpose of specifying the parameters of Eq. (15).²³
Experimental studies show that the sputter etch rates of low atomic weight metals in Ar plasmas are on the order of 5 Å/sec for bias voltages in the range of several keV. The sputter etch rates of oxides are lower, in the range of 1 Å/sec, owing to the higher bond strength in the oxide lattice.

The effective solubility parameter $\gamma$ should be larger than unity for most transition metals exhibiting stable oxides. The value is somewhat indeterminate, however, because plasma ionization and sputter etching processes modify the effective oxygen partial pressure at the target surface. Greiner's data for the oxidation of Pb targets in an oxygen plasma show that $\gamma$ is on the order of $10^3$ Å/sec.

The characteristic depth for the transition from metal to oxide sputter etching, $x_1$, should be on the order of the maximum depth of sputter etching, typically 5 to 10Å. Although the deep-rebound sputter mechanism is capable of sputtering from this depth, most of the sputter etching takes place closer to the surface.

The characteristic depth for oxidation, $x_o$, depends on the oxidation mechanism. For diffusion controlled oxidation in the large thermal gradient present at the target surface during sputter etching, $x_o$ is limited by the diffusion process; since most of the substrate heating is confined to the sputter etch range, $x_o$ should then be approximately equal to $x_1$. For oxidation by ion transport in an electrical field, $x_o$ is expected to be equal to the oxide thickness. For ion implantation, $x_o$ is the average range of ion implantation, which is on the order of 20 to 50Å for ion energies in the range of several keV, giving $x_o > x_1$. 
It is evident from these estimates that \( x_o \geq x_1 \) and that \( \gamma > R_{sp,m} > R_{sp,o} \). Consequently, the time dependence of oxide growth in a plasma for which \( y > \gamma^{-1}R_{sp,m} \) is approximately

\[
x \approx x_o \left( \ln \frac{\gamma y}{R_{sp,o}} - e^{-\frac{R_{sp,o}x_o^{-1}t}{x_o}} \right), \quad t > x_o R_{sp,o}^{-1}
\]

where \( R_{sp} \) is the oxide sputter etch (<5 Å/sec) and \( x_o \) is the oxidation range (~50 Å). The oxidation time is approximately 50 sec and the time constant for oxidation transients is then 10 to 50 sec.

The critical oxygen partial pressure below which no oxidation occurs is comparable to the critical plasma oxygen mole fraction \( y^* \) given by

\[
y^* = \begin{cases} 
\gamma^{-1}R_{sp,m} \sim 5 \times 10^{-3}, & \text{y increasing} \\
\gamma^{-1}\left(\frac{x_o}{x_1} - 1\right) R_{sp,o} \sim 4 \times 10^{-3}, & \text{y decreasing}
\end{cases}
\]

(with \( x_o > x_1 \)). These estimates depend, however, on the validity of the rate expressions used in the model, and on estimated values of the parameters.
III. EXPERIMENTAL APPARATUS AND PROCEDURES

A. Equipment

1. rf Sputtering Apparatus

The primary piece of experimental equipment consisted of an R. D. Mathis diode sputtering system together with a 1-kilowatt rf power supply. The sputtering system was attached to a vacuum system consisting of an NRC series VHS 6-in. diffusion pump with a pumping speed of 2400 liters air/sec,* a Welsch liquid nitrogen cold trap and a 7 liters air/sec centrifical roughing pump.** This system, shown in Fig. 3, could achieve an ultimate pressure below $10^{-7}$ mm Hg.

Chamber pressure was monitored simultaneously by a Pirani GP-310 Gauge (range 0-100 millitorr Hg) and an Autovac Type 3294-B Gauge (range 1-100 millitorr Hg and 100 millitorr to 1 atm). The main purpose of the dual meter system was to eliminate errors due to meter fluctuations after calibration. For better flow control, a thermocouple ionization gauge was installed in the diffusion pump foreline.

2. Gas Metering System

A very critical parameter in reactive sputtering is the precisely controlled reactive gas fraction in the plasma. For this reason, considerable effort was expended in designing an adequate gas supply system. A schematic of the flow system is shown in Fig. 4.

The $O_2$ flow was monitored by means of a microflowmeter capable of measuring flow rates between 0.2 and 15 ml/min. When operating

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*NRC, Newton, Massachusetts.

Fig. 3. rf sputtering system and ancillary apparatus.
Fig. 4. Gas metering system.
at low flow rates, it is essential that the inlet pressure to the meter be constant; a Matheson Model 70 regulator was incorporated with a standard tank regulator to restrict the outlet pressure to 30 psi. The delivery pressure was then more accurate, and hence the rate more constant than could be achieved with the standard regulator alone. In addition, for very dry gases at low flow rates, a static electric charge builds up on glass rotameter walls, inducing reading error in the position of the ruby rotameter sphere in the meter. A staticmaster unit (containing a polonium alpha emitter) was positioned next to the rotameter to dissipate any charge that might accumulate.

The gas passed from the flowmeter through a shut-off valve, an in-line filter and a double-pattern needle valve for flow control. The filter removed particles above 7 micron diameter, which might have obstructed flow through the needle valve. The oxygen was mixed with the argon stream and passed through a Hastings-Raydist massflowmeter, where the total gas flow and, by difference, the argon flow rate were measured.

Beyond the Hastings meter, the gas could be sent through a positive displacement flowmeter to vent, or directly into the sputtering chamber. The positive displacement meter provided a means for periodic detection of any fluctuations in the meter calibration. Located immediately before the chamber inlet was a Cartesian Manostat #6A, which provided pressure regulation in the flowline.

The Ar feed was similar to the O₂ line, except that the tank regulator sufficed to control delivery pressure; there was no micro-flowmeter in this line. The Ar gas was certified by the supplier as
99.998% pure. Also, an oxygen gettering furnace was used to remove any oxygen impurity in the feed argon. The furnace contained titanium sponge heated to 800°C, over which the gas was passed. All tubing was of stainless steel, to prevent atmospheric impurities from contaminating the feed.

Maximum gas throughput was determined by the limitations of the diffusion pump. The maximum foreline pressure was chosen as a conservative 200 millitorr. At this pressure, the argon flow rate reached an upper limit of 150 ml/min. Since the microflowmeter could resolve as low as 0.2 ml/min, the minimum measurable O₂ volume fraction attainable was 0.0013. The volume fraction of O₂ is identical to the mole fraction at the low chamber pressures involved (25 millitorr).

Another consideration for the flow system design was the adequate distribution of gas in the chamber, to ensure that the O₂:Ar ratio in the feed line is maintained in the cathode-anode gap. The distribution is a function of two parameters, the system mean free path and the rate of oxygen entrainment in the deposited films.

Appendix A contains a calculation of the mean free path as a function of the system temperature and pressure. Figure A-1 shows the mean free path λ vs pressure for a typical plasma positive ion temperature of 400°K in relation to the sputtering system dimensions. This figure was used to determine operating pressures. Davidse and Maissel have reported that the distance between the cathode ground shield and the electrode should be less than or equal to the thickness of the dark space which is directly proportional to the electron mean free path. If the ground shield spacing is much smaller than the dark space thickness,
the low impedance at radio frequencies between cathode and ground will allow most of the rf power to drain to ground, and the sputtering rate will decrease. This distance then is very critical and should be kept as close to the dark space thickness as possible without exceeding it. This criterion was used in selecting the operating point shown in Fig. A-1. At the operating pressure, the mean free path is considerably shorter than the cathode–anode distance, and many collisions can be expected as the gas traverses this gap, assuming adequate O\textsubscript{2} distribution in the plasma.

A calculation of the amount of O\textsubscript{2} removed from the plasma during the deposition of stoichiometric TiO\textsubscript{2} film is presented in Appendix B. The results indicate that negligible oxygen partial pressure change occurs by the deposition reaction. Only 1.3% of the total gaseous O\textsubscript{2} will be entrained at an oxygen plasma mole fraction of 0.007 provided maximum gas throughput is maintained.

3. Density and Deposition Rate Measurements

The deposition rate of TiO\textsubscript{x} was obtained from the measured thickness of the film deposited in a given time. Film thickness was measured using a Clevite Surfalyzer Model 150, which had a resolution of 25Å. A step height change from a masked part of the substrate was taken as the film thickness.

Film density was determined from the measured substrate weight change produced by sputtering, combined with the film thickness and area. Substrates were weighed immediately before and after deposition on a Mettler HT-20 balance which had a resolution of 10^{-5} gm.
4. Additional Equipment

Titanium targets 6 in. in diameter were fashioned from 0.32 in. sheet metal.* The purity was assayed at 99.9% and the results of a spectrographic analysis are given in Appendix C. Several targets were used, to ensure oxide-free surfaces for each phase of the research. The anode was covered with a Ti disk, to minimize film impurities due to back-sputtering.

Three different substrates were used: ordinary microscope slides for thickness measurements, microscope cover slides for weight change and masking, and type 10 quartz plate for all other measurements. The cover slides were ideal for obtaining weight change, by virtue of their small size and mass, and yielded a higher percent change in mass. They also provided a more definitive step-height change because the shadowing effect of slide edges during deposition was minimized. A thicker mask, such as a microscope slide produces a broad transition in height between the masked and unmasked surface due to shadowing. The cover slides, however, tend to warp from the heat generated during deposition after long sputtering times.

The quartz plates were cut into 13×13 mm squares, for electron microscopy and spectrophotometric analyses. High optical quality is essential to obtain reliable uv spectra.

* Continental Metals, North Hollywood, CA.
B. Experimental Procedure

1. Reactive Deposition of Titanium Oxide Thin Films

Sputtering was performed in the range of oxygen mole fraction $y$ ranging from 0 to 0.15. Titanium was sputtered in pure Ar ($y = 0$) as a standard for comparison in assessing the effects of O$_2$ on sputtering parameters. For this series of runs, a deposition time of 30 min was chosen, to generate films sufficiently thick for characterization purposes. Previous work on sputtering TiO$_x$ films showed that this amount of time would produce films at least 0.1 μm thick.$^{1,7}$

A sputtering pressure of 24 millitorr, determined by mean free path considerations, produced the optimum initial power match. Forward and reflected power settings were normally 500 watts and 90 watts, respectively, delivering a dc bias voltage of about 1.9 kilovolts. These values were not constant throughout a run, however, and provided an early indication of change in the target surface state, which was subsequently interpreted as oxidation. The chamber pressure remained constant during all experiments.

Specimens were examined by reflection electron microscopy to determine their structure. The reflection mode minimized any interference by the quartz substrate which could have occurred with transmission electron microscopy. Spectral absorbance of the samples was measured in the ultraviolet, visible, and infrared regions of the optical spectrum. The uv and visible absorbances were obtained on a Cary Model 118 spectrophotometer, while the Perkin-Elmer Model 421 spectrophotometer was used for the IR spectra.

A four point conductivity apparatus was constructed to measure the conductivity of the sputter-deposited films at room temperature.
The application of 1.0 keV across the probe was not sufficient to produce a detectable current, indicating extremely high resistivities in samples of titanium oxide deposited in the higher range of y.

The cooling water temperature rise and flow rate were recorded to provide information concerning heat transfer and power dissipation in the system.

2. Investigation of Target Oxidation Phenomena

A new target was utilized for this phase of the investigation, as the previous one had become completely oxidized. These experiments were performed without any substrate present on the titanium disk supported by the water-cooled Cu anode. The target was sputter-etched in Ar, then O\textsubscript{2} and Ar were simultaneously admitted at a given y for a measured time interval. The O\textsubscript{2} flow was then shut off, the target sputter-cleaned in Ar, and the etch time recorded. Sputter conditions were very much the same as in part 1.

During these runs, the target temperature was measured to provide insight into the activated nature of the oxidation kinetics. Two techniques were employed: phase change observation and infrared pyrometry. Tempilstik, a commercially-available, wax-like material designed to melt irreversibly at a specified temperature was tested for sensing substrate temperatures. The wax was applied to the target surface and a visual observation of melting was noted. The second measurement method utilized an Infra-Scope.* This device senses the

*Huggins Lab., Inc.
infrared, blackbody radiation of a heated surface to determine its temperature. Readings were taken through the transparent Pyrex observation window on the sputtering system.

Long-term (over 20 hr sputtering time) as well as short term depositions were made. These runs provided insight into oxide layer thickness and supplied thicker films for more accurate characterization.

Possible contamination of the system by atmospheric oxygen was minimized by completely evacuating the system for 30 min before each run. After each opening of the system to air, a complete sputter-cleaning was required before a new run was possible. A minimum of 10 min was necessary to remove the chemisorbed oxide layer which formed on the target surface. The in situ determination of the target oxidation state was made from measurements of reflected power bias potential and plasma color.
IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Characterization of Deposited Films

The titanium oxide films deposited under various conditions were characterized for two purposes: first, to study the effect of target oxidation and reactive sputtering variables on the physical, optical, and electrical properties of deposited films, and second, to delineate the film properties for their direct application to protective coatings, as well as potential utilization in microelectronics applications.

1. Density and Deposition Rate

A significant transition in density and deposition rate was observed at an oxygen mole fraction \( y^* = 0.007 \), as shown in Figs. 5 and 6. Deposition rates and film densities were independent of \( y \) for \( y > y^* \).

Bulk density values of Ti(c) and TiO\(_2\) (rutile) are 4.5 gm/cc and 4.26 gm/cc respectively.\(^{14}\) Table III summarizes the experimental results.

The thin films themselves were very durable and substrate adhesion was excellent, resisting both scraping with a razor blade and pulling with adhesive tape. The films were, however, easily etched in concentrated H\(\text{NO}_3\).

Lakshmanan and Mitchell have reported that TiO\(_2\) films produced by dc sputtering of Ti in Ar/O\(_2\) possess the same resiliency.\(^{15}\) Fitzgibbons reported that crystalline forms of TiO\(_2\) (rutile and anatase) are quite etch resistant, while the amorphous phase etches readily at 50Å/sec in concentrated H\(\text{NO}_3\).\(^{16}\)

Deposition rate data showed a decrease by an order of magnitude near \( y^* \), as shown in Fig. 6. The significance of these results becomes apparent when one contemplates the conditions needed to deposit films
Fig. 5. TiO\textsubscript{x} film density vs O\textsubscript{2} mole fraction in the plasma.
Fig. 6. TiO$_x$ film deposition rate vs O$_2$ mole fraction in the plasma.
Table III. Deposited film densities.

<table>
<thead>
<tr>
<th>Species</th>
<th>Plasma Composition</th>
<th>( \rho ) (gm/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>( y = 0 )</td>
<td>2.05</td>
</tr>
<tr>
<td>TiO</td>
<td>( y &lt; y^* )</td>
<td>6 to 6.5</td>
</tr>
<tr>
<td>TiO(_x)</td>
<td>( y &gt; y^* )</td>
<td>3.9</td>
</tr>
</tbody>
</table>
of constant and reproducible properties. For \( y > y^* \), the data indicate film properties are invariant with \( y \), which allows for easy control of film parameters, particularly in large volume commercial applications. However, the low deposition rate for \( y > y^* \) represents a drawback for operations requiring rapid throughput. Hence, an individual evaluation is required to determine the optimum operating parameters for each system based on the particular production requirements involved.

2. **Structure from Electron Microscopy**

The rapid etching characteristics of reactively sputtered TiO\(_x\) films suggest that the films are amorphous. This assumption was born out by electron microscopy studies, using a Hitachi HU-125 operated at 100 keV. Figure 7 shows a reflection electron diffraction pattern from an oxide film which demonstrates the amorphous structure of the films. The ring pattern is attributed to a gold foil evaporated over the oxide to prevent electrostatic charging of the surface. The Au coating thickness was critical as too thin a layer did not prevent electrostatic charging, while too thick a layer interfered with the reflection pattern. A 200Å coating initially selected proved too thick, completely dominating the diffraction pattern, while a 50Å layer was found to be satisfactory. Nevertheless, a 50Å film superimposed a ring pattern on the reflection diffraction pattern. This effect had to be subtracted from the composite pattern to yield the TiO\(_x\) diffraction pattern alone.

A photodensitometer evaluation of the sample of Fig. 7 with Au coating and of a Au foil alone were compared to compensate for the ring
Fig. 7. Reflection electron diffraction pattern from a TiO$_2$ film deposited at $y = 0.015$. 
diffraction pattern contributed by the Au. The photodensitometer records the relative photographic intensity of the micrograph along a radial distance from the electron beam centerline. Figure 8a shows the photodensitometer trace of the sample of Fig. 7, while that of Au is shown in Fig. 8b. The graphical subtraction of Fig. 8b from Fig. 8a is presented in Fig. 8c and represents the photodensitometer plot of the TiO\textsubscript{x} film alone.

The phase diagram for the Ti-O system shown in Fig. 1 indicates that the anatase phase of TiO\textsubscript{2} would be expected for low temperature deposition. Presumably the amorphous phase persists because of the high impact energy of the depositing atoms, which destroys any crystalline lattice which would otherwise form. In order to deposit a crystalline phase, it will be necessary to provide an external substrate heating source capable of maintaining the substrate several hundred degrees above its unheated temperature. This will provide sufficient kinetic energy to the already-deposited material for annealing.

Several suggestions of Howie, et al. in their monograph on interpreting the microscopy of amorphous materials have proven useful in identifying the structure of the deposited films.\textsuperscript{17}

3. Optical Spectra

The oxide films were studied in three regions of the electromagnetic spectrum: infrared, visible and ultraviolet. The specimens were examined while supported on the substrate. An alternate technique not used here is colorimetry, where the film is dissolved in an etchant, and analyzed in solution. Optical absorption measurement technique requires substrates of high optical quality, to minimize absorption by the
Fig. 8. Photodensitometer traces of reflection electron diffraction patterns from (a) the Au coated TiO$_2$ film shown in Fig. 7, (b) a vacuum deposited Au film, and (c) a composite of the sample shown in (a) and (b) showing the reflection diffraction pattern for the TiO$_2$ sample without the Au reflections.
substrate. All films deposited at \( y > 0.035 \) showed essentially no absorption in the visible range, and were in fact transparent to the eye. Films deposited at very low \( y(\ll 0.002) \) were metallic and showed some visible absorbance while films deposited at \( y = 0.02 \) possessed a slight gold tint. From the optical data of Table I, it can be inferred that the yellow-gold colored sample is TiO.

The uv spectra show an absorption edge at about 330 nm, as shown in Fig. 9, corresponding to a band gap of 3.76 eV for TiO\(_2\). Lakshmanan reports spectra for TiO\(_2\) reactively deposited in pure O\(_2\) remarkably similar both in shape and value that shown in to Fig. 9. The band gap energy of 3.65 eV which he reports agrees quite closely with the value of 3.76 eV obtained from Fig. 9.

The spectrum for the sample deposited at \( y = 0.02 \) shows low absorption throughout the uv range and is probably TiO. The films deposited at 0.05, 0.10 and 0.15 mole fraction of O\(_2\) in the plasma all absorb strongly below 300 nm and are probably amorphous Magneli phases. The species deposited at \( y = 0.15 \) represents an anomaly in that it absorbs less below 330 nm than the oxide films formed with lower \( y \). This anomaly is considered in more detail at the end of this section.

Infrared spectra for films deposited at low and high plasma oxygen compositions were measured and compared to the standard spectrum for rutile shown on Fig. 10. The low O\(_2\) samples gave spectra which are markedly different from the TiO\(_2\) standard as shown in Fig. 11. This result would be expected if the films were metallic \( \alpha \)Ti or TiO. All samples deposited with \( y \ll 0.02 \) exhibited an absorption transition around 2100 cm\(^{-1}\).
Fig. 9. uv spectrograph of TiO$_2$ thin films deposited at several oxygen plasma conditions.
Fig. 10. ir spectrograph of TiO₂ rutile standard.*

*After Nyquist and Kagel.¹⁸
Fig. 11. IR spectrograph of TiO$_x$ thin films deposited at low plasma O$_2$ concentrations.
Fig. 12. IR spectrograph of TiO\textsubscript{x} thin films deposited at high plasma O\textsubscript{2} concentrations.
Infrared spectra for films deposited from plasmas containing high $O_2$ are shown in Fig. 12. These spectra do resemble the standard spectra of $TiO_2$ and show high absorbance above 2100 cm$^{-1}$. The rutile standard absorbs below 900 cm$^{-1}$ (Fig. 11). Thus, the regular lattice array of the crystal provides a more well-defined absorption band edge than do the amorphous samples.

B. Target Oxidation Phenomena

1. Target Oxidation Effect on Deposited Films

The films deposited with $y = 0.035$ were shown in Fig. 12 to give less absorbance than did films deposited at $y = 0.05$ or $y = 0.10$. The order of deposition of the films shown in Fig. 12 corresponded to $y$ values of $0, 0.02, 0.15, 0.075$ and $0.035$. Because no target etching was performed before each successive deposition, the oxidation state of the target will affect the amount of oxygen incorporated into successively deposited films. This hysteresis effect is evident in the data of Fig. 12.

This target oxidation state hysteresis effect is apparent in both the uv and ir spectral data and demonstrates the critical necessity to control all possible sources of $O_2$ in the system, as the target oxidation state can significantly affect reactively deposited film properties.

The absorbance spectra for films deposited at high oxygen mole fractions resemble the spectrum for $TiO_2$ rutile, but show high absorbance above 2100 cm$^{-1}$, whereas the rutile spectrum showed high absorption above 900 cm$^{-1}$, as shown in Figs. 12 and 10, respectively. It is possible that the amorphous structure of the reactively sputtered
films causes the absorbance edge to be less sharp than for a crystalline phase.

The conclusion to be drawn from spectral data is that the TiO\textsubscript{x} films deposited from plasmas containing high percentages of oxygen are nearly stoichiometric, while films deposited with y < y* are primarily metallic. This result was confirmed by 4-point conductivity measurements of these samples. Only the film deposited at y ≤ 0.02 has any detectable room temperature conductivity.

2. In Situ Observation of Target Oxidation

The investigation of the target oxidation phenomena was considered significant because this condition so critically affects the operating parameters of the system as well as the film characteristics. The factors determining the onset of target oxidation, and the conditions under which it is sustained, are most important to anyone working with reactive gases and target materials.

The onset of target oxidation could be established quite clearly from a number of indications. The plasma color while sputtering Ti under non-reactive conditions was deep blue. Once an oxide layer formed the color became pink, attributable to intermediate oxide species such as TiO existing in the plasma, or to optical emission from excited O\textsuperscript{2+} ions. The transition period could be noted by the time required for the color change. Concurrent with the change in color of the plasma, the dc bias voltage showed a drop of about 30%, and the circuit impedance match deteriorated, resulting in a decrease in forward power. The oxide layer formed on the target surface in effect interposed a dielectric
material into the cathode-anode region increasing the impedance and detuning the power matching circuit.

The effects of oxidation on the observable system parameters is illustrated in Figs. 13 and 14. Figure 13 shows the plasma intensity in the pink spectral range, the rf forward power, and the dc bias voltages vs time following the admission of oxygen into the plasma for $y > y^*$, while Fig. 14 shows these changes for $y \gg y^*$. Similar transitions are shown following the replacement of the Ar-$O_2$ mixture with pure Ar. The clear transition of each at $y > y^*$ indicates a basic change in the oxidation state of the target.

The pressure dependence of the critical mole fraction of oxygen in the plasma required for target oxidation was studied by varying the total system pressure. At each pressure the target surface was first etched in pure Ar for a period of 10 min. Then the oxygen mole fraction in the plasma was slowly raised until changes in plasma color, bias voltage and reflected power were observed. The magnitude of the change was then noted as a function of $y$. The critical mole fraction $y^*$ was then obtained by extrapolating the magnitude of the changes to zero. It was found that the measured $y^*$ was essentially independent of system pressure over the range from 5 to 30 mTorr. No measurements were made outside this range because of power matching problems. The critical plasma oxygen mole fraction was found to be 0.007, in close agreement with that predicted from the target oxidation model given in Section II-B.
Fig. 13. Change in sputtering conditions during oxidation \( y \gtrsim y^* \).
Fig. 14. Change in sputtering conditions during oxidation ($y > y^*$).
3. **Effect of Target Oxidation on the Reactive Sputtering Process**

The dependence of the deposition rate on \( y \) is shown in Fig. 15. An order of magnitude decrease in the deposition rate occurs near \( y^* \). The initial rise in rate as \( y \) increases from 0 to 0.002 did not support the hypothesis that the Ti sputtering rate is constant for \( y < y^* \), and indicates that \( O_2^+ \) ions enhance sputter etching of the target. Part of the rise in deposition depicted in Fig. 15 is probably due to an increasing oxygen incorporation in the deposited film provided by \( O_2 \) in the plasma, and to a lesser extent, to an increasing sputter rate due to \( O_2^+ \) ions, superimposed on a constant Ar sputter etch rate. The non-reactive Ti sputtering rate of 5.6 Å/sec is an order of magnitude higher than the extrapolated sputtering rate of 0.48 obtained for \( y \gg y^* \), indicating that titanium metal has a much higher sputter yield than does TiO\(_2\). This disparity is larger than would be expected since the Ti-Ti bond energy is 112.6 kcal/mole compared to a Ti-O bond energy of 157 kcal/mole\(^{14} \) and since the sputter yield should vary with the square root of the bond energy.

Film physical properties also exhibited a strong dependence on the state of target oxidation. In particular, film density followed the same trend as did the deposition rate, with increasing \( y \), as shown in Fig. 5. The obvious transition at \( y^* \) is again apparent, with film density remaining constant for \( y \) above this value. The invariance of both deposition rate and density for \( y \) above \( y^* \) can be taken as an indication that film stoichiometry no longer changes, and that the target oxide here in fact is stoichiometric TiO\(_2\).
Fig. 15. Target etch time vs $O_2$ mole fraction in the plasma.
The effects of exposing a clean titanium target to an oxidizing plasma were studied as a function of exposure time and oxygen concentration. The steady-state target oxide thickness was formed by oxidation in an \( \text{Ar/O}_2 \) plasma for a time sufficiently long to achieve steady-state. The dependence of the steady-state oxide thickness developed on the target at different oxygen molar concentrations in the plasma was measured indirectly by the time required to etch the target clean of oxide in an Ar plasma. Figure 15 shows the dependence of the etch time on the plasma oxygen mole fraction. In this figure, the end of the etching period was determined from the color change of the plasma. The etch times shown are the average of several experiments for each value of \( y \). Since the Ar-plasma etch time is the product of sputter yield times the oxide thickness, the proportionality between oxide thickness and etch time holds only if the oxide properties are independent of \( y \).

It is possible that the sputter yield for films deposited for \( 0.01 < y < 0.02 \) are lower than for \( y > 0.02 \) to give the peak observed in Fig. 15. A low sputter yield is expected for the highly stable phases \( \text{Ti}_2\text{O}_3 \) and \( \text{Ti}_3\text{O}_4 \).

Fig. 15 shows that no oxide formed on the target for \( y < y^* = 0.007 \). There was an increase in etch time at \( y^* \), then a drop and a gradual rise with increasing \( y \). The initial increase can be attributed to the formation of a highly stable phase such as \( \text{Ti}_2\text{O}_3 \) or \( \text{Ti}_3\text{O}_4 \) on the target surface. The dashed line tangent to the curve for \( y > 0.03 \) delineates the approximate increase in \( \text{O}_2^+ \) ions resulting from a rise in \( y \) and indicates that target oxide thickness is proportional to \( y \).
in that range. This result is in contradiction to the growth rate model developed in Section II-B, which predicts that the oxide thickness is proportional to ln(\(\gamma yR_{sp}^{-1}\)).

The transient growth of oxide on the Ti target in an Ar/O\(_2\) plasma for which \(y = 0.014 = 2y*\) was also studied by measurement of Ar-plasma sputter etching times needed to remove the oxide films. Again, the oxide thickness was assumed proportional to the Ar-plasma etch time provided that the sputter yield of the oxide is independent of oxide thickness. The data is shown in Fig. 16. The oxide thickness increased monotonically with time. If the steady state oxide thickness corresponds to a target oxide sputter-etch time of 400 sec, then the time constant for transient oxidation can be found by comparing the data with Eqs. (4), (13) or (15).

The data of Fig. 16 does not show a parabolic oxidation rate as would be required by diffusion controlled kinetics. The time constant for the exponential time dependence of Eqs. (13) and (15) is found to be

\[x_o R_{sp,o}^{-1} = 67 \pm 11\]  \(\text{(20)}\)

Since the oxide sputtering rate at a bias voltage of 1.9 kV was independently measured experimentally to be 0.48 Å/sec, the apparent oxidation constant is \(x_o = 32\) Å, and the oxide thickness is \(x = 141\) Å, larger than that is obtainable by anodic oxidation at zero bias, but in reasonable agreement with visual inspection. If a steady state thickness of 141Å is assumed, however, the steady state thickness Eq. (16) gives \(\gamma yR_{sp,o}^{-1} = 82.1\), and since \(y = 2y*\) and \(R_{sp,o}\) are experimentally known, it follows that \(\gamma = 2820\), in agreement with the magnitude expected from Section II-B-2.
Fig. 16. Target etch time vs target oxidation time (error bars denote limit of data accuracy attributable to subjective determination of plasma color change.)
The value of the parameter $\gamma$ can also be estimated from Eq. (14), from the increased sputtering rate for $\alpha$Ti, and the critical value $y^* = 0.007$. The effective solubility rate parameter predicted by Eq. (14), for the condition $x_o = x_1$ with $\Delta R_{sp,m} = 9.5 \text{ Å/sec}$ becomes

$$\gamma = (y^*)^{-1} \Delta R_{sp,m} = 1357.$$  \hfill (21)

The value of $\gamma$ predicted by Eq. (15) in the steady state with $y = y^*$ and $R_{sp,m} = 10 \text{ Å/sec}$, is

$$\gamma = (y^*)^{-1} R_{sp,m} = 1430.$$  \hfill (22)

Both sputter etch models agree closely with the anticipated value of $\gamma$ on the order of $10^3$, estimated from the plasma oxidation of Pb. The deposition rate data of Fig. 6 indicates that $R_{sp,m}$ varies significantly with $y$, and reaches a maximum of $10 \text{ Å/sec}$. Then $\gamma$ becomes

$$\gamma \geq (y^*)^{-1} R_{sp,m} = 1140.$$  

The data of Fig. 16 indicates the difficulties associated with relying on color change as a sensitive indication of oxidation state. It is a somewhat subjective decision as to exactly what moment constitutes a completely blue or pink plasma color change since during the color change some trace of each color remains. Also, the intermediate oxide species in the plasma, to which the pink color is attributed, remain in the plasma for an indeterminate time after the oxide is etched. How long these remain after the oxide is etched will affect the observed time for color change.

Figure 16 was produced with $y = 0.014$. Data used to compile these figures are taken from Table IV. The data show that as the oxide growth
time increases at constant $y$, the etch time approaches an asymptotic limit. This relationship would be expected for a target where the oxide layer thickness asymptotically approaches a certain value and remains constant thereafter.

The existence of an oxide layer on the target after reactive sputtering can readily be determined by visual examination. Figure 17 shows a photograph of the oxidized surface of a titanium target following plasma oxidation to steady state at $y \geq 0.15$. The color fringes indicate changes in oxide thickness. This target was attached to the water cooled cathode by a central retaining screw machined from Ti stock and by 3 Ti clips equispaced about the circumference. The target oxidized rapidly during initial experimental runs. Where good thermal contact was provided by the screw and clips, little oxidation occurred (one clip failed to make contact and allowed that site to oxidize).

A second target was bonded to the surface of the water-cooled cathode with a thermally conducting Eccobond epoxy.* The clip-mounting allowed the targets to be interchanged more readily than did epoxy mounting but the heat transfer characteristics of the latter were more desirable.

---

* Emerson and Cuming, Inc., Gardena, California.
Table IV. Experimentally measured plasma oxidation and etch times and power settings at different plasma $O_2$ concentrations.

<table>
<thead>
<tr>
<th>$y$ (Mole Fraction)</th>
<th>$O_2$ Exposure Time</th>
<th>Time to start of color change</th>
<th>Time to Etch Voltage Target</th>
<th>Bias Voltage (keV)</th>
<th>rf Forward Power (Watts) Before/After $O_2$ Admitted</th>
<th>rf Reflected Power (Watts) Before/After $O_2$ Admitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.007</td>
<td>180</td>
<td>105</td>
<td>182</td>
<td>1.1</td>
<td>310</td>
<td>90</td>
</tr>
<tr>
<td>0.007</td>
<td>300</td>
<td>138</td>
<td>178</td>
<td>1.1</td>
<td>320</td>
<td>90</td>
</tr>
<tr>
<td>0.008</td>
<td>80</td>
<td>55</td>
<td>468</td>
<td>0.75</td>
<td>220</td>
<td>110</td>
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<tr>
<td>0.008</td>
<td>100</td>
<td>37</td>
<td>465</td>
<td>0.7</td>
<td>220</td>
<td>110</td>
</tr>
<tr>
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<td>150</td>
<td>55</td>
<td>416</td>
<td>0.8</td>
<td>220</td>
<td>110</td>
</tr>
<tr>
<td>0.014</td>
<td>80</td>
<td>35</td>
<td>245</td>
<td>1.0</td>
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<td>100</td>
</tr>
<tr>
<td>0.014</td>
<td>100</td>
<td>25</td>
<td>364</td>
<td>0.9</td>
<td>250/200</td>
<td>100/100</td>
</tr>
<tr>
<td>0.014</td>
<td>120</td>
<td>22</td>
<td>320</td>
<td>0.85</td>
<td>220/200</td>
<td>105/100</td>
</tr>
<tr>
<td>0.014</td>
<td>120</td>
<td>20</td>
<td>321</td>
<td>0.9</td>
<td>270/200</td>
<td>105/120</td>
</tr>
<tr>
<td>0.014</td>
<td>150</td>
<td>20</td>
<td>390</td>
<td>0.85</td>
<td>220/200</td>
<td>100/120</td>
</tr>
<tr>
<td>0.014</td>
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<td>18</td>
<td>360</td>
<td>0.85</td>
<td>250</td>
<td>100/120</td>
</tr>
<tr>
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<td>22</td>
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<td>0.9</td>
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<tr>
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<td>1.2</td>
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<td>85</td>
</tr>
<tr>
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<td>1.2</td>
<td>350</td>
<td>90</td>
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<td>100</td>
<td>5</td>
<td>250</td>
<td>1.1</td>
<td>220</td>
<td>80</td>
</tr>
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</table>
Table IV. Continued.

<table>
<thead>
<tr>
<th>( y ) (Mole Fraction)</th>
<th>( O_2 ) Exposure (sec)</th>
<th>Time to start of color change (sec)</th>
<th>Time to Etch Target (sec)</th>
<th>Bias Voltage (keV)</th>
<th>rf Forward Power (Watts) Before/After ( O_2 ) Admitted</th>
<th>rf Reflected Power (Watts) Before/After ( O_2 ) Admitted</th>
</tr>
</thead>
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<tr>
<td>0.064</td>
<td>15</td>
<td>3</td>
<td>170</td>
<td>1.1</td>
<td>300</td>
<td>110</td>
</tr>
<tr>
<td>0.064</td>
<td>60</td>
<td>3</td>
<td>211</td>
<td>1.1</td>
<td>300</td>
<td>80</td>
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<td>3</td>
<td>235</td>
<td>1.1</td>
<td>300</td>
<td>80</td>
</tr>
<tr>
<td>0.175</td>
<td>80</td>
<td>15</td>
<td>112</td>
<td>1.3</td>
<td>350/200</td>
<td>80</td>
</tr>
<tr>
<td>0.175</td>
<td>80</td>
<td>13</td>
<td>180</td>
<td>1.0</td>
<td>300</td>
<td>90/120</td>
</tr>
<tr>
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<td>18</td>
<td>216</td>
<td>1.0</td>
<td>300</td>
<td>90</td>
</tr>
<tr>
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<td>15</td>
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<td>1.0</td>
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<tr>
<td>0.033</td>
<td>100</td>
<td>10</td>
<td>199</td>
<td>1.0</td>
<td>300</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig. 17. Photograph of oxidized Ti target.
4. Heat Transfer During Reactive Sputtering

The temperature of the Ti target during reactive sputtering was deduced from measurements of the cooling water temperature rise following the initiation of reactive sputtering. The calculations are summarized in Appendix D. The bulk target temperature is determined to be 20.3°C, only 6°C above the inlet water temperature. It was not possible to obtain an estimate of any local ("hot-spot") temperature fluctuation. The target was cool to the touch immediately upon opening the system after a sputtering run, confirming the low temperature estimate given above.

The oxidized state of the first target indicated that the reaction mechanism was thermally-activated. Therefore, the target temperature must have been elevated during sputtering due to the low thermal contact with the cooling system allowed by the clip-mounting. The same conclusion does not apply to later targets which were epoxy bonded to the Cu cooling circuit.

All attempts to measure target temperatures with thermocouples and infrared pyrometry did not give valid results, probably because the temperature rise was confined to the first few monolayers of the target exposed to the plasma. Carter and Colligon have reported temperatures of 1750°K at the target surface caused by ion bombardment. This condition endures only 10⁻¹³ sec and does not affect the bulk material temperature, which is the temperature measured by the thermocouple and pyrometer. Thus, neither of these techniques was applicable to measure local hot spots on the target.
The heat balance performed on the target has provided a means for obtaining the bulk temperature, however, as shown in Appendix D. If the major target heating is confined to only a few atomic layers, it would be expected that a thermally activated process requiring elevated temperatures would be limited to the high temperature region. Thus, the oxidation layer formed should be very thin.

C. Recommendations for Further Study

Further study is recommended in both of the areas considered in this work. Determination of conditions for crystalline phases of TiO$_x$ films should be made along with a quantitative measurement of the value of $x$ as a function of $y$. The film physical properties can then be ascribed to a definite composition of the films. Additional data is required on the transient and steady state thicknesses of target oxide as a function of time and $y$. Leslie and Knorr have already begun work in this area using ellipsometry to measure thickness.

Finally, an experimental determination of the effectiveness of rutile thin films as diffusion barriers for hot-pressing oxides is recommended. Sputtered rutile films deposited at high substrate temperatures and collected on graphite die substrates could be used in actual hot-press runs. The amount of interdiffusion of oxide and carbon could be established, and the diffusion profile would yield information on rates and thus on the effectiveness of the barrier layers.
V. SUMMARY OF RESULTS

This investigation has yielded results in the two areas under study. The characterization data indicate that the deposited films are amorphous and generally metallic for \( y < 0.002 \), and dielectric for \( y > 0.035 \).

The invariance of film density and deposition rate for \( y > 0.007 \) has been demonstrated. This result can be used to advantage in processes designed for depositing films of uniform and reproducible properties. However, this fact must be weighed against the order of magnitude reduction in deposition rate occurring for \( y < y^* \).

The spectroscopic evidence of the metallic to dielectric transition at \( y = y^* \) is confirmed by 4-point probe conductivity measurements. The only film with a measurable room-temperature conductivity was that deposited at \( y = 0.02 \). Films grown at larger \( y \) were non-metallic, which is expected of \( \text{TiO}_x \) films where \( x \approx 2.0 \).

A. Film Characterization

The characterization studies of the titanium oxide thin films were valuable in producing information on several features of sputter-deposited films. The electron diffraction results indicate that the films are amorphous rather than crystalline anatase as predicted from phase equilibria crystallinity. Presumably the impact energy of the depositing atoms destroys any crystal lattice which would otherwise form. In order to deposit a crystalline phase of \( \text{TiO}_2 \), it will be necessary to provide an external substrate heating system capable of maintaining the substrate at a temperature above 800°C. This will serve to increase the energy of the deposited material, and permit rearrangement after impact.
The characterization data has shown a dependence of deposition rate and density on the target oxidation state. These results are of importance for predicting conditions of depositing films of constant and reproducible properties. For \( y > y^* \), the data indicate film properties are invariant with \( y \), thus allowing for easy control of film parameters, particularly in large volume commercial applications. However, the deposition rate for \( y > y^* \) is one order of magnitude lower than for \( y < y^* \), requiring a much longer sputter time to deposit films of comparable thickness, a drawback for large volume operations where rapid throughput is essential. Hence, an individual evaluation is required to determine the optimum operating parameters for each system based on the particular production requirements.

The spectroscopic results show that the TiO\( _x \) films deposited from \( \text{TiO}_x \) plasmas containing high percentages of oxygen are nearly stoichiometric, while films deposited at \( y < y^* \) are primarily metallic. This conclusion is confirmed by four-point conductivity measurements of these same samples which show that only the film deposited at \( y \approx 0.02 \) had any detectable room temperature conductivity.

**B. Target Oxidation**

Research on plasma oxidation of Ti with O\( _2 \) has been furthered. A \( y^* \) value controlling the initiation of oxidation has been measured and found to be 0.007 for the Ti-O\( _2 \) system. This value is significant as it controls many of the film properties.

A model for describing the target oxidation phenomena has been developed which permits prediction of oxide thickness and growth rates.
The model was found to be a reasonable approximation of the cathodic reactive sputter oxidation phenomenon. It is hoped that the present study will lend insight into the complex mechanism of reactive sputtering.
ACKNOWLEDGEMENTS

The author is deeply indebted to the entire technical staff of IMRD for their unceasing assistance and advice. The machinists and electronic technicians imparted an appreciation of the practical aspects of engineering science not found in the classroom or the textbook; their expertise and skills have been invaluable in surmounting the many experimental problems encountered.

I should like to record a special gratitude to Tribhawan Kumar, who contributed a remarkable insight into the target oxidation phenomena, and whose guiding light illuminated the experimental paths.

Particular tribute must be paid to Professor Lee F. Donaghey whose overall skilled guidance and technical competence instilled greater self-confidence in my abilities. His patience and humane understanding is deeply appreciated.

The assistance of the U. S. Atomic Energy Commission in supporting the project is gratefully acknowledged.
APPENDIX A. CALCULATIONS OF Ar MEAN FREE PATH

The mean free path for low pressure gases is given by

$$\lambda = \frac{1}{\sqrt{2\pi d^2 n}}$$

where $n$ is the molecular concentration and $d$ is the molecular diameter. The molecular concentration is related to the molar volume of argon by

$$n = \frac{N_{Ar}}{v}, \text{ where } v = \frac{RT}{P}$$

For $p = 25 \times 10^{-3}$ Torr, the ideal gas law applies. If $400^\circ K$ is assumed for the plasma temperature, then

$$v = \frac{(82 \text{ cc atm/mole } ^\circ K)(400^\circ K)(760 \text{ Torr/atm})}{25 \times 10^{-3} \text{ Torr}} = 10.0 \times 10^8 \text{ cc/mole}$$

where $d_{Ar} = 2.9\AA$

$$n = \frac{N_{Ar}}{v} = \frac{6.023 \times 10^{23} \text{ atoms/mole}}{10.0 \times 10^8 \text{ cc/mole}} = 6 \times 10^{14} \text{ atoms/cc}$$

$$\lambda = \frac{1}{(1.414)(3.14)(2.9 \times 10^{-8} \text{ cm})^2 (6 \times 10^{14} \text{ atoms/cc})} = 0.447 \text{ cm}$$

The assumed temperature of $400^\circ K$ corresponds to the positive ion temperature in a typical rf plasma. From the restriction imposed by the spacing of the ground shield, the pressure is constrained to the range near $25 \text{ mTorr}$. The mean free path for molecular oxygen, $\lambda_{O_2}$, will be very close to that for Ar, $\lambda_{Ar}$, since there is practically no difference in molecular diameters---$d_{O_2} = 2.95\AA$ and $d_{Ar} = 2.9\AA$. The relationship between mean free path and pressure is shown in Fig. A-1.
Fig. A-1. Variation of argon mean free path with system pressure.
APPENDIX B. OXYGEN REQUIREMENTS FOR DEPOSITING STOICHIOMETRIC FILMS OF TiO$_2$

The amount of oxygen necessary to produce a film of TiO$_2$ for a given sputtering rate of the Ti target will establish the absolute minimum flow rate of O$_2$. Naturally, a much higher flow rate will be desired, in order that O$_2$ depletion will not significantly affect the measured O$_2$ mole fraction admitted.

If the rate of Ti mass deposition ($y = 0$) on a 6 in. diameter substrate is $2.2 \times 10^{-7}$ gm/sec then the molar rate is

\[
\frac{2.2 \times 10^{-7} \text{ gm/sec}}{47.9 \text{ gm/mole}}
\]

or $4.6 \times 10^{-9}$ moles/sec. Two moles of O are required for every mole Ti deposited. Assuming the Ti sputtering rate to be independent of $y$, $9.2 \times 10^{-9}$ moles/sec of oxygen are required for stoichiometry. This corresponds to an STP volume of

\[
(9.2 \times 10^{-9} \text{ moles/sec})(22.4 \text{ L/mole})(10^3 \text{ cc/L})
\]

or an STP flow rate of $0.012 \frac{\text{cc}}{\text{min}}$. The O$_2$ flow rate corresponding to a $y^*$ value of 0.007 was 0.95 cc/min. Thus, the oxygen entrained in the deposited film is only 1.3% of the total O$_2$ flow.
### Table A-1. Semi-quantitative spectrographic analysis of Ti sheet metal.*

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<thead>
<tr>
<th>Ti Principle Constituent</th>
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<tbody>
<tr>
<td>Fe</td>
<td>0.1%</td>
</tr>
<tr>
<td>Al</td>
<td>0.02%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.001%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.001%</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.001%</td>
</tr>
<tr>
<td>V</td>
<td>&lt;0.002%</td>
</tr>
</tbody>
</table>

*Analysis performed by: American Spectrographic Laboratories, Inc.
557 Minna Street
San Francisco, CA 94103

Metal Supplied by: Continental Metals
North Hollywood, CA
APPENDIX D. HEAT FLOW CALCULATION

An estimation of the cooling water temperature rise was made based on dissipation of input power to the plasma. Power dissipation on chamber walls was also included.

A typical rf forward power was 500 watts or 120 cal/sec input to the plasma. Since Ti target volume was \( \frac{\pi}{4} (6 \text{ in.})^2 (0.032 \text{ in.}) = 0.603 \text{ in.}^3 = 9.88 \text{ cm}^3 \), with a density \( \rho = 0.163 \text{ lb/in.}^3 = 4.5 \text{ gm/cc} \), the target mass was \( 9.88 \text{ cm}^3 \times 4.5 \text{ gm/cc} = 44.6 \text{ gm} \).

The number of moles of Ti in the target is

\[
\frac{44.6 \text{ gm}}{48 \text{ gm/mole}} = 0.93 \text{ moles}
\]

An engineering estimate of the percentage of heat removed by the cooling water for a flow rate of 1.0 GPM or 63.1 gm/sec follows:

1. Conduction through aluminum chamber wall follows Fourier's Law, \( q = -kA \frac{\Delta T}{\Delta x} \), where \( kA = 0.5 \text{ cal/cm sec}^\circ \text{C} \). Heat is conducted through the neck of the bell jar (approximately 100 cm long and 15 cm\(^2\) cross-section) to the water-cooled diffusion pumping station, and to the base of the system. The maximum jar temperature rise was found to be approximately 10°C. Therefore,

\[
q = (0.5 \text{ cal/cm sec}^\circ \text{C})(15 \text{ cm}^2)(10^\circ \text{C}) = 0.75 \text{ cal/sec}
\]

2. Convection through exciting gases can be established from:

\[
C_p \approx \frac{3}{2} RT = \frac{3}{2} (2 \text{ cal/mole}^\circ \text{K})(300^\circ \text{K}) = 900 \frac{\text{cal}}{\text{mole}}
\]

where the Ar flow rate was 125 cc/min. Therefore,
\[ q = \frac{(900 \text{ cal/mole})(125 \text{ cc/mole})}{(22400 \text{ cc/mole})} = 5.4 \text{ cal/sec} \]

3. Heat removed by cooling water was thus

\[ 120 \text{ cal/sec} - 0.75 \text{ cal/sec} - 5.4 \text{ cal/sec} \approx 113.8 \text{ cal/sec} \]

The percent of input power removed by cooling water was thus \( \frac{113.8}{120} \) or 95\%. Therefore,

\[ (0.95)(120 \text{ cal/sec}) = (63.1 \text{ gm/sec})(1 \text{ cal/gm°C}) \Delta T \]

\[ \Delta T = 1.8°C \]

This estimated value of \( \Delta T \) corresponds well with the measured 2°C rise under normal sputtering conditions.

The cooling water coils were attached to the back side of the 6 in. diameter copper cathode. Cathode disk thickness was 1/4 in. The coils were 3/16 in. ID Cu tubing, totaling about 1 1/2 ft in length. Figure A-2 shows the cathode section in cross-section and dimensions are given in Table D-1.

---

**Table D-1. General Data Table**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Cathode Mass</td>
<td>735 gms</td>
</tr>
<tr>
<td>Cooling Water Velocity at 1 GPM</td>
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</tr>
<tr>
<td>Cooling Water Residence Time in Coils</td>
<td>0.13 sec</td>
</tr>
<tr>
<td>Tubing Surface Areas</td>
<td>0.074 ft</td>
</tr>
<tr>
<td>Viscosity, ( \mu_{\text{H}_2\text{O}} )</td>
<td>0.827 cp</td>
</tr>
<tr>
<td>Density, ( \rho_{\text{H}_2\text{O}} )</td>
<td>62.4 lb/ft²</td>
</tr>
<tr>
<td>Thermal Conductivity, ( k_{\text{H}_2\text{O}} )</td>
<td>0.00148 cal/cm sec°C</td>
</tr>
<tr>
<td>Heat Capacity, ( C_{\text{P}_{\text{H}_2\text{O}}} )</td>
<td>1 cal/gm°C</td>
</tr>
</tbody>
</table>
Fig. A-2. Cutaway view of water-cooled Cu cathode.
The Reynold's number for flow through the cooling tube was

\[
\text{Re} = \frac{D \cdot \rho \cdot v}{\mu} = \frac{(3/16 \times 1/12)(11.5 \text{ ft/sec})(62.4 \text{ lb/ft}^3)}{5.5 \times 10^{-4} \text{ lb/ft sec}} = 20,200
\]

For \( \text{Re} > 20,000 \) the following equation holds for heat transfer (20, p. 399)

\[
\frac{\text{Nu}}{\text{k}} = 0.026(\text{Re})^{0.8} (\text{Pr})^{1/3} \left(\frac{\mu_b}{\mu_o}\right)^{0.14}
\]

Therefore

\[
\text{Pr} = \frac{C_p \mu}{k} = \frac{(1 \text{ cal/gm}^\circ C)(0.00827 \text{ gm/cm sec})}{(0.00148 \text{ cal/cm sec}^\circ C)} = 5.6
\]

The temperature rise is only 2°C, so \( \left(\frac{\mu_b}{\mu_o}\right)^{0.14} \approx 1 \). Then,

\[
h_1 = \frac{(0.00148 \text{ cal/cm sec} \circ C)(0.026)(20200)^{0.8}(5.6)^{1/3}}{0.48 \text{ cm}} = 0.43 \text{ cal/cm}^2 \text{ sec} \circ C
\]

The heat transfer resistance of the Cu tubing wall is negligible compared to \( h_1 \). Therefore,

\[
Q = UA \Delta T_{\text{in}} \approx h_1 A \Delta T_{\text{in}}
\]

For a surface area of \( A = 0.074 \text{ ft}^2 = 68.8 \text{ cm}^2 \), the temperature rise becomes

\[
\Delta T_{\text{in}} = (T - 16.5^\circ C) - (T - 14.5^\circ C) = -2^\circ C
\]

or

\[
\Delta T_{\text{in}} = \frac{(95)(130 \text{ cal/sec})}{(0.43 \text{ cal/cm}^2 \text{ sec} \circ C)(68.8 \text{ cm}^2)} = 4.67^\circ C
\]

Thus, the average target surface temperature should be \( T = 20.3^\circ C \).
APPENDIX E. DETERMINATION OF O\textsubscript{2} CONTENT OF SPUTTERED FILMS FOR y < y* 

For y < y*, the Ti sputtering rate should be constant, and equal to that for αTi in Ar, because no oxide layer exists on the target. Any increase in film weight during deposition for y < y* will be due to deposited oxygen in the film. With this information, it is possible to estimate the value of x in TiO\textsubscript{x} samples. Data are shown in Table E-1.

Table E-1. Sample for oxygen content determination in TiO\textsubscript{x} films.

| Weight change Δω\textsubscript{y=0} = 2.66×10\textsuperscript{-6} gm/sec |
| Weight change Δω\textsubscript{y=0.004} = 3.21×10\textsuperscript{-6} gm/sec |
| Weight change due to Oxygen along = Δω\textsubscript{y=0} - Δω\textsubscript{y=0.004} = 0.55×10\textsuperscript{-6} gm O/sec |
| moles Ti deposited = \frac{2.66 \text{ gm/sec}}{47.9 \text{ gm/mole}} = 5.58×10\textsuperscript{-8} moles/sec |
| moles O deposited = \frac{0.55×10\textsuperscript{-6} \text{ gm/sec}}{16 \text{ gm/mol}} = 3.44×10\textsuperscript{-8} moles/sec |
| molar ratio: x = \frac{\text{moles O}}{\text{moles Ti}} = \frac{3.44×10\textsuperscript{-8} \text{ moles/sec}}{5.58×10\textsuperscript{-8} \text{ moles/sec}} = 0.62 |
REFERENCES


17. A. Howie, O. L. Krivanck and M. L. Rudee, Phil. Mag. 27, 1, 235


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