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KINETICS OF THE REACTIVE SPUTTER DEPOSITION OF TITANIUM OXIDES

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The reactive sputtering of titanium was studied in an rf plasma containing argon and oxygen. The kinetics of the reactive sputtering process and the properties of deposited titanium oxide films were studied as a function of the oxygen partial pressure in the plasma, bias voltage and rf power. Models for the transient oxidation of titanium were explored in relation to oxidation mechanisms. Model parameters were determined from experimental studies. The sputter etch rate of the titanium target reached a maximum at an oxygen mole fraction of 0.002. The sputter deposition rate was found to decrease sharply at a critical oxygen mole fraction equal to 0.007, corresponding to the onset of target oxidation. The time dependence of the target oxidation process was found to be in qualitative agreement with a reactive sputter-oxidation model.

INTRODUCTION

Titanium dioxide is an important dielectric material for refractory, optical and electronic applications. In optical and microelectronics applications, TiO_2 thin films can be sputter deposited by the rf sputtering of titanium, or by the reactive sputtering of titanium in a plasma containing a partial pressure of oxygen.⁽¹⁻³⁾ The optical properties of TiO_2 , particularly its high refractive index, have proven invaluable to the optics industry for over 25 years, and much thin film research in this industry has been carried out in the preparation of TiO_2 lens coatings.^(4,5) Titania can also be deposited as a protective coating.⁽⁶⁾ In addition to the practical importance of titanium dioxide, the Ti - O system is of theoretical interest because of the large number of phases in this system, and because the kinetics of reactive sputter deposition of these phases have not been established. 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.⁽⁷⁾ The establishment of kinetic rates and conditions for the deposition of TiO , of the Magneli phases $\text{Ti}_n\text{O}_{2n-1}$, where $n \geq 2$, and of TiO_2 by reactive sputtering is the subject of the present study.

THE Ti - O SYSTEM

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.⁽⁸⁻¹⁰⁾ The low temperature portion of the phase diagram for the Ti - O system after Roy and White is reproduced in Fig. 1.⁽¹⁰⁾ This diagram indicates that

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temperatures above 800°C are required to produce rutile crystals under equilibrium conditions. Below this temperature, anatase is the stable phase. Thus, in order to obtain rutile it is necessary to insure that the effective 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_3O_5 and the Magneli phases with regard to temperature and oxygen fugacity were determined by Porter.⁽¹¹⁾ These studies confirmed the existence of an indeterminate number of intermediate oxide phases between TiO and TiO_2 . Of these, Ti_2O_3 and Ti_3O_5 are distinct phases, while the Magneli phases form a closely related series of shear-defect compounds with the homologous formula Ti_nO_{2n-1} , $4 \leq n \leq \infty$.⁽¹²⁾

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. For substrate temperatures below 800°C, TiO_{2-x} (anatase) should be the thermodynamically stable, but not necessarily the kinetically favored phase deposited by reactive sputtering with Ar/O_2 over a range of oxygen fugacity.

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. Reactive gaseous components in the plasma can react with the target causing oxidation of the target surface, and energetic ions have sufficient energy to be implanted into the target to cause internal oxidation.

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

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 oxidation reaction could occur at the target surface, on collision with the substrate, or by diffusion and reaction following deposition on the substrate. Oxidation reactions in the gas phase are negligible because of the low collision cross-sections and low pressures involved.

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 or rate kinetics. However, new contributions to the mechanisms of target oxidation are available from recent developments in the analogous field of plasma anodization and oxidation.⁽¹³⁻¹⁵⁾

THE PLASMA ANODIZATION MODEL

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.⁽¹⁴⁾ Plasma oxidation is virtually the same technique lacking only the externally applied bias voltage. The current interest in these technologies stems from their application to the fabrication of oxide tunnel barriers for thin-film Josephson junction devices.

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.⁽¹³⁾ They offered a qualitative explanation of the oxidation process, and 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, Schroen looked at the physics of the oxidation process, and presented a molecular model for the reaction.⁽¹⁴⁾ The initially neutral substrate is raised to a negative potential by the mobile plasma electrons. This negative potential attracts O^+ and 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, and lacks any quantifying formulae.

O'Hanlon⁽¹⁵⁾ reviewed plasma anodization, and presented a model very similar to Schroen's for the plasma anodization process in terms of two distinct mechanisms. One mechanism is that of Schroen, whereby O_2^+ ions dissociate upon impact, and diffuse into the target. A second mechanism is that O^+ and O_2^+ ions originating in the plasma are implanted directly into the oxide. This model is supported by Whitlock and Bounden⁽¹⁶⁾ and by Thompson,⁽¹⁷⁾ 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.⁽¹³⁾ 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 600 sec before applying a bias potential. Without the priming period, no oxide was formed.

The thin oxide layers ($<20\text{\AA}$) formed after the priming period by plasma anodization without external bias potentials was shown by O'Hanlon(15) to have a logarithmic dependence on time given by

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

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

$$x = k' \sqrt{t} \quad t > 0 . \quad (2)$$

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.(18) The oxidation time dependence can be described by the parabolic dependence of oxide thickness on time with a rate constant given by

$$K_p = 0.16 \exp (-45050/RT) , \quad (550-850^\circ\text{C}) \quad (3)$$

where K_p has the units $[\text{gm}^2 \text{cm}^{-4} \text{sec}^{-1}]$, $R = 1.98719 \text{ cal}_{\text{th}} \text{mole}^{-1} \text{K}^{-1}$ and T is in $^\circ\text{K}$. Thus, the TiO_2 oxide thickness x in cm has the time dependence,

$$x = \left\{ 10^{-1.027-4923T^{-1}} \right\} t^{1/2} \quad (4)$$

where time t is in seconds. This equation indicates that temperatures of $\sim 1000^\circ\text{C}$ are needed to form a $1 \mu\text{m}$ thick oxide layer in 10^3 sec , whereas an oxide layer of $10\text{\AA}$ forms at only 385°C in the same time. Although a water-cooled sputtering target remains within a few degrees of the coolant temperature during sputtering, the temperature at the sputtering collision site can reach a significant fraction of the melting point. Therefore, it can be anticipated that the oxidation rate in an oxygen-containing plasma is partly diffusion controlled, in spite of the finite sputtering process.

THE REACTIVE SPUTTER-OXIDATION MODELS

The first quantitative analysis of the oxidation phenomena was advanced by Greiner, who investigated rf sputter etching in oxygen.(19) The basis of Greiner's theory is the assumption that the sputtering and oxidation rates are independent and concurrent. The rate of change of oxide thickness on the target, dx/dt , is then

$$\frac{dx}{dt} = R_{\text{ox}} - R_{\text{sp}} \quad (5)$$

where R_{ox} is the oxidation rate, and R_{sp} is the sputter rate of the target phase. In this model, Greiner invokes two assumptions. First the oxide thickness follows a logarithmic time dependence given by $x = x_0 + k \ln t$, and second, the sputter etch rate, R_{sp} , is constant. Consequently

$$R_{ox} = K e^{-x/x_o} \quad (6)$$

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

$$\left(\frac{dx}{dt}\right)_{total} = K e^{-x/x_o} - R_{sp} \quad (7)$$

This differential equation has the integral form,

$$x = x_o \ln \left[\frac{K}{R_{sp}} - \left(\frac{K}{R_{sp}} - e^{x_i/x_o} \right) e^{-R_{sp} t/x_o} \right], \quad (8)$$

where x_i is the oxide thickness at time $t = 0$. This equation has a transient time constant x_o/R_{sp} and a steady state limit given by

$$\lim_{t \rightarrow \infty} x = x_o \ln (K/R_{sp}) \quad (9)$$

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_o/R_{sp} .

In a more recent model, Heller presented an analysis of the results of his work on reactively sputtering metals in oxidizing atmospheres.⁽²⁰⁾ Heller found the existence of a critical oxygen partial pressure in the plasma, $P_{O_2}^*$, below which no oxidation of the target takes place. For $P_{O_2} < P_{O_2}^*$, the sputter rate exceeded the oxidation rate and no oxide layer formed on the target. For $P_{O_2} > P_{O_2}^*$, 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.

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

$$R_{ox} = \frac{A(P)}{\rho} e^{-x/x_o} \quad (10)$$

where the parameter $A(P)$ is a pressure-dependent function and ρ 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 $x \rightarrow \infty$, i.e.,

$$\left(\frac{dx}{dt}\right)_{sp} = R_{sp} = R_{sp,o} + (R_{sp,m} - R_{sp,o})e^{-x/x_o} \quad (11)$$

where $R_{sp,o}$ and $R_{sp,m}$ are the sputtering rates of target oxide and metallic Ti, respectively. This model was tested in a second paper by Greiner who obtained sufficient data to determine the unknown parameters of the model.⁽²¹⁾

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.⁽²²⁾

EXPERIMENTAL

rf SPUTTERING APPARATUS

The experimental equipment consisted of modular 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. (15.2 cm) diffusion pump with a pumping speed of 2400 liters-air/sec, a Welch liquid nitrogen cold trap and a 7 liters-air/sec centrifugal roughing pump. This system, shown in Fig. 3, could achieve an ultimate pressure below 10^{-7} torr* (1.3×10^{-5} Pa).

Chamber pressure was monitored simultaneously by a Pirani GP-310 gauge for pressures below 0.1 torr and an Autovac Type 3294-B gauge for pressures in the range from 1 millitorr to 1000 torr. The main purpose of the dual meter system was to eliminate errors due to meter fluctuations after calibration.

The O_2 flow was controlled and monitored by means of a micro-flowmeter capable of measuring flow rates between 0.2 and 15 ml/min. The oxygen was mixed with Ti-getter purified argon stream and passed through a Hastings-Raydist mass flowmeter, where the total gas flow, and, by difference, the argon flow rate were measured.

The maximum volumetric gas flow through the chamber 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 O_2 volume fraction attainable was 0.0013. The volume fraction of O_2 is identical to the mole fraction at the low chamber pressures involved (25 millitorr).

A calculation of the amount of O_2 removed from the plasma during the deposition of stoichiometric TiO_2 film indicates that negligible oxygen partial pressure change occurs by the deposition reaction. Only

*1 torr = 133.3224 Pa

1.3% of the total gaseous O_2 would be entrained at an oxygen plasma mole fraction of 0.007 provided that the maximum gas flow rate is maintained.

MATERIALS

Titanium targets 6 in. (15.2 cm) in diameter were fashioned from 0.032 in. (0.081 cm) thick sheet metal.* The purity was assayed at 99.9% and the results of a spectrographic analysis indicated that iron was the only significant impurity (.1%). 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: microscope slides for thickness measurements, microscope cover slides for weight change measurements, and type 10 quartz plate for electron diffraction, optical and electrical measurements. The quartz plates were precut into 1.3x1.3 cm squares for electron microscopy and spectrophotometric analyses. High optical quality substrates were essential in order to obtain reliable uv spectra.

PROCEDURE

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. A minimum deposition time of 30 min² was chosen for this series to generate films sufficiently thick for characterization purposes.

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.

Following reactive sputtering, substrate specimens were examined by reflection electron microscopy to determine their structure. 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 metallic and semi-metallic films.

* Continental Metals, North Hollywood, CA.

The target oxidation phenomenon was studied by the following procedure. The target was first sputter-etched of all surface oxide in Ar. Then O_2 and Ar were simultaneously admitted at a given oxygen mole fraction y for a measured time interval. The O_2 flow was then shut off and the target again sputter-etched in Ar. The etch time was recorded.

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.

RESULTS

The titanium oxide films deposited under various conditions were characterized to determine the effects of reactive sputtering variables on the physical, optical and electrical properties of deposited films and to determine reactive sputtering rate kinetics.

DEPOSITION RATES

A significant transition in density and deposition rate was observed at an oxygen mole fraction $y^* = 0.007$, as shown in Fig. 4. Deposition rates and film densities were independent of y for $y > y^*$. Deposition rate data showed a sharp decrease by an order of magnitude as y increased above y^* , as shown in Fig. 4. The significance of these results becomes apparent when one contemplates the conditions needed to deposit films 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 processing rates.

PHYSICAL PROPERTIES

Films were found to etch rapidly in concentrated HNO_3 . The rapid etching characteristics of reactively sputtered TiO_x films with $x < 2$ suggests that the films are amorphous. This assumption was born out by electron microscopy studies, using a Hitachi HU-125 operated at 100 keV. Figure 5 shows the radial dependence of the photodensity of a typical film which demonstrates the amorphous structure of the films. The Au coating was applied by evaporation on the films to prevent electrostatic charging, but too thick a layer interfered with the reflection pattern. The photodensitometric effect of the 50Å Au film was subtracted from the composite pattern to yield the TiO_x diffraction pattern alone.

The density of reactively sputter-deposited films was determined from weight change and thickness measurements. The results are shown in Table 1. A significant increase in film density occurred for y near y^* . 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 $y (< 0.002)$ were metallic and showed some visible absorbance while films deposited at $y = 0.02$ possessed a slight gold tint. From optical data it was inferred that the yellow-gold colored samples were TiO .

The uv spectra of deposited films show an absorption edge at about 330 nm. These spectra are shown in Fig. 6 and correspond to a band gap of 3.76 eV for TiO_2 .

TARGET OXIDATION-ETCH RATES

Target oxidation at different oxygen partial pressures was studied by exposing the target to the reactive gas mixture for a fixed time, then measuring the etching time to remove the oxide. The experimentally measured oxidation and etch times are shown in Table 2.

DISCUSSION

The phase diagram for the Ti - O system shown in Fig. 1 indicates that the anatase phase of TiO_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. A heat transfer calculation showed that the substrate surface temperatures was 20.3°C. In order to deposit a crystalline phase, it will be necessary to provide an external 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.

Film physical properties exhibited a strong dependence on the state of target oxidation. In particular, film density followed the trend shown by the deposition rate with increasing y . An obvious transition at y^* was again found, 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 .

Lakshmanan reports spectra for TiO_2 reactively deposited in pure O_2 remarkably similar both in shape and value to that shown in Fig. 6. The band gap energy of 3.65 eV which he reports agrees quite closely with the value of 3.76 eV obtained in this study for amorphous TiO_2 . (23)

The spectrum for the sample deposited at $y = 0.02$ shows low absorption throughout the uv range, probably for 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 Magnell 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 .

The films deposited with $y = 0.035$ were found to give less uv absorbance than did films deposited at $y = 0.05$ or $y = 0.10$. Because no target etching was performed before each successive deposition of these samples, the oxidation state of the target should have affected the amount of oxygen incorporated into successively deposited films. This hysteresis effect is evident in experimental data.

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 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 8 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. 8. A low sputter yield is expected for the highly stable phases Ti_2O_3 and Ti_3O_4 .

Fig. 7 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 Ti_2O_3 or Ti_3O_4 on the target surface. The dashed line tangent to the curve for $y > 0.03$ delineates the approximate increase in 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 somewhat in contradiction to models for the reactive sputter-oxidation process which predicts that the oxide thickness is proportional to $\ln(KR_{\text{sp}}^{-1})$, unless different phases form on the target, each with different values of K and R_{sp} .

The dependence of the deposition rate on y was found to exhibit an order-of-magnitude decrease in the deposition rate occurs near y^* . Part of the rise in target oxide etch time depicted in Fig. 7 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-etch 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 if the sputtering process removed individual atoms from the target, since the Ti - Ti bond energy is 112.6 kcal/mole compared to a Ti - O bond energy of 157 kcal/mole⁽²⁴⁾ and since the sputter yield should vary with the square root of the atom binding energy. Thus, molecular groups such as TiO and TiO_2 are probably removed from the target during reactive sputtering at high values of y_{O_2} .

The transient growth of oxide on the Ti target in an Ar/ O_2 plasma for which $y_{O_2} = 0.014 = 2y^*$ 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 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) and (8). The experimental data was found not to show a parabolic oxidation rate as would be required by diffusion controlled kinetics. On the other hand, the time constant for the exponential time dependence of the reactive sputter-oxidation model, Eq. (8), was found to be

$$KR_{sp}^{-1} = 67 \pm 11. \quad (20)$$

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 for the anodic oxidation theory was $x_o = 32 \text{ Å}$. This data is in qualitative agreement with the reactive sputter-oxidation model, with significant deviations at short sputter-oxidation times.

CONCLUSION

This study of the reactive sputter deposition rates of titanium oxides showed that amorphous films were deposited at room temperature over the entire range of oxygen mole fractions studied. Deposited films were generally metallic αTi for oxygen mole fractions $y < 0.002$, and dielectric TiO_2 for $y > 0.035$. A sharp transition in deposition rate took place at $y^* = 0.007$, where TiO is deposited, and corresponded to the onset of oxidation of the titanium target.

Models describing the target oxidation phenomenon were tested against experimental data. The dependence of the target oxidation rate on oxygen mole fraction indicated that the target oxidation process is influenced by oxygen-atom incorporation in the target and by sputter etching of the target oxide by oxygen ions. The time dependence of the target oxidation process cannot be described by a parabolic time dependence. The reactive sputter-oxidation model is in qualitative agreement with the experimental data.

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Table 1. Reactively sputter deposited titanium oxide film densities.

Film Phase	Plasma Composition	ρ (gm/cc)
Ti	$y = 0$	2.05
TiO	$y \leq y^*$	~5
TiO _x , $x \lesssim 2$	$y \gg y^*$	3.9

Table 2. Experimentally measured plasma oxidation and etch times and power settings at different plasma O_2 concentrations.

y (Mole Fraction)	O_2 Exposure Time (sec)	Time to Start of Color Change (sec)	Time to Etch Target (sec)
0.007	180	105	182
0.007	300	138	178
0.008	80	55	468
0.008	100	37	465
0.008	150	55	416
0.014	80	35	245
0.014	100	25	364
0.014	120	22	320
0.014	120	20	321
0.014	150	20	390
0.014	200	18	360
0.014	250	22	400
0.022	100	20	174
0.022	150	12	162
0.022	200	12	164
0.040	82	5	284
0.040	100	5	250
0.064	15	3	170
0.064	60	3	211
0.064	100	3	235
0.175	80	15	112
0.175	80	13	180
0.175	100	18	216
0.175	150	15	288
0.027	100	10	199
0.033	100	10	199

XBL 746-6495

Fig. 1. Low temperature condensed phase diagram for the Ti-O system. The Magneli phases have the form $\text{Ti}_n\text{O}_{2n-1}$ where $n = 4, 5, 6, \dots \infty$.

XBL 746-6607

Fig. 2. Stability ranges of titanium oxides as a function of reciprocal temperature and oxygen fugacity.

XBL746-6496

Fig. 3. RF sputtering system and ancillary apparatus.

Fig. 4. TiO_x film deposition rate vs O_2 mole fraction in the plasma.

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- (a) Reflection electron diffraction pattern from reactively sputtered TiO_2 .

XBB 746-4100

- (b) Photodensitometer trace for an Au-coated TiO_2 film.

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- (c) Photodensitometer trace calculated for the TiO_2 film without the Au reflections.

XBL 746-6612

Fig. 5. Reflection electron diffraction of a TiO_2 film.

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Fig. 6. UV spectrograph of TiO₂ thin films deposited at several oxygen plasma conditions.

Fig. 7. Target etch time following target oxidation
as a function of y_{O_2} .

XBL746-6494

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