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Effect of Target Oxidation on Reactive Sputtering Rates of
Titanium in Argon-Oxygen Plasmas

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Abstract

Reactive sputtering rates of titanium in argon-oxygen plasmas are studied as a function of oxygen and argon partial pressures. The sputtering rate changes by an order of magnitude at a critical oxygen mole fraction in the plasma equal to 0.0070. This transition corresponds to the onset of target oxidation. The threshold for target oxidation is independent of the total plasma pressure.

Introduction

The reactive sputtering of titanium is an important industrial process used for the preparation of dielectric films for optical and electronic applications.¹⁻² The reactive sputtering process is carried out in an inert gas plasma containing a partial pressure of a reactive gas such as oxygen or nitrogen. An important problem with this process is that the sputtering target can be oxidized by the reactive gas. As a consequence of target oxidation, significant transients can occur in reactive sputter rate processes and also in the stoichiometry of the deposited compound film. It is important to establish the criteria for the onset of target oxidation and its effect on rate processes for the optimal design of industrial reactive sputtering processes. In this study, the factors determining the onset of target oxidation are explored for r.f. sputtering of titanium in an argon-oxygen plasma.

Step-like transitions in reactive sputtering rates of metals have been reported in several earlier studies of reactive sputtering.³⁻⁶ Stirling and Westwood found a transition in the sputtering rates of aluminum in an argon-oxygen plasma which was closely related to a chemical surface reaction on the aluminum target.⁵ Heller performed similar experiments to determine the target oxidation threshold for the reactive sputtering of iron, cobalt and silver in an argon-oxygen plasma.⁶

Hiller has proposed that the target oxidation effect should occur at a critical partial pressure of the oxidizing component,

the target oxidation rate exceeding the sputtering rate for reactant partial pressures above this critical value. Although the criterion -- that the oxidation rate should exceed the sputter etch rate for target oxidation -- is intuitively valid, it is anticipated that the reactant mole fraction rather than its partial pressure should be the controlling process variable. In addition to pressure effects, the materials properties of the target metal and its oxide, as well as the sputtering energy density, should contribute to the criterion for the onset of target oxidation.

Mechanisms of Target Oxidations

The oxidation of metallic targets during reactive sputtering can occur by several mechanisms involving collision of oxygen species from the plasma with the target, or by chemisorption of oxygen followed by an oxidation reaction. Schroen examined the physics of the oxidation process during plasma anodization, and presented a molecular model for the reaction.⁷ The initially neutral substrate is raised to a negative potential by the mobile plasma electrons. This negative potential attracts O_2^+ oxygen ions as well as A_r^+ ions to the target surface. The O_2^+ 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 quantifying formulae. O'Hanlon reviewed plasma anodization mechanisms, and presented a model very similar to Schroen's.⁸ O'Hanlon proposed an addition mechanism to that of Schroen: O_2^+ ions

originating in the plasma are accelerated by the bias field and implanted directly into the target. This model is supported by measurements of Whitlock and Bounden⁹ and by Thompson¹⁰ who were unable to detect any measurable negative ion current density in the negative glow of an oxygen discharge. The target oxidation mechanism proposed by Greiner is similar, involving incorporation of atomic oxygen in the oxide during rf sputtering, followed by diffusion to the metal-oxide interface.¹¹ Notwithstanding the efforts to arrive at a quantitative model for 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.¹²

The rate of target oxidation by either of these mechanisms is

$$R_{ox} = \alpha_{O_2^+} N_{O_2^+} \quad (1)$$

where $N_{O_2^+}$ is the flux of the species O_2^+ , to the target and $\alpha_{O_2^+}$ is the oxidation probability, provided that the process of O_2^+ collision with the target surface is rate controlling. The partial pressure of O_2^+ should be proportional to the concentration of oxygen in the plasma, since the degree of ionization is known to be small.

The rate of sputter etching of the target can be represented by

$$R_{sp} = N_{Ar^+} S_{Ar^+} + N_{O_2^+} S_{O_2^+} \quad (2)$$

where $N_{A_r}^+$ is the argon flux to the target surface, here taking into account both charged and uncharged species, and S_i is the sputter yield of species i . According to the theory of Sigmund,¹³ S_i is inversely proportional to E_b , the target surface binding energy, and proportional to the molecular weight of the sputtering ion. The experimental work of Almén and Bruce¹⁴ and of Rosenberg and Wehner¹⁵ show that E_b can be assigned a value equal to the heat of vaporization for the target metal, and to the heat of atomization of its oxide.

The onset of target oxidation occurs when the sputtering rate and oxidation rate are equal. Equating Eqs. (1) and (2) then gives

$$\frac{S_{A_r}}{\alpha_{O_2}^+} = \frac{N_{O_2}^+}{N_{A_r}^+ + N_{O_2}^+ g\left(\frac{M_{O_2}^+}{M_{A_r}^+}\right)} \approx \frac{P_{O_2}}{P_{Ar} + 0.81 P_{O_2}} \quad (3)$$

where g is a function of the molecular weights of O_2^+ and A_r^+ , which is approximately equal to $M_{O_2}^+/M_{A_r}^+$, or 0.801. Therefore, the onset of target oxidation corresponds to a constant partial oxygen flux to the surface. It can be expected that pressure effects and sputtering ion energies contribute to the threshold for target oxidation by affecting the fluxes of O_2^+ and A_r^+ ions, and neutral species, to the target surface.

Experimental

The sputtering apparatus used in this study was a diode sputtering system attached to an oil diffusion-pumped vacuum system

consisting of an NRC series VHS 6-in. diffusion pump, a Welch liquid nitrogen cold trap and a Welch 7 liters air/sec centrifical roughing pump. This system could achieve an ultimate pressure below 10^{-7} mm Hg, with a maximum argon flow rate of 150 S.T.P. ml/min.

The chamber pressure was monitored simultaneously by a Pirani GP-310 Gauge (range 0-100 millitorr Hg and 100 millitorr to 1 atm). The flow rates of oxygen and argon were controlled by pressure regulators and microflowmeters. The oxygen flow-meter was capable of metering flow rates between 0.2 and 15 ml/min. A titanium gettering furnace operated at 850°C was used to remove oxygen impurities from the high purity argon gas. 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.

Results

The bias voltage was maintained at 2 keV for all experiments. Film deposition experiments were conducted using optical-grade quartz and thin glass slides as substrates. The film deposition rate was measured by the weight gained by the substrate as a consequence of sputtering for a fixed period of time, up to 30 min. The dependence of the deposition rate as a function of plasma oxygen mole fraction for a total plasma pressure of 25 mtorr is shown in Fig. 1. The critical mole fraction required for the detection of oxidation products on the target is denoted by $y_{O_2}^*$. For oxygen mole fractions greater than $y_{O_2}^*$, the deposition rate and film properties were invariant

with y_{O_2} , which allows easy control of the reactive sputtering process, whereas for $y_{O_2} < y_{O_2}^*$ the rate varied markedly with y_{O_2} .

The onset of target oxidation could be established quite clearly from a number of indications. The plasma color while sputtering Ti in pure argon under non-reactive conditions was deep blue. Once an oxide layer formed on the target, the color became pink, attributable to intermediate oxide species such as TiO present in the plasma, or to optical emission from excited O_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 decrease of as much as 30%, and the circuit impedance mismatch increased, resulting in an increase in reflected power. The effect of the oxide layer formed on the target surface was to interpose 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 Fig. 2, which shows the plasma intensity in the pink spectral range, the rf forward power, and the dc bias voltages versus time following the admission of oxygen into, or removal from, the plasma, for $y_{O_2} \geq y_{O_2}^*$. The effect of oxidation on system parameters for $y_{O_2} \approx 15 y_{O_2}^*$ is shown in Fig. 3. The transitions are significantly slower than for $y_{O_2} \geq y_{O_2}^*$. The clear transition of each experimental variable indicates a basic change in the oxidation state of the target. The oxidation of the target above the threshold was confirmed by removing the target from the sputtering chamber for visual inspection and surface conductivity measurements with a 4-point conductivity probe. The pressure dependence of the critical oxygen mole fraction in the

plasma required for onset of target oxidation was studied by varying the oxygen flow rate to the sputtering chamber at fixed values of the argon flow rate. The total system pressure was limited to the range between 5 and 30 mtorr because of power matching problems. Before each experiment the target surface was etched in pure argon for a period, typically 10 min., sufficient to produce the characteristic spectral color of an oxygen-free plasma. A given oxygen flow rate was then turned on and changes in plasma color, bias voltage and reflected power were observed. The critical mole fraction and partial pressure of oxygen were then obtained by extrapolating the magnitude of the operating parameter changes to zero. These results are shown in Fig. 4. It was found that the measured critical mole fraction, $y_{O_2}^*$, was independent of total system pressure, whereas the oxygen partial pressure varied linearly with total pressure. The critical plasma oxygen mole fraction was found to be 0.0070.

Reactively sputtered films were produced for oxygen mole fractions in the range from 0 to 0.15. A total sputtering pressure of 25 mtorr produced the optimal power match. This pressure corresponds to a mean-free path of 0.45 cm, and is near, but less than, the ground shield spacing of 0.5 cm.

The sputtered films were characterized by reflection electron microscopy, electrical conductivity and uv-visible spectroscopy. All the films sputtered at room temperature were amorphous. The density of sputtered films followed closely the trend found in the sputtering rate dependence on oxygen mole fraction, with an obvious

transition at $y = y^*$. The sputtered film density was independent of y for $y > y^*$. In this range of y the band gap energy of 3.65 eV was found for sputtered films, which is close to the value found by Lakshmanan for TiO_2 .⁽¹⁶⁾

Discussion

An order of magnitude change in sputtering rate was found to occur at a critical plasma-oxygen mole fraction $y_{O_2}^*$ equal to 0.0070. This transition in rate was confirmed to correspond to the onset of oxidation of the target surface. The reactive sputtering rate declined as the oxygen mole fraction was varied from 0.3 $y_{O_2}^*$ to 1.3 $y_{O_2}^*$, indicating a continuous change in the stoichiometry of the amorphous TiO_x oxide layer on the target.

The critical oxygen partial pressure of 0.0070 can be substituted into Eq. 3 to determine the approximate relation between the argon sputtering rate and the oxidation probability. The derived relation is

$$S_{Ar}^+ \approx .007 \alpha_{O_2}^+ \quad (4)$$

This results indicates that bound oxygen is not sputtered with the same sputter yield as is titanium on the target surface.

The experimental results showed that the critical oxygen mole fraction $y_{O_2}^*$, was independent of the total plasma pressure, whereas the critical oxygen partial pressure increased linearly with total system pressure. This result is in agreement with the theoretical

model presented above, which predicts that the onset of target oxidation corresponds to a constant partial oxygen flux to the target surface. The theoretical model is limited to the pressure range where $P_{O_2} \ll P_{Ar}$, which is satisfied by the experimental conditions.

The target oxidation effect has an impact on industrial, reactive sputtering processes. In the preparation of thin-film capacitors by the reactive sputtering of titanium, a layer of metallic titanium is deposited, followed by a layer of TiO_2 .¹⁶ When the plasma gas is changed from pure argon to an argon-oxygen mixture, an order of magnitude change in sputtering rate takes place gradually as y_{O_2} increases. As a consequence, the stoichiometry of the deposited material can vary with thickness unless the target is shielded during the gas-exchange process.

An important result of this study is that the reactive sputter deposition of TiO_2 can be achieved with as an argon plasma containing oxygen mole fractions in excess of 0.0070. The fact that the sputter deposition rate is independent of y_{O_2} in the range $0.09 \leq y_{O_2} \leq .15$ indicates that TiO_2 films can be sputter deposited without precise control of the reactive gas composition.

Acknowledgment

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List of Figures

- Fig. 1. Deposition rate of TiO_x films by r.f. reactive sputtering of Ti in argon as a function of the oxygen mole fraction in the plasma. The total system pressure is 25 mtorr, and the forward power density is 2.7 watt/cm^2 .
- Fig. 2. Changes in observable parameters during reactive sputtering during target oxidation with $y_{\text{O}_2} \approx 1.4 y_{\text{O}_2}^*$, and during target-oxide reduction in pure argon.
- Fig. 3. Change in observable system parameters during target oxidation with $y_{\text{O}_2} \approx 15 y_{\text{O}_2}^*$, and during reduction of the target oxide in pure argon.
- Fig. 4. Dependence of the critical threshold oxygen mole fraction and partial pressure in the argon plasma required for target oxidation, as a function of total system pressure.

Fig. 1.

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Fig. 2.

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Fig. 3.

Fig. 4.

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