

Lawrence Berkeley National Laboratory

Recent Work

Title

EFFECT OF TARGET OXIDATION ON REACTIVE SPUTTERING RATES OF TITANIUM IN ARGON-OXYGEN PLASMAS

Permalink

<https://escholarship.org/uc/item/6qz5t9j0>

Author

Geraghty, Kenneth G.

Publication Date

1976-03-01

0 0 0 0 4 3 0 0 2 3 7

Submitted to Thin Solid Films

LBL-4110 Rev.
Preprint c.1

EFFECT OF TARGET OXIDATION ON REACTIVE SPUTTERING
RATES OF TITANIUM IN ARGON-OXYGEN PLASMAS

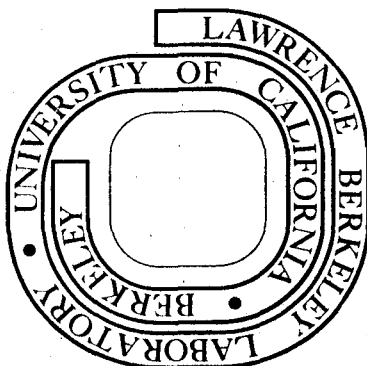
Kenneth G. Geraghty and Lee F. Donaghey

March 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-4110 Rev.
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-4110

REVISED

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

Kenneth G. Geraghty^{*} and Lee F. Donaghey

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering, University of California,
Berkeley, California 94720

March, 1976

Abstract

Reactive sputtering rates of titanium in argon-oxygen plasmas were studied as a function of oxygen and argon partial pressures in an rf diode sputtering system at 2 keV bias voltage. The sputtering rate changed 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 shown to be independent of the total plasma pressure, and to be specified uniquely by a critical mole fraction of oxidant in the plasma.

[†]This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the authors and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

^{*}Current address: General Dynamics/Pomona Division, Pomona, Calif. 91766.

Introduction

Reactive sputtering is an important industrial process used for the preparation of dielectric films for optical and electronic applications.¹⁻² The reactive sputtering process involves the sputtering of a target material in a plasma containing a partial pressure of a reactive gas such as oxygen. 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 of titanium are explored during r.f. sputtering 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

Heller has proposed that the target oxidation effect should occur at a critical partial pressure of the oxidizing component for which

the target oxidation rate equals the sputtering rate of the target by the reactive plasma. Although the criterion -- that the oxidation rate should exceed the sputter etch rate for target oxidation -- is intuitively valid, it was anticipated by the authors the reactant mole fraction rather than its partial pressure should be the controlling process variable. In particular, it is the relative rates of oxide formation and removal which are important in establishing a target oxidation threshold. The oxidation rate is of course controlled by the rate at which oxygen is made available to the target, whereas the sputtering rate is controlled by the sputtering conditions. Therefore, in addition to plasma partial pressure effects, the materials properties of the target metal and of its oxides, as well as the sputtering energy density should also contribute to the criterion for the onset of target oxidation. In this study, the plasma partial pressure dependence of the criterion are examined in detail at a constant bias potential, with other sputtering conditions held constant.

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 additional mechanism, namely, that 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 These conditions apply to the low range of sputtering energies below 5 keV, whereas at higher energies the sputtering yield also depends on the atomic numbers of the sputtering and target atoms.¹³

Actually, certain differences in target oxidation mechanisms of the two processes can be expected because the plasma anodization

process is carried out under conditions which are distinctly different from those of reactive sputtering. A significant difference is that the voltage developed on the target during reactive sputtering is much higher than for plasma anodization. Also, during plasma anodization the target surface is separated from the negative glow by an ion sheet which is short compared to the mean free path, whereas this is not so for reactive sputtering. Nevertheless, the target oxidation rate for both processes should be proportional to the flux of oxygen-containing species reaching metal target such as titanium because of the high reactivity of metallic titanium.

The rate of target oxidation by either of these mechanisms is

$$R_{\text{ox}} = \alpha_{\text{O}_2} N_{\text{O}_2} \quad (1)$$

where N_{O_2} is the flux of the neutral and charged species of O_2 toward the target and α_{O_2} is the oxidation probability, provided that the process of O_2 chemisorption on the target surface is rate controlling. The partial pressure of O_2 in the plasma should be the same as the concentration of oxygen entering the chamber, since the rate of the oxidation reaction is small compared to the flow rate.

The rate of sputter etching of the target by argon and oxygen species can be represented by

$$R_{\text{sp}} = N_{\text{Ar}} S_{\text{Ar}} + N_{\text{O}_2} S_{\text{O}_2} \quad (2)$$

where N_{Ar} 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,¹⁴ 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 Bruce¹⁵ and of Rosenberg and Wehner¹⁶ 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

$$\frac{S_{Ar}}{\alpha_{O_2}} = \frac{N_{O_2}}{N_{Ar} + N_{O_2} \left(S_{O_2} / S_{Ar} \right)} \approx \frac{P_{O_2}}{P_{Ar} + \beta P_{O_2}} \quad (3)$$

where β is the ratio of sputtering yields of T_i by O_2 to that by Ar , and is a function of the molecular weights of O_2 and Ar . For sputtering energies in the low keV range, Sigmund's theory as modified by Nghi and Kelly^{17,18} leads to the value

$$\beta = 1.02 \frac{\alpha(0.83)}{\alpha(0.665)} = 1.27 . \quad (4)$$

Alternately, on the basis of simple sputtering theory where β is equal to the molecular weight ratio we have

$$\beta = \frac{M_{O_2}}{M_{Ar}} = 0.801 . \quad (5)$$

Therefore, we can conclude that β is nearly unity. The actual value of β should differ from the above approximate value since simple sputtering theory should not hold for multi-element targets. However, the above approximation should not give significant error when $P_{\text{Ar}} \gg P_{\text{O}_2}$.

From Eq. 3 it can be anticipated that 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 Ar 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.¹⁹ This system could achieve an ultimate pressure below 10^{-7} torr* with a maximum argon flow rate of 150 S.T.P. ml/min. The sputtering target was a water-cooled, titanium disk 15.24 cm (6 inch) in diameter.** The titanium purity was 99.95% with Fe the major impurity.

The chamber pressure was monitored simultaneously by a Pirani GP-310 Gauge (ranges 0-100 mtorr and 100 mtorr to 760 torr). The flow rates of oxygen and argon were controlled by pressure regulators and microflowmeters in a metering system shown in Fig. 1.

* 1 torr = 133.322 Pa .

**Continental Metals, North Hollywood, CA.

The oxygen flow-meter was capable of metering flow rates between 0.2 and 15 ml/min. 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 greater than 7 μm in diameter, which might have obstructed flow through the needle valve. The oxygen was mixed with the argon stream and passed through a Hastings-Raydist mass flow meter, where the total gas flow and, by difference, the argon flow rate were measured. Following 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 O_2 line, except that the tank regulator sufficed to control delivery pressure; there was no microflowmeter in this line. The Ar gas was certified by the supplier as 99.998% pure. A titanium gettering furnace operated at 850°C was used to remove oxygen impurities from the high purity argon gas. The bias voltage was maintained at 2 keV for all experiments. Reactively sputtered films were produced for oxygen mole fractions in the range from 0 to 0.15. The total system pressure was limited to the range between

5 and 30 mtorr because of power matching problems. A total sputtering pressure of 25 mtorr produced the optimal power match. This pressure corresponds to a calculated mean-free path of 0.45 cm, and is nearly equal to, but less than, the ground shield spacing of 0.5 cm.

Film deposition experiments were conducted using optical-grade quartz and thin cover-glass slides as substrates. The film deposition rate was measured by masking part of the substrate during the sputtering period, then measuring the height of the step produced by the deposit with a Tally-Serf Analyzer. This method of measurement had an absolute accuracy of about $\pm 5\%$. The density, optical spectra and electron diffraction characteristics of sputter deposited films were also measured, and those properties are reported elsewhere.²⁰

Results

Film deposition experiments were conducted using optical-grade quartz and thin glass slides as substrates. The film deposition rate was measured by the thickness of the film deposited on the substrate as a consequence of sputtering for a fixed period of time, typically 30 min to 2h. 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. 2. 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

-9-

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. 3, which shows the relative 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 $y_{O_2} \approx 1.4 y_{O_2}^*$. The effect of oxidation on system parameters for $y_{O_2} \approx 15 y_{O_2}^*$ is also shown in Fig. 3. The transitions are significantly slower for $y_{O_2} \gg y_{O_2}^*$ than for $y_{O_2} \approx y_{O_2}^*$. 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. 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 plotting the magnitudes of process-sensitive parameter changes against oxygen mole fraction and then extrapolating the magnitude of the 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.

The sputtered films were characterized by reflection electron microscopy, electrical conductivity and uv-visible spectroscopy. All the films sputtered at room temperature were amorphous.¹⁹ The density of sputtered films followed closely the trend found in the sputtering rate dependence on oxygen mole fraction, with an obvious transition at $y_{O_2} = y_{O_2}^*$.²⁰ The sputtered film density was independent of y_{O_2} for $y_{O_2} > y_{O_2}^*$. In this range of y_{O_2} the band gap energy of

-11-

3.76 eV was found for sputtered films, which is close to the value found by Lakshmanan (3.65 eV) for TiO_2 .²¹

Discussion

An order of magnitude change in sputtering rate was found to occur at a critical plasma-oxygen mole fraction $y_{\text{O}_2}^*$ 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 $0.3 y_{\text{O}_2}^*$ to $1.3 y_{\text{O}_2}^*$, indicating an apparently continuous change in the stoichiometry of the amorphous TiO_x oxide layer on the target, or alternately, to a gradual change in surface coverage of a stoichiometric oxide.

The critical oxygen partial pressure of 0.0070 can be substituted into Eq. 3 with $\beta \approx 0.801$ to determine the approximate relation between the argon sputtering rate and the oxidation probability. The derived relation is then

$$\alpha_{\text{O}_2} \Big|_{y_{\text{O}_2}^*} = 143 S_{\text{Ar}} . \quad (6)$$

It is possible that the low apparent sputter yield at the critical mole fraction is caused by the formation of stable titanium oxides from chemisorbed oxygen on the target surface.

The experimental results showed that the critical oxygen mole fraction $y_{\text{O}_2}^*$, 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 .²¹ 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 time 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.

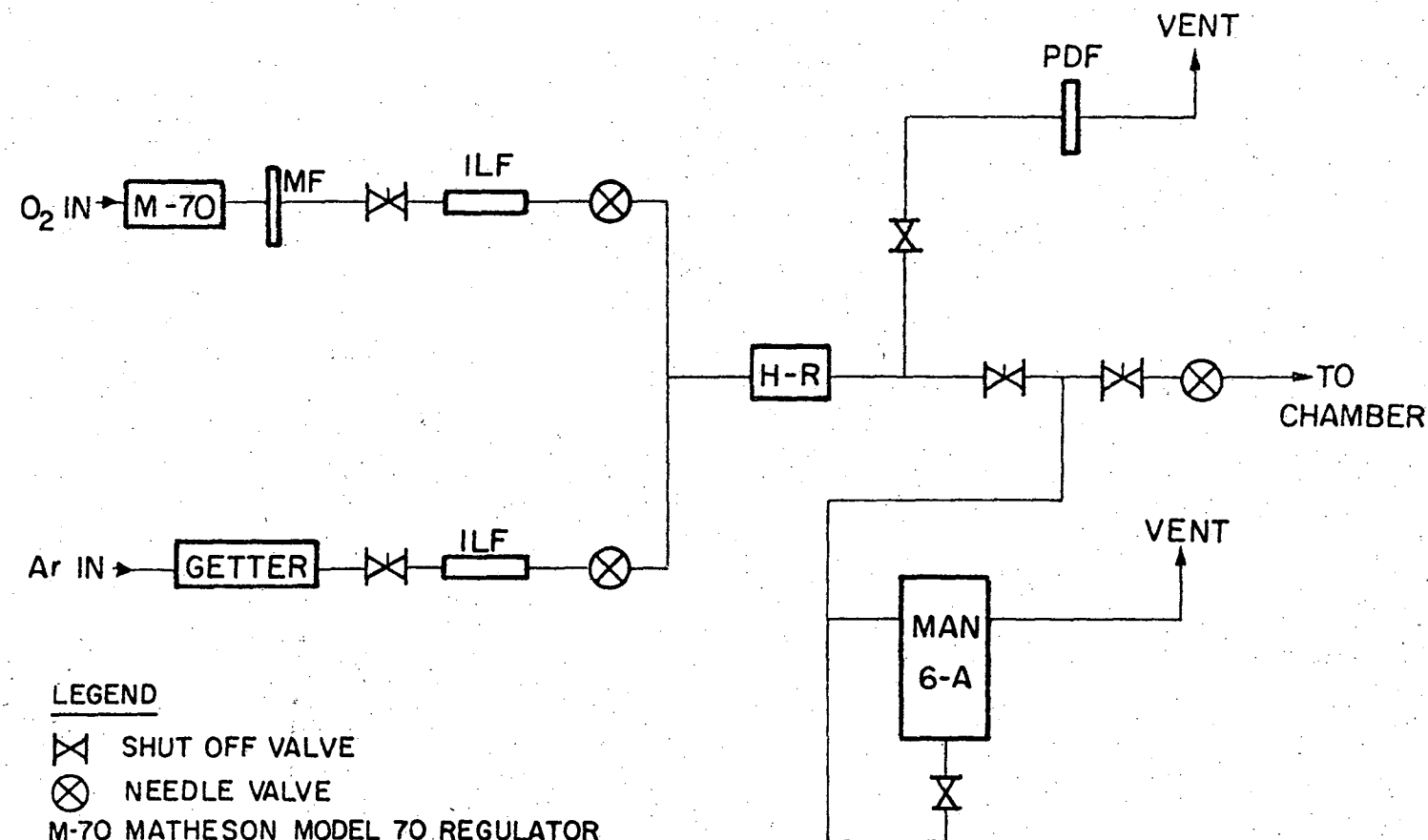
Acknowledgment

The financial support of the U.S. Energy Research and Development Administration is gratefully acknowledged.

References

1. K. Wasa and S. Hayakawa, Microelectronics and Reliability 6, 213 (1967).
2. G. Haas and A. P. Bradford, J. Optical Sci. of Amer. 47, 125 (1957).
3. R. M. Valetta, J. A. Perri and J. Riseman, Electrochem. Technol. 4, 402 (1966).
4. E. Hollands and D. S. Campbell, J. Mater. Sci. 3, 544 (1968).
5. A. J. Stirling and W. D. Westwood, Thin Solid Films 7, 1 (1971).
6. J. Heller, Thin Solid Films 17, 163 (1973).
7. W. Schroen, J. Appl. Phys. 39, 2671 (1968).
8. J. F. O'Hanlon, J. Vac. Sci. Technol. 7, 330 (1969).
9. W. S. Whitlock and J. E. Bouden, Proc. Phys. Soc. (London) 77, 845 (1961).
10. J. B. Thompson, Proc. Roy. Soc. (London) 262, 503 (1961).
11. J. H. Greiner, J. Appl. Phys. 45, 32 (1974).
12. J. D. Leslie and K. Knorr, J. Electrochem. Soc. 121, 263 (1974).
13. W. D. Davis and T. A. Vanderslice, Phys. Rev. 131, 219 (1963).
14. P. Sigmund, Phys Rev. 184, 383 (1969).
15. O. Almén and G. Bruce, Nucl. Instr. Methods 11, 257 (1961).
16. D. Rosenberg and G. K. Wehner, J. Appl. Phys. 33, 1842 (1962).
17. L. Q. Nghi and R. Kelly, Canadian J. Phys. 48, 137 (1970).
18. W. D. Westwood, R. J. Boynton and S. J. Ingrey, J. Vac. Sci. Technol. 11, 381 (1974).

19. K. G. Geraghty and L. F. Donaghey, Kinetics of the Reactive Sputter Deposition of Titanium Oxides, Proc. Conference on Chemical Vapor Deposition, The Electrochemical Society, 1975, p. 219.
20. K. G. Geraghty, Reactive Sputtering of Titanium Oxides: Target Oxidation Phenomena and Thin Film Characterization, LBL-2788, Lawrence Berkeley Laboratory, Berkeley, CA. (Sept. 1974)
21. T. K. Larshmanan and J. M. Mitchell, "Chemical Formation of Microcircuit Elements," Tech. Rept. AD 613563, March, 1965.

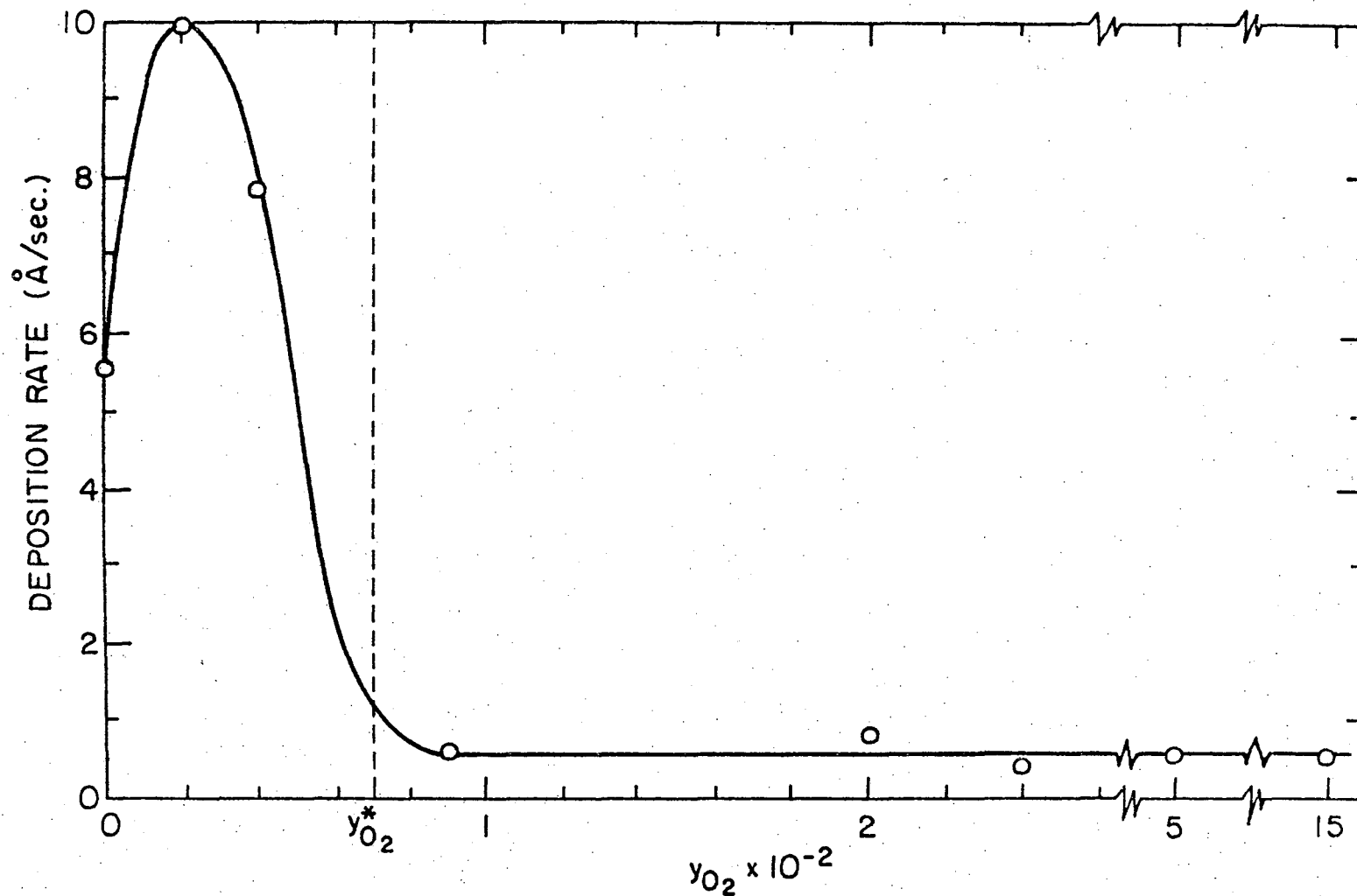


LEGEND

✕ SHUT OFF VALVE
 ⊗ NEEDLE VALVE
 M-70 MATHESON MODEL 70 REGULATOR
 GETTER TI-SPONGE OXYGEN REMOVAL FURNACE
 MF MICROFLOWMETER
 ILF IN-LINE FILTER
 H-R HASTINGS-RAYDIST MASS FLOWMETER
 MAN 6-A CARTESIAN MANOSTAT MODEL 6-A
 PDF POSITIVE DISPLACEMENT FLOWMETER

XBL746-6493

Fig. 1 Gas metering system.

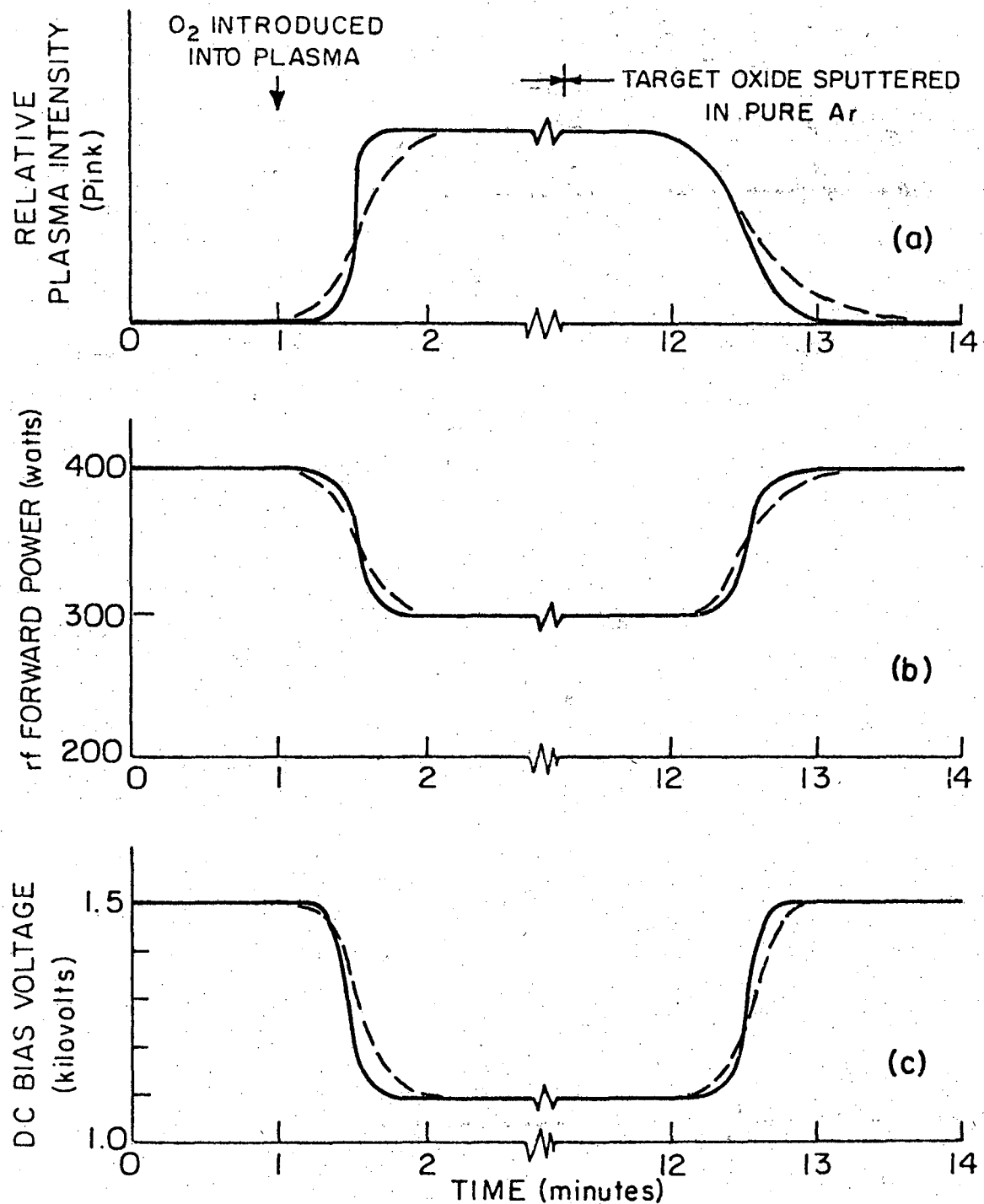


-16-

XBL 746-6485

Fig. 2 Deposition rate of TiO_x films by r.f. reactive sputtering of Ti as a function of the oxygen mole fraction in the argon-oxygen plasma, for a total system pressure of 25 mtorr and the forward power density of $2.7 \text{ watt}/\text{cm}^2$.

-17-



XBL746-6488

Fig. 3 Changes in observable parameters during reactive sputtering during target oxidation with $y_{O_2} \approx 1.4 y_{O_2}^*$ (—) and $y_{O_2} \approx 15 y_{O_2}^*$ (---), during target-oxide reduction in pure argon.

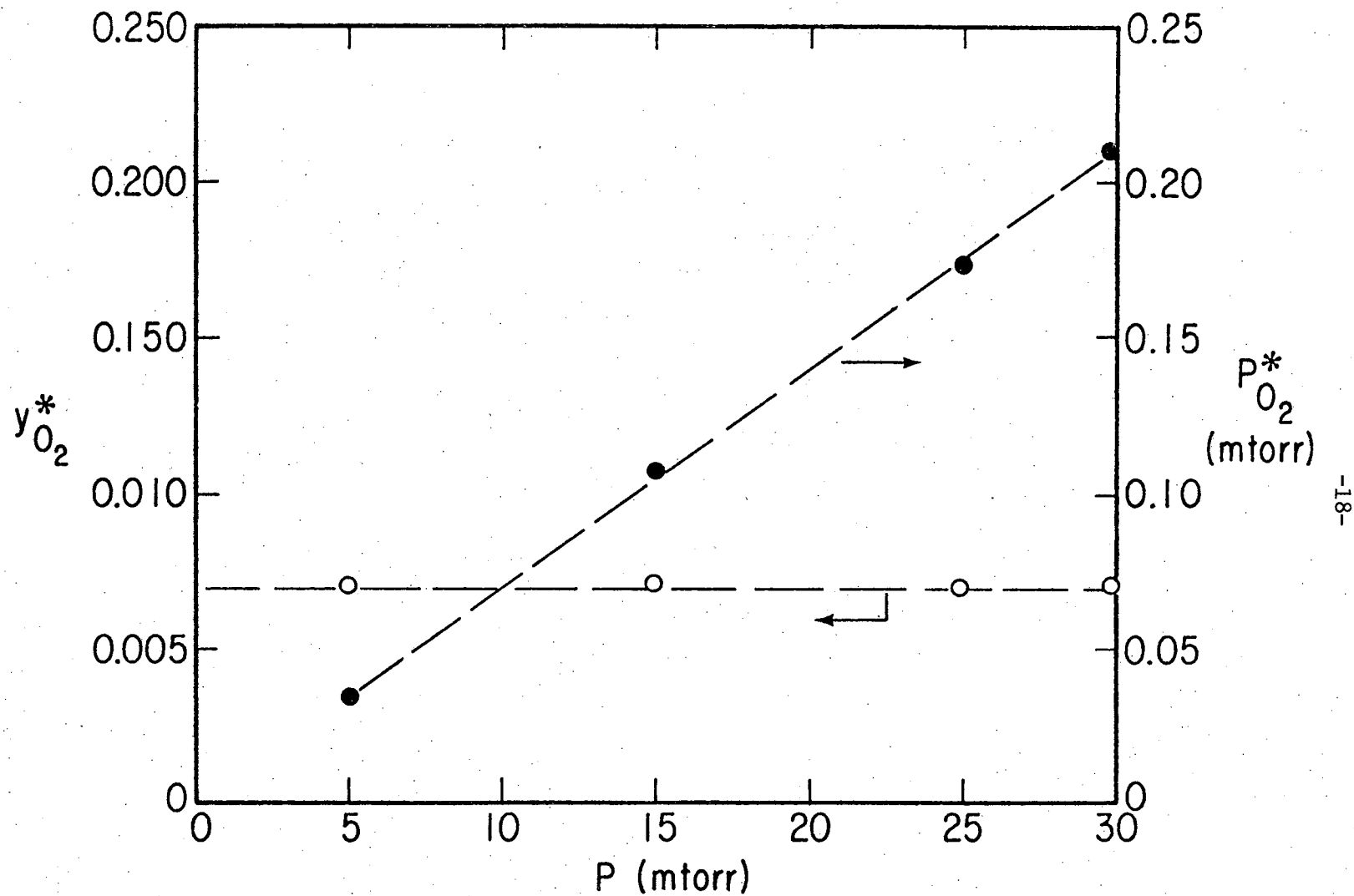


Fig. 4 Total system pressure dependence of the threshold mole fraction and partial pressure of oxygen in the argon plasma required for target oxidation.

XBL 757-6662

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720