

Vanadium reactive magnetron sputtering in mixed Ar/O₂ discharges

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Abstract

Due to the multitude of phases that may be deposited as a result of varying degrees of target poisoning, the vanadium oxygen system provides a vehicle for studying the reactive sputtering process. Examination of the consumed O₂ partial pressure, target voltage, deposition rate, and change in film composition as a function of the oxygen partial pressure, shows how the target is poisoned by oxygen. The sputtering yield for V as a function of O₂ partial pressure was measured by a novel technique that collects a known fraction of the sputtered flux. The V sputtering yields were used to help determine the O sputtering yield by an analytical model based upon the work of Berg et al. Target sputter cleaning in pure Ar and the oxidation of a partially oxidized metal surface exposed to an O₂ ambient are shown to approach completion following an exponential time dependence. The target and substrate oxidation are shown to be well simulated by a modified version of existing reactive sputtering models and give reasonable values for the sputtering yield of oxygen from the target surface. © 1997 Elsevier Science S.A.

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1. Introduction

Vanadium dioxide (VO₂) is well known for its semiconductor-to-metal transition at 67 °C with a corresponding resistivity change as large as 10⁵ in single crystals. This transformation leads to dramatic changes in optical properties such as the absorption coefficient. A wide variety of technological applications for VO₂ have been suggested such as electrical switches, holographic storage media, and thermal switches or sensors. For example, Boyle and Verleur designed a composite thin film structure including VO₂ to thermally stabilize bodies by radiant heat transfer [1]. One primary requirement for fabricating such composite optical structures is the ability to coat large-area substrates with films of uniform thickness and properties.

Reactive magnetron sputtering has been shown to permit fabrication of large-area, uniform coatings of both metallic and ceramic materials [2–4]. The process can be controlled to produce well-defined chemical compositions in the as-deposited films. With the addition of ion bombardment of the growing film, metastable compositions, improved micro-

structures, and improved conformal coverage has been achieved [5]. Thin, polycrystalline VO₂ films have been produced on glass and alumina substrates by magnetron sputtering which exhibit resistivity changes as large as a factor of 5 × 10³ with semiconducting-state resistivity comparable to that of single-crystal VO₂ films [6].

One limitation of VO₂ reactive magnetron sputtering, however, is that the target oxidation state and hence the deposited film composition can be extremely sensitive to the deposition conditions, especially the oxygen partial pressure in the sputtering gas. The binary V–O system includes a large number of phases ranging from VO_{0.3}, in which V has a mean valence between 0 and +2, to V₂O₅ where V exhibits a +5 valence. Intermediate phases include V₁₆O₃, V₉O₁₁, V₇O₁₃, VO₂, V₆O₁₃, and V₃O₇. To achieve the desired stoichiometry, VO₂, it is critical to understand the V–O reactive sputtering process in detail. Such an understanding is expected to permit, for example, modification of the deposition geometry to induce VO₂ formation in a pressure regime outside of the zone of unstable operating conditions, typically observed in reactive sputtering processes (see, for example, below). However, most published work available for vanadium–oxygen sputtering focuses on the properties of

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V_2O_5 films formed in the stable, fully-poisoned target state [7–11]. Some work has been published on the production of V–O films with lower oxidation states [12,13].

Much work has been done on the topic of reactive sputtering in order to develop a clear understanding of the target behavior [14,15]. For example, a large amount of experimental data has been acquired for other reactively-sputtered materials such as TiN [16–18]. Several models of the reactive sputtering process have been proposed including those of Berg (a steady-state analytical solution), Kusano (an iterative kinetics model), and Penfold (a generic model) [19–21]. Application of these models to the case of vanadium oxide reactive sputtering can yield the extent of target and substrate oxidation, for a given set of deposition conditions, and can aid in identifying the necessary conditions for formation of a specific oxide phase. In order to use the models it is necessary to determine the V and O sputtering yields from the target and the flux of O_2 and its sticking coefficient on the target and substrate as a function of surface chemistry.

This paper presents the results of experiments aimed at characterizing the V sputtering rate at the target as a function of O_2 fraction in the gas phase and the time constants for metallization of an oxidized surface and for sputter cleaning of an oxidized target. In addition, the changes in sputtering parameters, such as target voltage, associated with variations in the O_2 content of the sputtering gas and the rate of O consumption, are given. These are compared with predicted curves calculated using a modified form of the Berg model, which is used to extract estimates of the oxygen sticking probability.

2. Experimental

The experiments were conducted in a 31 cm diameter, high-vacuum chamber equipped with a 25 cm diameter diffusion pump with a throttled pumping speed of 230 l s^{-1} at 0.27 Pa. The system base pressure is 2×10^{-4} Pa (1×10^{-6} Torr). The chamber, shown schematically in Fig. 1, includes a 12.7 cm diameter d.c. magnetron (127 cm² target area) and a triple-gas mass-flow-control system, arranged to permit

introduction of Ar, O_2 , and N_2 (used only for venting) into the system. The total pressure is measured by an ionization gauge and, for pressures above 10^{-2} Pa, by a capacitance manometer. A quartz-crystal deposition rate monitor is used to determine the sputtered flux at the substrate as a function of deposition conditions. Analysis facilities include two optical-emission spectrometers for in-situ characterization of the plasma chemistry during deposition. In the present work, one spectrometer detected the 6965 Å Ar emission while the second monitored the 4111 Å V line. The Ar emission signal served as a standard, for a given Ar/ O_2 mixture, against which the V emission was compared. The ratio of the two emission signals is related to the partial pressure of V in the discharge which, in turn, is determined by the V sputtering rate.

For experiments measuring the oxygen reaction rates and wall metallization times, the area of the metal reacting to form oxide or the area to be metallized must be well characterized. (Throughout the paper, the term wall includes the substrate.) To achieve this, a cap of known surface area (1400 cm²) was placed over the target, acting as an unheated substrate. This cap was a 12.7 cm diameter, 12.7 cm high cylinder with one end closed and was mounted directly on the magnetron anode shield. The sputtering gas was injected into the cap through a 0.6 cm diameter hole in the end plate facing the target and escaped through a narrow channel between the anode shield and the target. The pumping speed of this channel was measured as 20 l s^{-1} at a pressure of 0.267 Pa (2.0 mTorr) into the remainder of the chamber. A pressure manometer was mounted directly on the cap end plate so that the pressure differential across the cap wall could be determined. The deposition uniformity on the cap, required to calculate the effective cap area A_w , was determined by comparing the deposited film thicknesses across the end diameter and along the sides of the cap. The deposition rate varied across the cap end-plate by 33% and along the cylinder sides by 67%.

Experiments performed in this apparatus included measurements of the V sputtering yield for a partially oxidized target, characterization of deposited film compositions and deposition rates as a function of sputtering parameters, and measurement of the time constants for wall metallization and target sputter cleaning. Typical deposition conditions included O_2 /Ar flow-rate ratios ranging from 0 to 0.35 at target currents of 2.0 and 1.0 A. Experiments were also conducted at flow-rate ratios of 0.12, 0.50, 0.64, and 0.72 as a function of target currents in the range 0.25–3.0 A.

The target sputtering yield may be found by measuring the V flux leaving the target surface. Sputtering yields for V were determined as a function of O_2 flow by deposition on two unheated, 218 cm², triangular, aluminum-foil substrates. These substrates were cleaned with acetone and weighed in a microbalance prior to insertion into the vacuum system. They were symmetrically mounted on a 16 cm diameter, hemispherical cage and were arranged so that they collected 33% of the sputtered flux. This design permits unimpeded

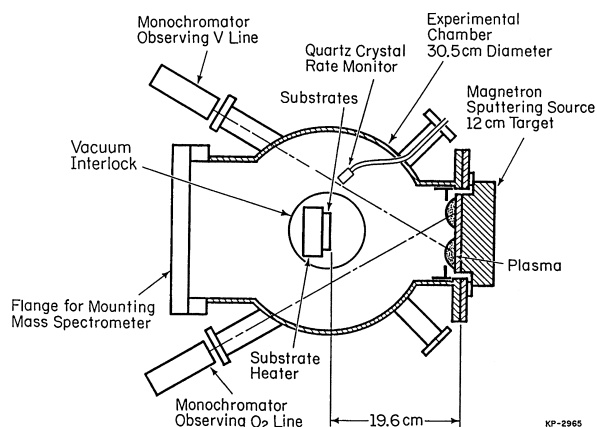


Fig. 1. A schematic diagram of the VO_2 deposition system.

gas flow to the target from essentially any direction while sampling sputtered material across the entire hemisphere. Films were deposited for a series of gas compositions ranging from pure Ar to pure O₂ at a sputtering current of 2.0 A. The total amount of film deposited in each run was determined by weighing the substrates. Film compositions were estimated by deposition under identical conditions on glass slides mounted in positions comparable to those used with the Al substrates. The compositions of these films were then determined by inductively-coupled atomic emission spectroscopy. From these data the deposition rate of V was determined and the sputtering yield calculated assuming positive singly-charged ions.

The partially oxidized surface was formed by coating an oxidized substrate (the target cap) by sputtering the (initially oxygen-saturated) target in pure Ar for times ranging from 1 to 30 min at a current of 2 A. The resulting surface was then oxidized in an atmosphere obtained by injection of pure oxygen at a rate of 10 standard cm³ min⁻¹ (sccm) with the chamber isolated from external pumping.

3. Results

Initial experiments concerned characterization of the sputtering parameters of the deposition chamber as a function of growth conditions. Figs. 2–4 show the target voltage, plasma V emission intensity relative to the Ar emission, and the change in total pressure in the cap upon discharge ignition. It should be noted that the target voltage (Fig. 2) and the ratio of V line plasma emission intensity ratio (Fig. 3) show an inverse relationship with one another. Fig. 4 shows the pressure change from the plasma-off partial pressure, and the steady-state value. Another way of looking at the plot is that it is a plot of the oxygen consumed by the reactive sputtering processes. The change in total pressure shown in demonstrates that at low oxygen partial pressures, some oxygen is being consumed, and that the rate of change is initially linear.

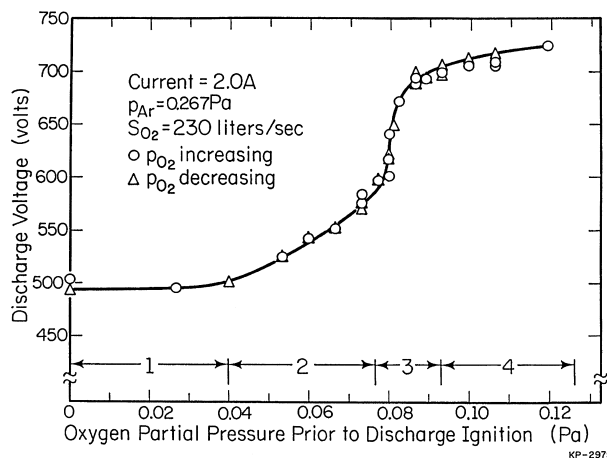


Fig. 2. Discharge voltage as a function of the oxygen partial pressure in the discharge, with the four operating regimes described in the text indicated.

However, between about 0.3 and 0.6 mTorr (0.040 and 0.080 Pa) (0.3 and 0.6 mTorr), there is a slight downward deviation. The curves exhibit four distinct operating regimes with respect to pressure [22]. The significance of the four operating regimes will be discussed below.

Figs. 5 and 6 show the change of the deposition parameters, the mass deposition rate at the substrate, and the V atom fraction in the film as a function of the O₂ partial pressure in the sputtering gas with respect to the oxygen partial pressure. The total mass deposition rate slightly increases at low oxygen partial pressures, but decreases steeply about 0.077 Pa (0.58 mTorr). The atomic fraction of vanadium in the films follows a sublinear decrease with respect to oxygen partial pressure, except for a slight discontinuity that corresponds to the abrupt decrease in the deposition rate. These regions correspond to region 3 shown in Fig. 2.

The sputtering yield for V is a function of the local target chemistry, the bombarding ion species, and the ion energy distribution. The sputtering yield remains relatively constant until about 0.080 Pa (0.6 mTorr) oxygen partial pressure

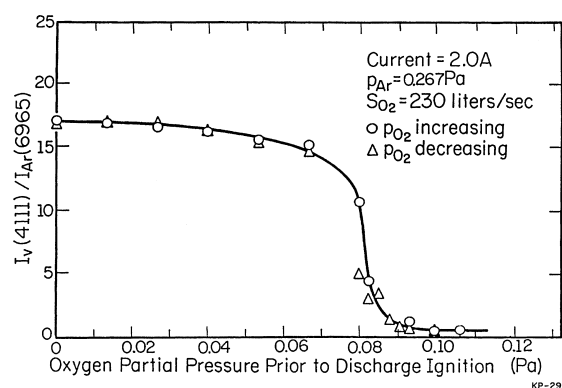


Fig. 3. The ratio of the characteristic V emission intensity in the discharge to the Ar intensity (not accounting for Ar dilution by O₂), plotted as a function of the oxygen partial pressure in the discharge. The four operating regimes described in the text are indicated in Fig. 2.

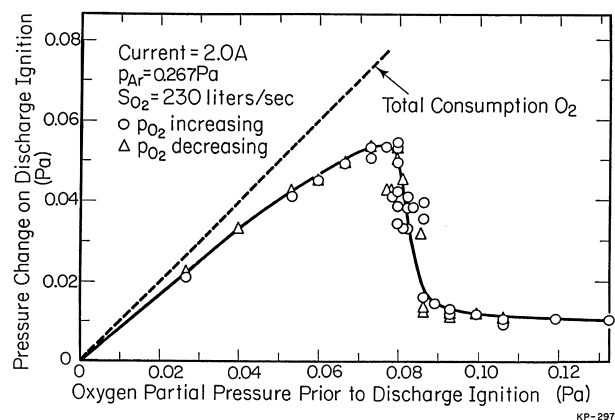


Fig. 4. The total pressure change on discharge ignition plotted as a function of the oxygen partial pressure in the discharge. The dashed line indicates consumption of all of the injected oxygen. The four operating regimes described in the text are indicated in Fig. 2.

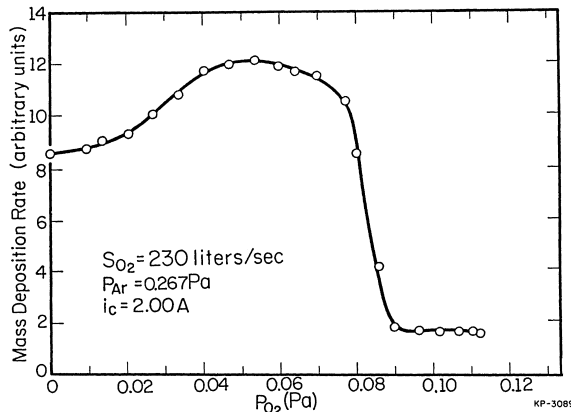


Fig. 5. Deposition rate plotted as a function of the oxygen partial pressure in the discharge.

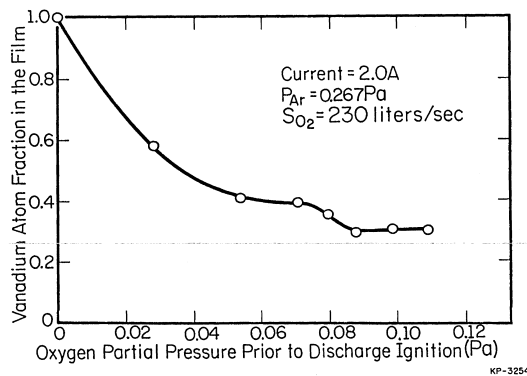


Fig. 6. V atom fraction in the sputtered films plotted as a function of the oxygen partial pressure in the discharge.

when it decreases abruptly until about 0.093 Pa (0.7 mTorr). The bare target V sputtering yield was found to be 0.53 vanadium atoms per incident 500 eV Ar^+ ion, in good agreement with the results of Laegrid and Wehner [23]. At partial pressures above 0.093 Pa (0.7 mTorr), the sputtering yield decreases to about 0.05, a factor of 10 decrease from the 0 mTorr Pa (0 mTorr), (bare target) condition. The measured sputtering yield for V as a function of oxygen partial pressure in the discharge is shown in Fig. 7.

The characteristic wall metallization time τ_m was determined indirectly as a function of sputtering current by meas-

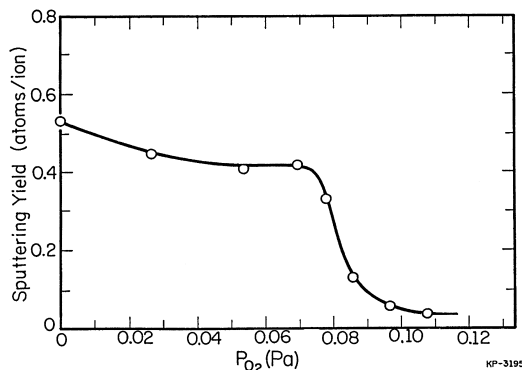


Fig. 7. The effective sputtering yield for V determined from the mass deposition rate, the V atom fraction in the films, and the total target current.

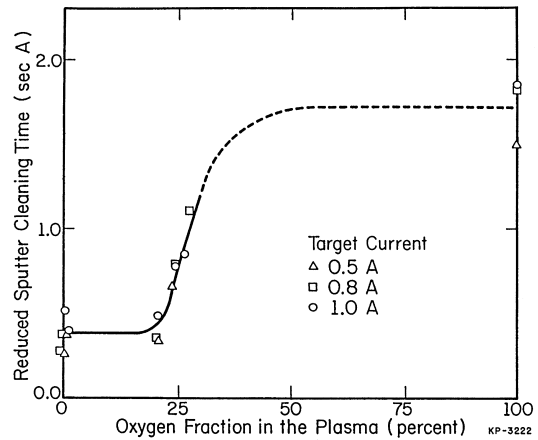


Fig. 8. The reduced sputter cleaning time (the measured time multiplied by the sputtering current) for three target currents. The solid curve represents a possible behavior in the region in which data was not acquired.

uring the time required for the surface to absorb a saturation coverage of oxygen from an O_2 atmosphere. A curve of consumed oxygen as a function of metallization time was constructed by measuring the pressure rise in the cap for a partially metallized surface relative to that for a fully oxidized surface as shown in Fig. 8. The data is normalized with respect to the target current. The τ_m remains flat until about 25% oxygen fraction in the plasma, then increases by almost a factor of 3 by about 28%. These oxygen fraction values correspond to 0.58 and 0.65 mTorr 0.077 and 0.087 Pa (0.58 and 0.65 mTorr), respectively.

4. Discussion

4.1. Film growth and vanadium oxidation

The curves shown in Fig. 2 exhibit four distinct operating regimes [22]. These may be described in terms of degree of target oxidation, and can be related to the change in the flux rates of various components onto the target and wall surfaces. In the first regime, also referred to as the low-oxygen region, the sputtered V flux is sufficient to getter most of the injected oxygen in the deposited film. For a pure Ar discharge the V emission intensity is at its highest, consistent with the sputtering rate for the pure metal. Increasing the O partial pressure in the discharge initially affects the V emission only slightly because most of the oxygen is getterred by the growing film, resulting in a gradual increase in mass deposition rate at the substrate and in the oxygen content of the growing film, shown in Fig. 5. The sputtering parameters, such as target voltage at constant current, are unaffected by oxygen flow in low-oxygen-flow region.

The second region begins when the sputtered V flux decreases enough that the overall deposition rate begins to decrease (see Fig. 5). Oxygen not getterred by the film is partially pumped by the vacuum system and partially adsorbed on the target. A gradual decrease in V emission

intensity and increase in target voltage demonstrate that significant steady-state oxidation of the target has begun and that the V sputtering rate has decreased. Oxidation decreases the secondary electron emission rate of the target surface requiring a higher target voltage to achieve the same current. The decreasing sputtering yield lowers the V mass deposition rate which is partially offset by an increase in oxygen content of the film, however. However, the net effect is to lower the overall deposition rate.

In the third region, the target coverage by oxygen increases abruptly as the oxygen sputtering rate decreases below the oxygen adsorption rate. In this regime the secondary electron emission coefficient drops abruptly resulting in a sharp rise in target voltage. The sputtering and mass deposition rates decrease rapidly due to the lower sputtering rate of the oxidized target surface. Oxygen saturation of the wall surface prevents oxygen uptake from offsetting the decreasing mass deposition rate. The O_2/Ar flow-rate ratio at the onset and termination of rapid target oxidation was found to increase approximately linearly with target current. Finally, in the fourth regime both the target and wall surfaces are saturated with oxygen and further increases in O_2 partial pressure produce little or no change in the film or target compositions.

It is assumed that ion-assisted oxidation occurs primarily at the target while reactions at the wall are mostly thermally activated. The consequence is that the oxygen sticking coefficient is expected to be higher on the target than on the wall for a single reactive gas partial pressure. In addition, the added energy introduced at the target should promote formation of more stable V oxidation states by enhancing the oxidation kinetics while preferentially removing less strongly bound oxygen. At low oxygen partial pressures the enhanced oxidation rate is more than offset by sputter cleaning which removes much of the absorbed oxygen.

To understand the dynamics of the reactive sputtering process, it is necessary to know the rate at which clean metal sites are created on the wall as a function of the deposition parameters. One method is to define time constants that relate to the adsorption and sputter removal rates for the reaction components. For example, the characteristic wall metallization time τ_m was determined indirectly as a function of sputtering current by measuring the time required for the surface to absorb a saturation coverage of oxygen from an O_2 atmosphere. This time was assumed to be directly proportional to the fractional V coverage of an otherwise oxygen-saturated surface.

The rate of creation of metal sites was found to be well fit by an exponential time dependence. This dependence follows from a first-order reaction mechanism which is the standard description for the deposition of sputtered target material. Following Penfold [21], a characteristic time constant τ_m was defined for wall metallization which represents the time required to cover a portion of the oxidized surface sites. The time evolution of the fractional completion, c , of the surface metallization is given by

$$c(t) = \exp\left\{\frac{-t}{\tau_m}\right\} \quad (1)$$

where t is the elapsed time. The fraction of sites on a wall that have been metallized by sputtering from a clean metal target is simply $n(t) = n(0) [1 - c(t)]$ where $n(0)$ is the total number of surface sites to be metallized and $\tau = \tau_m$. In this case, τ_m is given by

$$\tau_m = \frac{n_v A_w}{J_t Y_v A_t} \quad (2)$$

for which n_v is the maximum V surface site density on the wall and A_w is the effective wall area accounting for V which does not strike the wall and non-uniformities in the V flux (which causes some areas of the target to be metallized more slowly than others). A_t is the effective target area, J_t is the mean target current density, and Y_v is the V sputtering yield from the target in units of sputtered particles per coulomb of bombarding ion charge. The non-area terms (n_v , J_t , and Y_v) describe a characteristic removal time of the bulk target material from the target. The area ratio is a scaling term since it is assumed the physical processes scale with area.

It should be noted that certain terms have implied assumptions that must be accounted for when applying the model to a real reactive sputtering system. For example, the value of A_t may be less than the actual target area because of the non-uniform sputtering rate of the target in a magnetron. A_t is computed as a weighted average where the weighting factor is the local current density relative to the average current density at the target. In addition, both the target and wall areas are increased by microscopic roughness. If the target is oxidized, Y_v is decreased because the binding energy of the compound is greater than that of the metal, a fraction of the sputtered atoms is not V, and the sputtered O must be covered if it condenses on the wall. These effects increase the value of τ_m for a wall being metallized from an oxidized target or in an oxidizing atmosphere. The metallization time was determined based on fitting consumed oxygen data with curves determined using Eqs. (1) and (2). The resulting value of τ_m was approximately 13 min for sputtering in a pure Ar discharge.

4.2. Target behavior

The measured sputtering yield for V as a function of oxygen partial pressure in the discharge is shown in Fig. 7. The yield decreases with increasing oxygen content in the sputtering gas and due to target oxidation, which reduces the V surface site density; an increase in surface binding energy; and the intrinsically lower sputtering yield of V by O relative to Ar. Calculations of the V sputtering yield using the TRIM [24] program predict no significant change in the sputtering yield between Ar^+ and O_2^+ . However, as expected, the sputtering yield was predicted to decrease for O^+ sputtering relative to Ar^+ .

The sharp decrease in Y_v above an oxygen partial pressure of 0.077 Pa (0.58 mTorr) corresponds to the onset of massive target oxidation. The formation of vanadium oxides increases the binding energy of V on the surface which accounts for a significant decrease in sputtering yield. As an estimate of the magnitude of this contribution, the enthalpy of formation of V_2O_5 from V metal is 370 kcal mole⁻¹ while the enthalpy of condensation of V is 120 kcal mole⁻¹ [25]. This suggests an approximately threefold increase in surface binding energy for V in the form of V_2O_5 as compared to the pure metal, corresponding to a decrease in sputtering yield of approximately a factor of three [24–26]. Because oxygen can react at either the wall or the target surface, it was not possible, based on these measurements, to determine the oxygen sputtering yield explicitly.

The efficiency of sputtering as a process for removing oxygen from the target surface can be established in a manner similar to that used to find the wall metallization efficiency. As for metallization, a characteristic time for sputter cleaning the target, τ_{sc} , is defined using a first-order reaction rate. This is given by

$$\tau_{sc} = \frac{n_O}{J_t Y_O} \quad (3)$$

where n_O is the maximum oxygen site density on the target surface and is a function of oxide stoichiometry and Y_O is the sputtering yield of oxygen by Ar. The definition is very similar to that of the metallization time constant, however, since sputtering only occurs on the target, the area ratio is unity. The time constant is essentially the time it takes to remove the adsorbed gas from the target by sputtering. A flux of oxygen from the vapor phase due either to residual gas or to sputtered oxygen returning to the target increases τ_{sc} by reoxidizing the target surface.

The characteristic target sputter cleaning time was measured as a function of target current and O_2/Ar flow-rate ratio by presputtering the target in a mixed Ar + O_2 discharge until the target surface composition reached steady state, as determined by the V/Ar spectral emission intensity ratio. At this point the O_2 flow was terminated and the Ar flow was adjusted, with the sputtering current switched off, to return the total pressure to the typical operating value of 0.267 Pa (2.0 mTorr). The target was then sputtered until the spectral intensity ratio returned to the clean-target value. The intensity ratio was recorded as a function of time during the cleaning process and τ_{sc} was determined by fitting the spectral data with Eqs. (1) and (3). When oxygen is present in the plasma the target does not clean completely but rather reaches a steady-state oxygen content determined by a dynamic balance between the oxygen sputtering and adsorption rates. In this case, τ_{sc} represents the time to reach steady-state conditions. The values for τ_{sc} multiplied by the sputtering current as a function of the oxygen fraction in the plasma during cleaning are plotted in Fig. 8. Note that the points for different sputtering currents fall on top of each other. This demonstrates

that reoxidation of the target during sputter cleaning due to residual oxygen in the chamber or sputtered oxygen is negligible. The sputter cleaning time is constant up to approximately 22% O_2 in the cleaning plasma. However, with further increases in plasma O_2 , τ_{sc} increases rapidly until it reaches the value for pure O_2 (essentially no target cleaning).

4.3. Process simulation

The reactive sputtering process was simulated based on a model of reactive sputtering proposed by Berg et al. for TiN [27]. The Berg model calculates the target and wall surface coverage by the reactive gas and target elements by solving the steady state mass balance solution. It uses the flux of gas atoms incident at the surfaces, the gas sticking coefficients on either oxidized or clean metal sites (no provision for intermediate values is made), sputtering yields of the metal and oxide due to Ar, and the deposition parameters such as sputtering pressure to achieve its solution. The primary advantage of this model its relative simplicity and speed of calculation. In Section 3, results for the sputtering rate of V in Ar and mixed Ar/ O_2 discharges as well as target sputter cleaning data were presented. These values were used as the basis for simulating the sputtering process. Fig. 9 shows a plot of the experimentally measured and calculated values of O_2 consumption by the film at steady state as a function of injected O_2 flow rate. The calculation makes use of the measured values of pumping speed from under the cap (20 l s^{-1}) and a wall-to-target area ratio of 17.9. The calculation further assumes a unity sticking coefficient for O_2 on clean V, and no O_2 adsorption on a fully oxidized surface. The data were fit by adjusting the value of Y_O with a best match obtained for $Y_O = 0.027$. This value is in general agreement with the sputtering yield of V from a fully oxidized surface (Fig. 7). Such agreement is required to maintain the surface stoichiometry.

For comparison, Y_O can be estimated based on the fraction of current used to sputter oxygen and the flux of oxygen

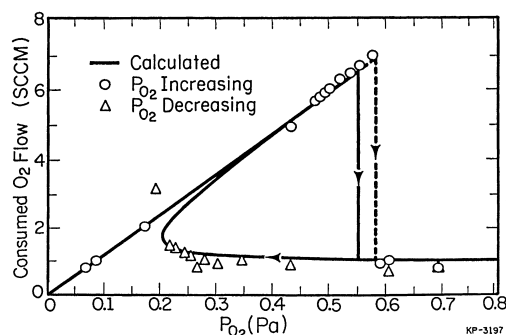


Fig. 9. The equivalent pumping rate (flow rate) of oxygen resulting from reaction with the wall during deposition plotted as a function of oxygen partial pressure in the discharge. The solid line was calculated using a modified form of the Berg model while the data points were recorded for a target current of 2.0 A and an Ar flow rate of 36.3 sccm. Points at which the system becomes unstable and the target composition switches to a different point on the curves are indicated by vertical lines.

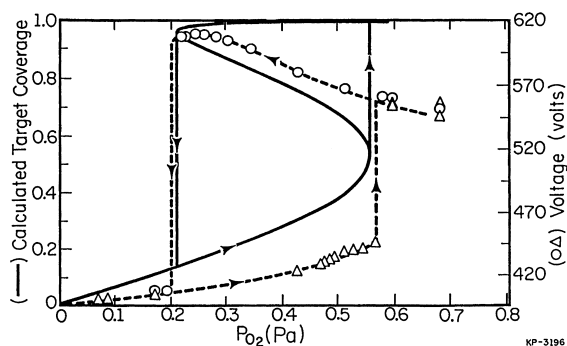


Fig. 10. Target voltage expressed, as points and the dashed curve, as a function of oxygen partial pressure in the discharge recorded with a target current of 2.0 A and an Ar flow rate of 36.3 sccm. \circ , increasing oxygen partial pressure direction; \triangle , the decreasing oxygen partial pressure direction; —, the calculated fractional coverage of the target with oxygen (full coverage corresponds to the V_2O_5 stoichiometry) for the oxygen partial pressures corresponding to the experimental data. Points at which the system becomes unstable and the target composition switches to a different point on the curves are indicated by vertical lines.

leaving the target. The current consumed in sputtering oxygen I_O is simply the total sputtering current I less the current used to sputter vanadium atoms, I_V : $I_O = I - I_V$. The V sputtering current I_V is then given by the sputtered V flux density divided by the V sputtering yield. The sputtered oxygen flux is equal to the incident, sticking oxygen flux at steady state. The sticking flux is found by multiplying the arriving flux (calculated from the O_2 partial pressure) by the sticking coefficient. While the sticking coefficient is not known exactly, it may range from 6×10^{-4} (the value observed on the oxygen-saturated V_2O_5 wall surfaces) to unity. This gives a range of possible values for Y_O between 3.5×10^{-4} and 0.33. The fit value of Y_O reflects the change of sticking coefficient of oxygen on the target as oxidation takes place. The value is reasonable for the given deposition conditions.

The target oxygen coverage was calculated using the model and is shown, along with experimental values, in Fig. 10. The model estimates that approximately 50% of the V surface sites are filled at the onset of the sputtering rate instability. However, only 5% of these sites are cleaned before the reverse instability occurs causing target cleaning. By comparing two of the major kinetic processes, metallization and sputter cleaning, it shows how the target coverage breakpoints are affected by the relative sputtering yields of various materials on the target, and the relative surface areas of the target and wall.

5. Conclusions

The reactive magnetron sputtering of V in a mixed Ar/ O_2 discharge has been studied and the results simulated using a modified form of an analytical sputtering model. For the sputtering system described here, the onset of target poisoning occurs at 0.077 Pa (0.58 mTorr), and is complete at about 0.087 Pa (0.65 mTorr). As with all reactive sputtering proc-

esses, the target gradually adsorbs oxygen until a critical point is reached at which the sputtering rate drops and the oxidation of the target rapidly increases. The sputtering yield was measured and found to decrease by a factor of 10 during poisoning from 0.53 to 0.05. The analytical model that was used was found to estimate the sputtering yield of oxygen from the target to be about 0.03. It was proposed that the decrease in the sputtering yield is, in part, dependent upon the change in the chemical binding energy of V and O. Two process time constants related to the sputtering processes were defined, and τ_{sc} was shown to vary as a function of the oxygen partial pressure. No evidence of a favored oxide phase was found based on the sputtering conditions or oxygen consumption. The desired material, VO_2 , is produced in a narrow range of sputtering parameters in which the system is unstable. Thus, to grow VO_2 in a controllable manner it will be necessary to modify the oxygen content of the deposited film relative to the target composition by changing the system geometry.

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