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The Mechanism of Reactive Sputtering

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The reactive sputtering of tantalum in mixed argon/oxygen atmospheres at a total pressure of 3.0×10^{-4} torr has been investigated by means of measurements on deposition and growth rates, density, electrical properties and electron diffraction. The main controlling factor on all of the parameters was found to be the partial pressure of oxygen.

The deposition rate was determined by the partial pressure of oxygen and assumed one of two values – either that associated with a clean tantalum target or that characteristic of an oxidised target. In the former region the oxygen content of the sputtered film was mainly dependent on the partial pressure of oxygen in the sputtering atmosphere and could range from zero to 100%. In the latter region, the films were always oxidised, but were deposited at a rate which was a fifth of that of the oxidised films sputtered under the former conditions.

It is concluded that there is a critical oxygen pressure, below which tantalum metal is sputtered and undergoes reaction at the substrate, and above which tantalum oxide is sputtered from an oxide surface as the result of reaction at the target.

1. Introduction

Reactive sputtering is one of a number of different methods for the preparation of the thin films of metallic compounds, e.g. oxides and nitrides, which are an integral part of microcircuitry. In this technique the required compounds are produced by sputtering the relevant metal in a reactive atmosphere. The characteristics which make it an attractive technique for this application are versatility and the ease with which the range of composition, and hence of electrical characteristics, from pure metal to complete stoichiometry can be produced. The mechanism by which films are formed in reactive sputtering is, however, imperfectly understood, and this paper is the result of an investigation aimed at gaining a better insight into the mechanism of the process, with a view to possible improvements in the electrical properties of the sputtered films.

For this investigation, tantalum was sputtered in argon/oxygen atmospheres which contained 0 to 100% of oxygen. Tantalum was chosen because of the interest existing [1, 2] in its use for thin film capacitors and resistors. The effect of additions of oxygen to the atmosphere when tantalum is sputtered has already been studied by Gerstenberg [3], Krikorian [4], and Schwartz [5]. These workers were however more concerned with the electrical properties of the sputtered films than with the possible sites of oxidation, although the last two do devote small sections of their respective papers to this subject.

2. Experimental Details

The films were sputtered in mixed argon/oxygen atmospheres at a total pressure which was always 3.0×10^{-4} torr. The vacuum chamber consisted of a six-armed glass cross shown schematically in fig. 1. The ions required for sputtering were generated by injecting electrons from a source mounted in one of the arms into an axial magnetic field of 500 Oe. Rhenium was used for the filament in the electron source, because it was found to have ten times the life of a tungsten filament when working in an all

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*Current address: The Plessey Company Limited, Components Group, Capacitor Division, Bathgate, West Lothian, UK oxygen atmosphere. The ion density was increased fourfold by an electron reflector placed in the arm opposite to the electron gun [6] and ion currents up to 50 mA were obtainable. The tantalum target, which was mounted in one of the four remaining arms, was inserted into the plasma, rather as a Langmuir probe, and material was sputtered on to the substrate located in the opposite arm. Because of the high magnetic field, the electron beam diameter was only ~ 0.1 mm, and hence there was only a low probability of interaction between the sputtered material and the electron beam. Targets of two sizes (1.0 cm^2 and 36.4 cm^2) were used at constant sputtering conditions of 2.0 kV and 1 mA/cm^2.

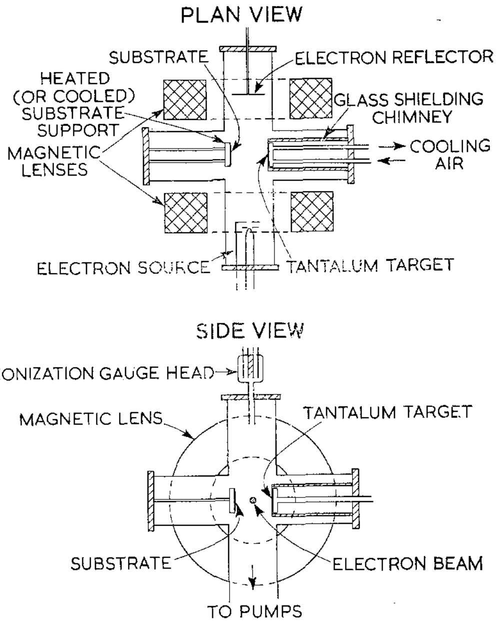

Figure 1 Sputtering chamber.

The substrate was clipped to a holder which could be heated or cooled as required, and which was located 4 cm away from the target. A shutter was provided to permit presputtering of the target before the films were deposited on the substrate. The remaining two arms of the chamber were occupied by a pumping port, and ionisation and mass spectrometer heads, respectively.

By use of baking techniques and liquid nitrogen traps, the residual pressure achieved was of the order of 10^{-8} torr, of which 9.0×10^{-9} torr was shown by mass spectrometry studies to be due to water vapour. The oxygen (99.8 %) and argon (99.9 %) were transferred from standard cylinders to the chamber through needle valves, which were adjusted to give the required composition and pressure in the sputtering atmosphere.

1.0 × 2.0 cm substrates of Corning 7059 microsheet, on to which five equally spaced 0.275 cm wide strips of aluminium had been evaporated, were used for the preparation of specimens for the measurement of film thickness and electrical properties. The aluminium strips provided the base electrodes for capacitance and resistance measurements. When dissolved in dilute caustic potash they also released portions of the sputtered film for electron diffraction examination, as well as leaving a series of thickness steps across the substrate. Electrical measurements were made on the film with a Keithley 600A electrometer (resistance) and a Wayne Kerr universal bridge B221A (capacitance and loss). The film thickness was measured with a Taylor Hobson Talysurf probe.

The densities of the films were determined by weighing the amount of material sputtered through a 1.2 cm square mask on to 1.5 × 2.0 cm glass substrates. This size of aperture was chosen because it was found to be the largest area over which the films showed a thickness variation of not greater than 5 %.

3. Results

3.1. Oxygen Pressure Effects

The effect of oxygen concentration on the density and deposition rate of tantalum films sputtered from the large (36.4 cm^2) target on to substrates at 80° C can be seen in fig. 2. The rate

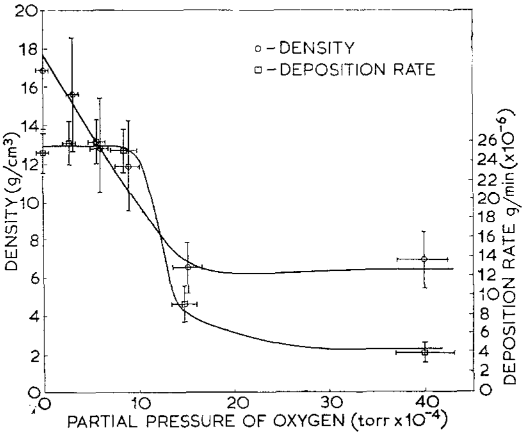

Figure 2 Density and deposition rate versus partial oxygen pressure. Substrate temperature 80° C; sputtering condition – 2.0 kV, ~ 30 mA.

of deposition was apparently independent of the oxygen concentration until the oxygen pressure was increased to ~ 1.25×10^{-4} torr. At this level the deposition rate fell sharply from 2.6×10^{-5} to 6.0×10^{-6} g/min. If the rate of deposition is expressed as grams per coulomb it can be shown that when the oxygen pressure was increased from zero to 1.0×10^{-4} torr (i.e. 30% of total pressure) the deposition rate rose by a factor of 1.3. This value is close to that which would be expected if the tantalum film which was deposited in 100% argon was deposited as Ta_2O_5 in 30% oxygen, i.e.

$$\frac{\text{Mass } (Ta_2O_5)}{\text{Mass } (2Ta)} = \frac{442}{362} = 1.22$$

In contrast to the above rate of deposition behaviour, the density exhibited a steady decrease with increase of oxygen pressure. This decrease continued until the partial pressure of oxygen had risen to 1.5×10^{-4} torr when the density reached a constant value of 6.5 g/cm^3. It is of interest to note that the fall in deposition rate approximately coincided with the levelling off of the density curve.

The growth rate of films sputtered from the large and small targets showed a similar pattern of variation with oxygen pressure. In the case of the small target, the growth rate rose, at room temperature, from 14 Å/min in 100% argon to a maximum of 32 Å/min at 6.0×10^{-5} torr (i.e. 20%) of oxygen, and then fell sharply to 4 Å/min in 100% oxygen.

The effect of the oxygen concentration in the sputtering atmosphere on the structure and composition of the sputtered films has been examined by electron diffraction. In 100% argon, films up to 100 Å thick were found to possess a fcc structure ($a_0 = 4.45$) similar to that found by Denbigh and Marcus [7] in thin films and by Chopra, Randlett and Duff [8] in thick films (up to 2 μm). This was gradually replaced by the normal bcc structure ($a_0 = 3.37$) as the films increased in thickness. Above 200 Å the films were entirely bcc in structure. As the oxygen concentration was increased, the films became amorphous (crystallite size < 10 Å) and the diffraction patterns changed smoothly from that due to bcc tantalum (100% argon atmospheres) to one which was identical with the patterns obtained from anodised tantalum (100% oxygen atmospheres). This is shown in fig. 3, where the diffraction patterns are presented in the form of densitometer traces. These traces have been transposed vertically for the sake of clarity but no horizontal adjustments have been made, so that the relative positions of the peaks may be taken as significant. The patterns derived from films sputtered in 100% oxygen have been subjected to radial distribution analysis in an attempt to identify the compounds present. Evidence was found for the presence of Ta-O bonds and free tantalum metal, but no definite (Ta, O) compounds, e.g. TaO, TaO_2, Ta_2O_5, were identified. Thus films sputtered in 100% oxygen appear to have an "average" (Ta, O) structure.

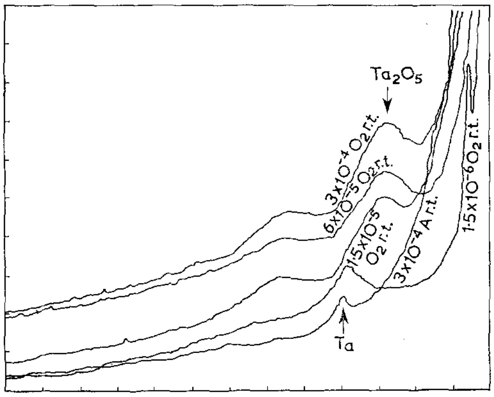

Figure 3 Effect of oxygen concentration on composition of sputtered films. Densitometer traces of electron diffraction patterns.

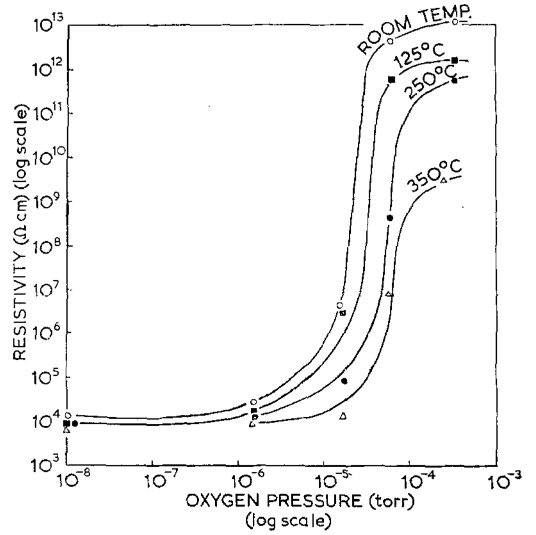

Figure 4 Resistivity versus partial oxygen pressure. Resistivity measured at room temperature. The temperatures quoted are those of the substrates during deposition.

The variation of the resistivity of the sputtered films with the oxygen concentration in the sputtering atmosphere (measured at room temperature for various deposition temperatures) is shown in fig. 4. The large increase in resistivity over a relatively small pressure range has been previously observed by Krikorian [4].

3.2. Substrate Temperature Effects

The density of films sputtered from the large target varied with substrate temperature, as shown in fig. 5, for atmospheres containing 100 % argon, 1.5×10^{-5} and 6.0×10^{-5} torr of oxygen. As can be seen from fig. 2, the rate of deposition for these atmospheres was unaffected by the composition of the sputtering atmosphere, and was constant at $\sim 2.6 \times 10^{-5}$ g/min. The effect of substrate temperature on density was, however, a function of the partial oxygen pressure. The density of films produced in atmospheres containing 1.5×10^{-5} torr of oxygen or less, increased towards the value of bulk tantalum with increase of substrate temperature, whereas at 6.0×10^{-5} torr of oxygen the density exhibited a sharp initial decrease, and then assumed a constant value of ~ 9.0 g/cm^3 above 125° C. The effect of substrate temperature on growth rate is shown in fig. 6 which is substantially the inverse of fig. 5. The good agreement between the measured growth rate and that predicted from density measurements (see fig. 6) indicates that there is no variation of growth parameters, e.g. condensation coefficient, over the temperature range considered.

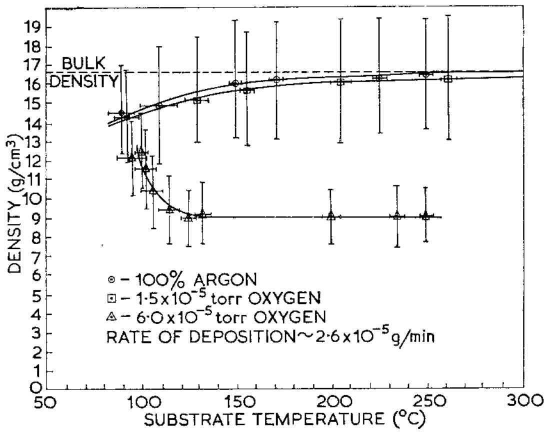

Figure 5 Density of sputtered film as a function of substrate temperature.

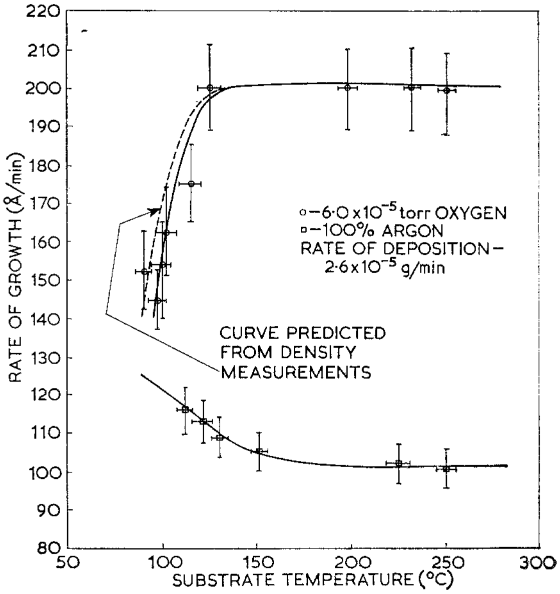

Figure 6 Growth rate (as measured by thickness) versus substrate temperature.

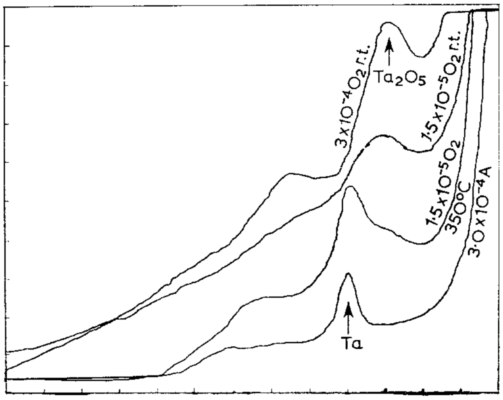

Figure 7 Effect of substrate temperature on composition of films sputtered in 1.5×10^{-5} torr oxygen. Densitometer traces of electron diffraction patterns.

Electron diffraction studies, using the films sputtered from the small target, indicated that the effect of an increase in substrate temperature was to increase the metal content of the sputtered films. This is illustrated in fig. 7 for atmospheres containing 1.5×10^{-5} torr of oxygen, and in fig. 8 for atmospheres containing 6.0×10^{-5} torr of oxygen. In both figures the traces illustrating the effect of temperature are bracketed by traces obtained in high and low oxygen atmospheres to aid identification of the various peaks. The effect of temperature was much more pronounced at 1.5×10^{-5} torr of oxygen than at 6.0 ×

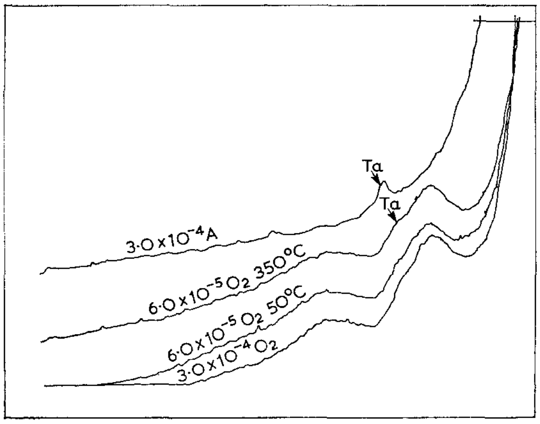

Figure 8 Effect of substrate temperature on composition of films sputtered in 6.0 × 10^{-5} torr oxygen. Densitometer traces of electron diffraction patterns.

10^{-5} torr, where the effect was identical with that observed in 100% oxygen (i.e. 3.0 × 10^{-4} torr) atmospheres.

The results of electrical measurements also indicate an increase in the metal content of the sputtered films with increased substrate temperature. This is shown by the decrease of resistivity (fig. 4) and also by the measured increase of permittivity and loss with increase of temperature. The permittivities of films sputtered from the small target in 100% oxygen and 6.0 × 10^{-5} torr of oxygen were 10 and 30 respectively. (The low value of the permittivity is due to the formation of γ-alumina on the base electrode.) These values remained constant up to 250° C and then increased sharply at higher temperatures. Dielectric loss of films produced in both atmospheres remained at < 1.0% up to 250° C and again increased sharply above this temperature (fig. 9).

4. Discussion

4.1. Introduction

The mean-free-path of sputtered tantalum atoms at a pressure of 3.0 × 10^{-4} torr is about 50 cm. Thus the number of possible collisions between tantalum atoms and oxygen molecules which can occur between the target and substrate at 4 cm distance is almost zero. Consequently, the possibility of oxidation in flight can be discounted as making a significant contribution to the formation of oxidised films, even in 100% oxygen atmospheres.

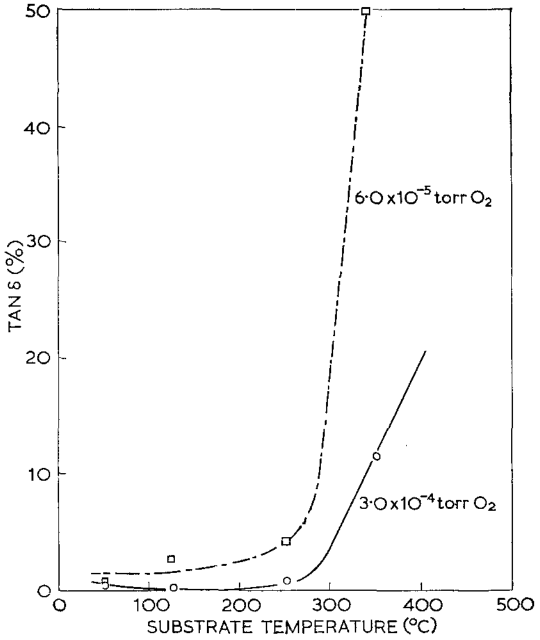

Figure 9 Loss versus substrate temperature.

4.2. Effect of Oxygen Pressure, below Critical Pressure

The results quoted above show that, in the reactive sputtering of tantalum, there is a critical oxygen pressure, below which the deposition rate is that characteristic of 100% argon atmospheres, and above which the rate of deposition falls sharply by a factor of about five. The magnitude of the deposition rate observed in the subcritical region indicates that the tantalum target surface was substantially free of oxide. Any significant amount of oxide on the target surface would have resulted in a drop in the deposition rate below that observed in argon, whereas a slight, but significant, rise was in fact observed (fig. 10). Thus, in the subcritical oxygen pressure region, the oxide films were formed by reaction between metallic tantalum and gaseous oxygen at the substrate. The apparent increase in growth rate with partial oxygen pressure observed in the subcritical region was due to a decrease in the density of the tantalum, caused by incorporation of oxygen into the growing tantalum film. The ratio between the growth rates of films sputtered at the critical oxygen pressure and in 100% argon (32/14 = 2.29 for the 1.0 cm^2 target at 6.0 × 10^{-5} torr of oxygen) indicates that at the critical pressure oxidised films are produced (density (Ta_2O_5)/density (Ta) = 2.3). The actual value of the critical pressure depends upon the relative arrival rates of tantalum and oxygen. Thus the critical pressure of 6.0×10^{-5} torr, observed when the 1.0 cm^2 target was used, rose to 1.25×10^{-4} torr for the larger target.

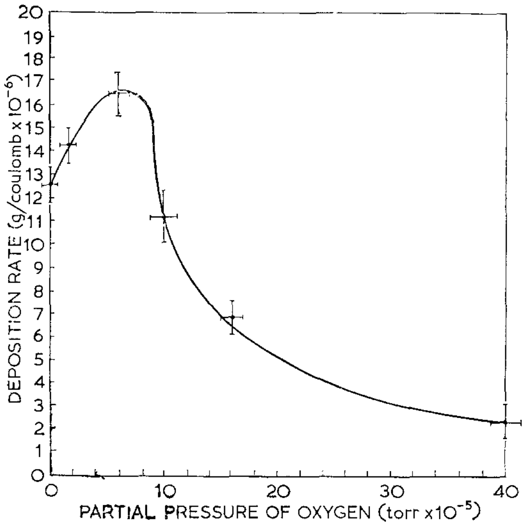

Figure 10 Rate of deposition versus partial pressure of oxygen. Sputtering conditions 2.0 kV, 30 mA.

The formation of oxidised films in the subcritical oxygen pressure region depends upon the incorporation of oxygen-atoms into the growing tantalum films. Only oxygen-atoms which have energy above that of the activation energy for the absorption process will succeed in reacting.

The surface concentration of oxygen-atoms, with energy above the activation level, depends on the product of two terms – the total concentration of adsorbed oxygen, and the proportion with $E > E_a$ (E = general energy term, E_a = activation energy). Thus at constant temperature, i.e. at constant rate per atom for the absorption reaction, the oxidation of the film should bear some direct relationship to the oxygen pressure – the exact form of this relationship depending upon the adsorption process.

At any given temperature, and at a constant rate of tantalum deposition, the degree of oxidation of the sputtered films increases with the partial pressure of oxygen. (This was shown by density (fig. 2), resistivity (fig. 4), weight and thickness determinations.) This pressure-dependence suggests that a chemisorption equilibrium precedes the rate-determining step of oxide growth. This process can be expressed as

$$\text{Site} + \tfrac{1}{2}\,O_2 \rightleftharpoons \text{O-chemisorbed} \qquad (1)$$

$$\text{O-chemisorbed} + \text{Ta} \xrightarrow{\text{absorption}} \text{Ta/O solid solution} \qquad (2)$$

Reaction 1 represents two or more steps which involve chemisorption of an oxygen molecule, followed by dissociation of that molecule. The concentration of chemisorbed oxygen atoms can be expressed as

$$[O^-]_{\text{chemisorbed}} = K\,[O_2]^{\frac{1}{2}} \qquad (3)$$

where K is the chemisorption equilibrium constant. Substitution of p/RT for $[O_2]$ according to the ideal gas laws gives

$$[O^-]_{\text{chemisorbed}} = \frac{K\,p_{O_2}^{\frac{1}{2}}}{(RT)^{\frac{1}{2}}} \qquad (4)$$

Thus at constant temperature the rate of oxidation will be approximately proportional to the square root of the oxygen pressure. In the subcritical pressure region, the growth rate of the sputtered tantalum films exhibits this type of pressure-dependence (fig. 11), which was also described by Cowgill and Stringer [9], and Kofstad [10], for the oxidation of bulk tantalum at low oxygen pressures.

4.3. Effect of Oxygen Pressure, above Critical Pressure

The abrupt fall in the deposition rate at the critical pressure suggests that at this pressure the condition of the target surface undergoes a significant change. The fall in the deposition rate is the same as the decrease in the sputtering yield observed by Wehner [11] when he sputtered from pre-oxidised tantalum surfaces. Thus the reduction in the deposition rate was most likely due to oxidation of the target surface. The presence of an insulating layer on the target surface results in the build-up of a positive charge which exerts a retarding influence on the bombarding ions, thus reducing the sputtering yield from the target.

4.4. Effect of Substrate Temperature, below Critical Pressure

At constant pressure the temperature-dependence of the rate of oxidation will be more complex than the pressure-dependence at constant temperature, for it in turn depends on two

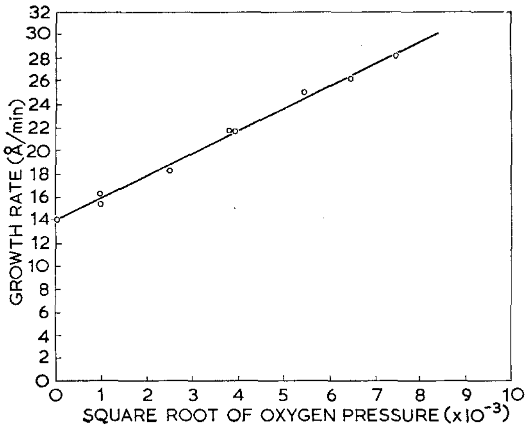

Figure 11 Growth rate versus square root of partial oxygen pressure.

opposing terms. The effect of an increase in temperature is to increase the reaction rate per atom, but at the same time the concentration of adsorbed atoms will decrease according to Langmuir's isotherm

$$\frac{\theta}{(1-\theta)} = \text{const.} \exp (E_b/kT)$$

where θ = fraction of surface covered with adsorbed molecules, and E_b = heat of adsorption.

The actual effect of an increase of temperature on the reaction rate depends upon the temperature-dependence of these two processes, and also upon the magnitude of the surface concentration of adsorbed molecules due to the partial pressure of oxygen which is employed.

The form of the effect of temperature on the oxidation of tantalum films will depend upon the magnitude of the partial oxygen pressure. When the pressure is high enough, and the temperature low enough for the surface to be substantially saturated with oxygen, then the temperature-dependence of the rate is the same as for the rate-controlling absorption reaction. This situation was found when the films were grown at a deposition rate of 2.6×10^{-5} g/min in an atmosphere containing 6.0×10^{-5} torr of oxygen. Here the relative arrival rates of tantalum and oxygen at 50° C were 1.16×10^{16} atom/cm^2 sec and 2.18×10^{16} mol/cm^2 sec respectively. An Arrhenius plot of the growth rate is shown in fig. 12. The slope of this line yielded an activation energy of 6.7 kcal/mole, which is the same value as that quoted by Kofstad [10] for the oxidation of bulk tantalum under conditions where the rate constant was proportional to the square root of the oxygen pressure. At 125° C it appears that the reaction per molecule has risen to such a level that all of the arriving oxygen reacts with the tantalum. Hence the rate shows no change for temperatures above 125° C.

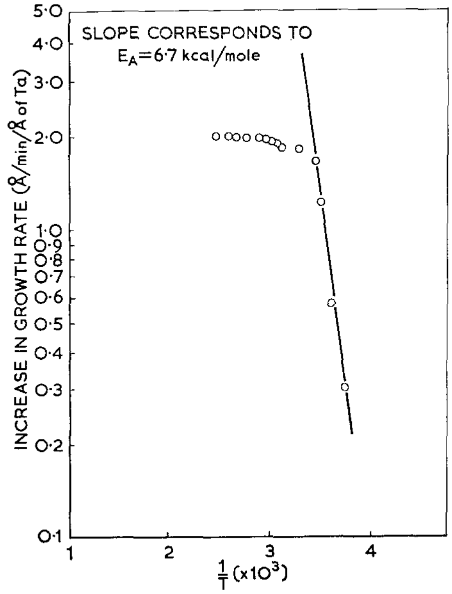

Figure 12 Growth rate versus $1/T$. 6.0×10^{-5} torr oxygen pressure.

At very low oxygen pressures, the growth rate measurements indicate that there is, making allowance for density changes, no detectable temperature effect on the absorption of oxygen. In this region the surface concentration of adsorbed oxygen is below saturation, even at the lowest temperatures employed. This concentration decreases even further with increase of temperature. Hence the concentration of molecules with $E > E_a$ is low at all times, and appears from the electron diffraction and resistivity evidence to actually decrease with increase of temperature. As tantalum films can form solid solutions containing up to 20 at. % of oxygen [3] these films retain many of the characteristics of a metal, e.g. low resistivity, and exhibit an increase of density with temperature.

At partial oxygen pressures corresponding to the critical value, films are formed which exhibit oxide characteristics. Because oxides are more difficult to sinter than metals, these films show little change in density and apparent growth rate with temperature.

4.5. Effect of Substrate Temperature, above Critical Pressure

The electron diffraction evidence shows that an increase of substrate temperature results in an increase of metallic tantalum in the sputtered films. This effect is most pronounced in the subcritical region (fig. 7), but is also present, although on much reduced scale, in films sputtered in 3.0×10^{-4} torr of oxygen (fig. 8).

The maximum substrate temperature employed (350° C) was too low to cause dissociation of stoichiometric Ta_2O_5, so it appears that incompletely oxidised tantalum is sputtered from the target in high oxygen atmospheres. At low substrate temperatures the surface concentration of adsorbed oxygen is high enough to restore the oxide to its fully oxidised state. As the substrate temperature is raised the surface concentration of adsorbed oxygen is reduced according to Langmuir's isotherm, and at 350° C it is apparently too low to allow complete oxidation.

The electrical results, discussed in section 4.7 below, also indicate that non-stoichiometric tantalum oxide is sputtered under conditions where the target surface is oxidised.

4.6. Effect of Target Temperature

A limited series of experiments have been carried out on the effect of variations of oxygen pressure and target temperature on the sputtering yield of tantalum. The results indicate that, as at the substrate, there are two competing oxidation processes – an activation energy effect causing an increase of oxidation with temperature, and a reduction in the concentration of adsorbed oxygen with temperature tending to decrease oxidation.

This work is continuing and will be reported at a future date.

4.7. Electrical Results

Electrical results have been obtained on resistivity versus oxygen pressure (fig. 4) and loss versus substrate temperature (fig. 9). Because of the effect of the substrate temperature on resistivity, it must be concluded that even at the higher oxygen pressures the material arriving at the substrate is not completely oxidised. This is confirmed by the loss/temperature relationship (fig. 9), where an increase in loss with substrate temperature is evident even for oxygen pressure of 3.0×10^{-4} torr. However, in this last case there appears to be little change of loss for temperatures below 200° C. If the material is acting electrically as an amorphous dielectric, it could be conducting by means of a large number of structural traps, [12] (cf Walley and Jonscher [13] for amorphous germanium), and in this case would be relatively insensitive to impurities. Thus the loss would remain fairly constant until fairly high levels of free tantalum are present in the material. The electron diffraction evidence would indicate that there is very approximately 5% of free tantalum in the films deposited at 350° C and at this temperature the loss is rising.

The curve of loss versus substrate temperature for an oxygen pressure of 6.0×10^{-5} torr shows a similar behaviour but in this case the general loss level is higher because of less complete oxidation at all temperatures.

4.8. Supporting Evidence

The results stated here are largely in agreement with those of Gerstenberg and Calbick [3], Krikorian and Sneed [4] and Schwartz [5] who have worked with glow discharge systems. Gerstenberg, with reference to nitrogen, and Schwartz, with reference to nitrogen, oxygen, methane, and carbon monoxide, found that the deposition rate of tantalum was constant, at a value characteristic of all argon atmospheres, up to partial pressures of the order of 10^{-4} to 10^{-3} torr. Schwartz concluded that reaction in flight and at the substrate were the dominant processes. From the effect of substrate bias and temperature on the growth of tantalum films sputtered in argon/oxygen atmospheres, Krikorian also placed the dominant reaction site at the substrate. Thus is would appear that the mechanism of reactive sputtering is substantially the same in both glow discharge and low pressure systems, and for other reactive gases besides oxygen.

Finally, supporting evidence for the pressure-dependence of the site of oxide formation has been supplied by the results of an investigation into the stress present in reactively sputtered tantalum films [14]. At high partial pressures of oxygen it has been found that the films are in tensile stress, which indicates that they are formed by condensation, nucleation, and growth, as in the evaporation of metals [15]. At low oxygen partial pressures, the films are in compressive stress, which indicates that the reaction to form the oxide occurred at the substrate (see Campbell [16] for a general discussion of the development of stress in thermally and anodically grown oxides, and Pawel and Campbell [17] for a report on the stress present in gaseously oxidised tantalum).

5. Summary and Conclusions

The site of oxidation in the reactive sputtering of tantalum is principally determined by the partial pressure of oxygen in the sputtering atmosphere. From 0% of oxygen up to a critical pressure determined by the relative arrival rates of oxygen and tantalum, oxidation occurs mainly at the substrate. In this region the oxygen content of the sputtered films depends on the partial pressure of oxygen. Above the critical oxygen pressure oxidation occurs mainly at the target and the films are formed by sputtering of the oxide from the target surface. In atmospheres containing the critical pressure of oxygen, oxidised films are deposited at approximately five times the rate of those grown in higher oxygen atmospheres. It is thus apparent that there is no advantage to be gained, in the preparation of dielectric films by reactive sputtering, from working at high oxygen partial pressures. Films which are electrically identical can be deposited at higher rates by working at the lowest oxygen pressure which is consistent with complete oxidation. The actual value of this optimum oxygen pressure will depend on the rate of deposition of tantalum and the "apparatus" factor which appears to play such a large part in sputtering work.

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