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# Ta thin film resistors reactively sputtered onto substrates mounted on a rotating carousel

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Ta thin film resistors have been reactively sputtered in $1.5 \times 10^{-5}$ Torr oxygen and $1.5 \times 10^{-5}$ Torr nitrogen simultaneously, using a d.c. diode system in which the anode is formed by a carousel. The substrates are mounted on this carousel and can be rotated through the discharge. For non-heat-treated films the resistivity increases and the TCR becomes more negative as the carousel rotation speed increases. These changes in electrical properties are attributed to the observed increase in the oxygen concentration and a simultaneous decrease in the nitrogen concentration in the films. The electrical properties are further perturbed by an elongation of the physical structure of the films as a result of carousel rotation. This elongation, which can produce an increased resistivity for a given TCR, is attributed to oblique incidence effects as the substrate rotates into, and out of the discharge. Changes produced in the electrical and structural properties of the films during heat-treatment at 500° C are shown to depend on carousel rotation speed: recrystallization and surface oxidation occur for films deposited onto a rotating carousel, whereas films deposited onto a stationary carousel undergo surface oxidation only, as indicated by the kinetics of the conductance change and the lack of structural changes as shown by transmission electron microscopy.

## 1. Introduction

Owing to their small size and high degree of stability, Ta films are often used as resistance elements in microelectronic circuits. In order to obtain a high resistivity for a given TCR, these films may be reactively sputtered [1] in oxygen or in nitrogen. However, it may be advantageous to reactively sputter Ta films in oxygen and nitrogen simultaneously since it has been shown [2] that such films can have a higher resistivity for a given TCR than for films sputtered in oxygen or nitrogen separately.

The present investigation shows that, for a given TCR, the resistivity of Ta films reactively sputtered in oxygen and nitrogen simultaneously, can be further increased if the substrate is mounted on a rotating carousel in such a fashion that the substrate can be rotated through the discharge. The structure and composition of the resulting Ta films are investigated by transmission electron microscopy and electron microprobe analysis. These results are then correlated with the observed changes in electrical properties which result from different carousel rotation speeds as well as those changes produced by a stabilizing heat treatment of the films.

## 2. Experimental equipment

Ta films were sputtered in a d.c. diode system in which the anode consists of a carousel (Fig. 1). A substrate was mounted on the carousel so that the substrate could be rotated through the discharge during sputtering. Films were deposited either with the carousel rotating or with the carousel stationary, the latter condition maintaining the surface of the substrate parallel to the cathode with an anode-cathode spacing of 2 in. Sputtering was done at 4 kV in an atmos-

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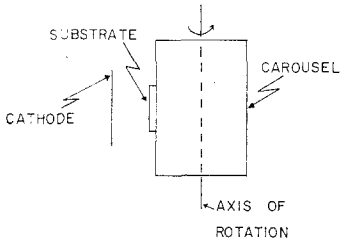


*Figure 1* Sputtering system showing substrate mounted on rotating carousel.

phere consisting of $1.5 \times 10^{-5}$ Torr oxygen, $1.5 \times 10^{-5}$ Torr nitrogen and 30 mTorr argon, producing a sputtering current of 100 mA.

Pre-sputtering was done for 30 min onto a region of the carousel adjacent to the substrate. The substrate temperature, as measured by a thermocouple wedged between the back surface of the glazed ceramic substrate and the carousel was $325 \pm 25°C$ after the deposition of the films, independently of whether or not the carousel was rotating. No substrate bias was employed.

Gold pads were used to make electrical contact to the films. Standard photoetching techniques were used to form a straight-line resistor pattern of 50 squares, or a zig-zag resistor pattern of 1000 squares; all etched resistors have the same orientation relative to the axis of the substrate which was vertical during sputtering. Films which are investigated after this point of the production cycle will be referred to as non-heat-treated, whereas films which have been stabilized [1] by baking will be referred to as heat-treated. Film resistance was measured with a Wayne-Kerr model B 641 bridge which has an accuracy of 0.01%. Low-temperature resistance measurements were carried out by mounting the samples in a cryogenic refrigerator [3] which is capable of reaching a temperature of 30K. The film thickness was measured by a Talysurf moving stylus instrument. A Cambridge electron microprobe was used to measure the tantalum, oxygen, and nitrogen X-ray count rate from the films at a beam voltage of 20 kV and a beam current of $5 \times 10^{-7}$ A. The relative oxygen and nitrogen concentration is obtained from the ratio of the oxygen or nitrogen count rate obtained from the film to that obtained from an $Al_2O_3$ or a BN bulk standard. Transmission electron microscopy results were obtained using a Philips EM 300 electron microscope at a voltage of 100 kV. These films were removed from the substrate by a parlodion stripping technique.

## 3. Experimental results

Table I shows the film resistivity and TCR both before and after heat-treatment at 500°C for selected carousel rotation speeds. In all cases, the TCR was measured over the temperature range +25 to −196°C. The resistivity of the non-heat-treated films is seen to increase with rotation speed, with the largest change occurring between 0 and 1 rpm. The resistivity of the heat-treated films exceeds that of the non-heat-treated films deposited at the same carousel rotation speed. Heat-treatment does not affect the TCR of films deposited onto a stationary carousel or onto a carousel rotating at 1 rpm, in contrast to films

TABLE I Resistivity and TCR of Ta films reactively sputtered in $1.5 \times 10^{-5}$ Torr oxygen and $1.5 \times 10^{-5}$ Torr nitrogen with the substrates mounted on a carousel rotating at different speeds.

| Rotation speed (rpm) | Non-heat-treated films | | Heat-treated films | |
|---|---|---|---|---|
| | $\rho(\mu\Omega\,cm)$ | TCR (ppm °C$^{-1}$) | $\rho(\mu\Omega\,cm)$ | TCR (ppm °C$^{-1}$) |
| 0 | $5.0 \times 10^{2}$ | −143 | $7.0 \times 10^{2}$ | −145 |
| 1 | $2.5 \times 10^{3}$ | −265 | $4.7 \times 10^{3}$ | −257 |
| 10 | $4.2 \times 10^{3}$ | −312 | $1.2 \times 10^{4}$ | −436 |
| 20 | $4.8 \times 10^{3}$ | −485 | $1.1 \times 10^{4}$ | −360 |

TABLE II Electron microprobe results for Ta films reactively sputtered in $1.5 \times 10^{-5}$ Torr oxygen and $1.5 \times 10^{-5}$ Torr nitrogen with the substrates mounted on a carousel rotating at different speeds.

| Rotation speed | Relative oxygen concentrations ±10% | Relative nitrogen concentrations ±10% | Ta counts/film thickness (Å$^{-1}$) ±10% |
|---|---|---|---|
| 0 | 0.082 | 0.379 | 304 |
| 1 | 0.127 | 0.328 | 278 |
| 10 | 0.151 | 0.274 | 282 |
| 20 | 0.148 | 0.219 | 282 |

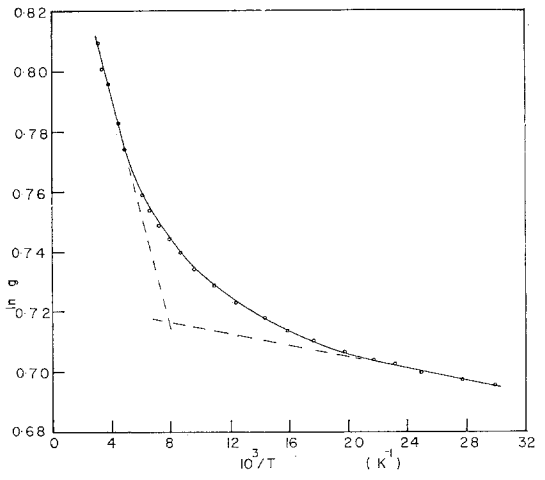


*Figure 2* Arrhenius plot of film conductance for a heat-treated film sputtered during carousel rotation at 10 rpm.

deposited during carousel rotation at 10 or at 20 rpm.

Electrical properties of the films were further investigated by measuring the conductance over the range of 293 to 30K. Fig. 2 illustrates an Arrhenius plot for a film sputtered onto a carousel rotating at 10 rpm. The results for this film are qualitatively similar to those results for films deposited at other carousel rotation speeds in that the Arrhenius plot does not yield a single activation energy, but apparently yields two values of activative energy. For Fig. 2, these values are $2.0 \times 10^{-3}$ and $8.6 \times 10^{-5}$ eV.

The relative oxygen and nitrogen content of the films as measured by the electron microprobe are summarized in Table II. It is seen that as the rotation speed of the carousel is increased, the oxygen content of the films is increased, while the nitrogen content is simultaneously decreased for a fixed partial pressure of oxygen and nitrogen. This table also shows that the ratio of the Ta X-ray count rate to film thickness is independent of rotation speed. Since the reciprocal of the X-ray self absorption coefficient for Ta ($\sim 5\ \mu$) and the mean range of the electron beam in Ta (calculated [4] to be 7000 Å) greatly exceeds the film thickness (1000 Å), the Ta X-ray count rate is proportional to the surface density of Ta atoms. Since the atomic weight of Ta exceeds that of oxygen and nitrogen by more than an order of magnitude, the Ta X-ray count rate per unit film thickness can be taken to be proportional to the film density. Thus, the results of Table II show that, within experimental error, the film density is independent of the rotation speed of the carousel.

Fig. 3 shows the transmission electron microscope results for a non-heat-treated film deposited during carousel rotation at 1 rpm. The diffraction pattern of Fig. 3a is quite diffuse, indicating a grain size [5] of about 15 Å. The bright-field micrograph of Fig. 3b is typical of an amorphous film. Fig. 4 is a bright field micrograph of a non-heat-treated film sputtered during carousel rotation at 20 rpm. This micrograph shows that the films have an elongated, worm-like structure. The diffraction pattern corresponding to Fig. 4. contains diffuse rings and appears very similar to the diffraction pattern of Fig. 3a.

The structure of the films was also studied during *in situ* heat-treatment in the electron microscope at a vacuum of $10^{-5}$ Torr. Fig. 5a shows the resulting diffraction pattern for a film

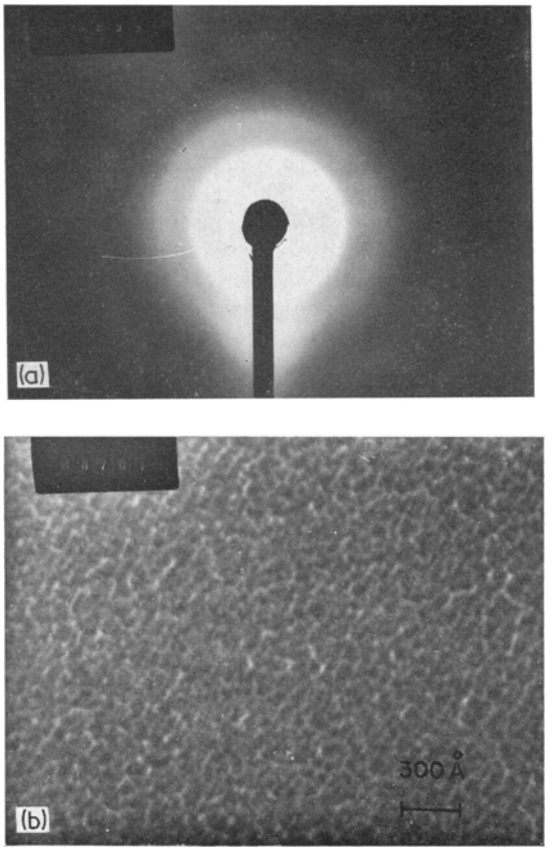


*Figure 3* Transmission electron microscopy results for a non-heat-treated film sputtered during carousel rotation at 1 rpm. (a) diffraction pattern, (b) corresponding bright-field micrograph.

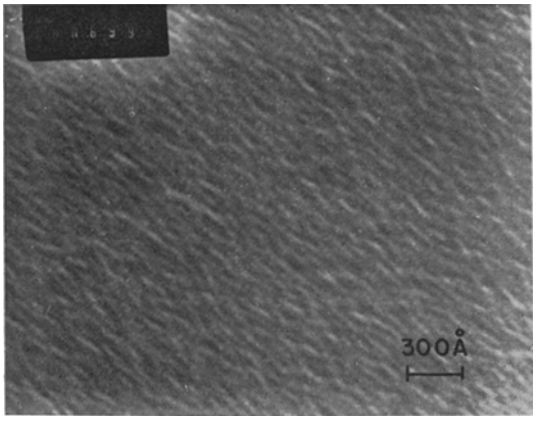


*Figure 4* Bright-field micrograph of a non-heat-treated film sputtered during carousel rotation at 20 rpm.

deposited during carousel rotation at 1 rpm. In contrast to Fig. 3a, the rings are quite sharp and somewhat discontinuous. The diffraction pattern is attributed to a combination of $\beta$-Ta and $\beta$-$Ta_2O_5$. Table III gives a comparison between the measured $d$-values and the standard $d$-values for these two materials. Of the known Ta-O-N structures, the $d$-value of 5.38 Å can be uniquely attributed [6] to $\beta$-Ta, while $d$-values of 3.87 and 3.15 Å can be uniquely attributed [7] to $\beta$-$Ta_2O_5$. Many of the remaining rings in the diffraction pattern can be attributed to $\beta$-Ta or $\beta$-$Ta_2O_5$, as well as to other Ta-O-N structures. These diffraction results are typical of films which were deposited at different carousel rotation speeds and which could be recrystallized by heating at 500° C. The major difference in the films deposited at different carousel speeds is the time required for recrystallization to occur at 500° C. For films deposited at a carousel rotation speed of 20 rpm, recrystallization occurred after 15 min, while for a carousel rotation speed of 1 rpm recrystallization occurred after 30 min. For films deposited onto a stationary carousel, recrystallization had not occurred by 45 min. Fig. 5b and c shows the bright-field and dark-field micrographs corresponding to the diffraction pattern of Fig. 5a. These micrographs show a grain size of about 500 Å.

The effect of heat-treatment on the films was further investigated by heating the films at 500° C in an air ambient and measuring the film conductance at room temperature as a function of the heat-treatment time. Fig. 6 shows the conductance decrease as a function of the square root of the heat-treatment time. The curve for films sputtered onto a stationary carousel is linear for the complete measurement time. For films deposited onto a carousel rotating at 1 rpm,

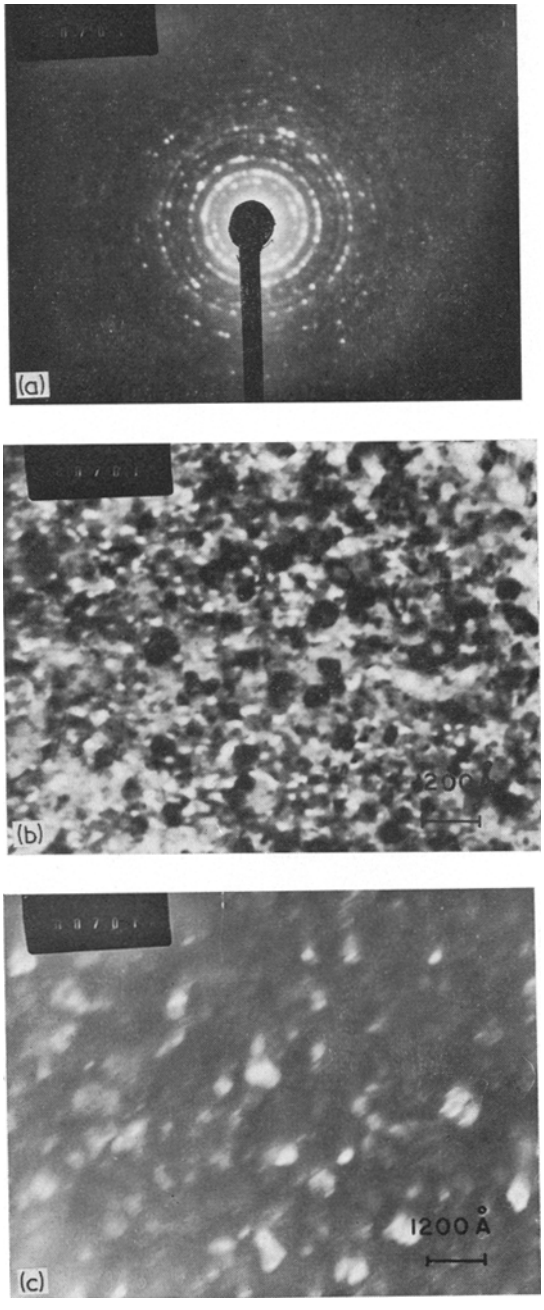


*Figure 5* Transmission electron microscopy results for a heat-treated film sputtered during carousel rotation at 1 rpm. (a) diffraction pattern, (b) bright-field micrograph, (c) dark-field micrograph.

TABLE III Comparison of measured $d$-values with standard $d$-values for $\beta$-Ta and $\beta$-$Ta_2O_5$.

| Measured film $d$-values (Å) | $\beta$-Ta standard | | $\beta$-$Ta_2O_5$ standard | |
|---|---|---|---|---|
| | $d$-value (Å) | $hkl$ | $d$-value (Å) | $hkl$ |
| 5.45 | 5.38 | 100 | | |
| 3.95 | | | 3.87 | 001 |
| 3.16 | | | 3.15 | 110 |
| 2.79 | 2.80 | 103 | | |
| 2.55 | 2.50 | 201 | | |
| 2.28 | 2.25 | 104 | | |
| 2.10 | 2.14 | 212 | | |
| 2.00 | 2.00 | 005 | 2.02 | 211 |
| 1.87 | 1.81 | 204 | 1.83 | 020 |

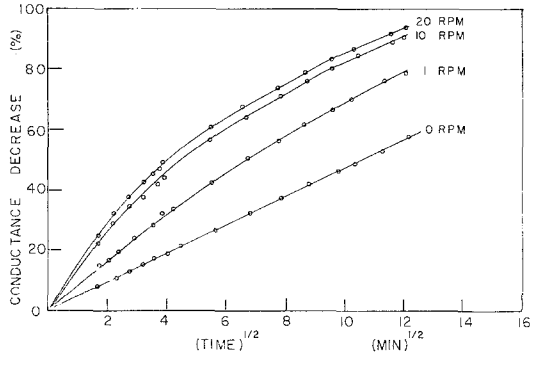


*Figure 6* Conductance decrease produced by heat-treatment of Ta films at 500° C in an air ambient as a function of the square root of the heat-treatment time.

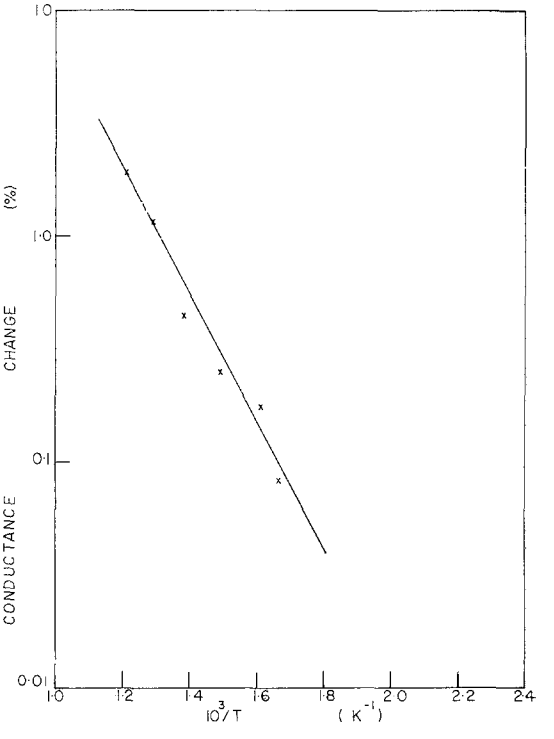


*Figure 7* Arrhenius plot of the conductance change produced by heat-treatment of a Ta film deposited onto a stationary carousel. The heat-treatment was done in an air ambient.

the experimental points can be approximated by a linear relationship for the first 10 min. For longer times the curve becomes non-linear. For films sputtered onto a carousel rotating at either 10 or 20 rpm, the curve is non-linear for the entire measurement time.

Fig. 7 shows an Arrhenius plot of the conductance change of a film deposited onto a stationary carousel, but heat treated at various temperatures in an air ambient. All conductance measurements were made at room temperature. The measured activation energy for the conductance change is 1.2 eV.

## 4. Discussion

### 4.1. Non-heat-treated films

The oxygen content of the films is shown to increase and the nitrogen content of the films to decrease with increasing rotation speed. Since the resistivity and TCR of Ta films reactively sputtered in oxygen and nitrogen simultaneously are mainly determined [2] by the oxygen content in the films, and since the resistivity increases and the TCR becomes more negative with an increasing oxygen content, it is proposed that it is this change in impurity concentration which largely produces the change in electrical properties with carousel rotation speed. The fact that the observed increase in oxygen concentration in the films does not produce a correspond-

ing decrease in film density might be attributed to the simultaneous decrease in the nitrogen content of the films, producing a compensating increase in film density.

During deposition onto a rotating carousel, a layer of Ta is deposited and this freshly deposited layer then rotates out of the discharge region and into a region of an oxygen-nitrogen ambient. In this latter region, oxygen and nitrogen can be adsorbed by the top surface of the freshly deposited Ta. These adsorbed gases can then be incorporated into the film the next time it passes through the discharge. The greater the carousel rotation speed, the greater is the number of times a freshly deposited Ta surface is exposed to the oxygen-nitrogen ambient outside the discharge, and thus the greater is the impurity content in the films. It has been shown [8] by monitoring the sputtering process with a mass spectrometer that oxygen is adsorbed more rapidly and desorbed more slowly by sputtered Ta films than is nitrogen. This indicates that oxygen is the more strongly bound species, and suggests that an increasing oxygen exposure with an increasing carousel rotation speed may cause some of the adsorbed nitrogen to be displaced, accounting for the increasing oxygen content and decreasing nitrogen content in the films with increasing carousel rotation speed.

The electron micrographs of non-heat-treated films illustrate that the physical structure of the films becomes elongated with an increase of carousel rotation speed during sputtering. A similar observation has been made for NiCr films [9] sputtered in the same apparatus. In analogy to the NiCr films, the worm-like structure which is observed for Ta films may be attributed to oblique incidence effects as the substrate rotates into, and out of, the discharge. The increased degree of elongation of the Ta films with increasing carousel rotation speed may be due to the increased surface oxygen concentration since the adatom surface mobility is expected to decrease with an increase in the surface oxygen concentration [10] and oblique incidence effects, to which the elongated worm-like structure is attributed, will increase as the adatom surface mobility decreases [10].

The diffuse electron diffraction patterns obtained from the present films are to be contrasted to the diffraction patterns of sharp rings [2] which have been obtained from films sputtered in the same bell jar at the same partial pressures of oxygen, nitrogen and argon, but using a conventional diode system in which the substrates are heated to 400°C prior to deposition. The present diffuse patterns may be a result of deposition onto unheated substrates since such deposition in a conventional diode system results in diffuse diffraction rings for Ta films [11]. This observation is in agreement with the results of other authors who have found that films of other transition metals (Nb [12], W [13], Mo [14]) deposited onto room temperature substrates produce a diffuse diffraction pattern, whereas deposition of these films onto substrates at 250 to 400°C results in a sharp, polycrystalline diffraction pattern.

Sputtering Ta films onto a rotating carousel is advantageous in that it is possible to obtain a higher resistivity for a given TCR than for the sputtering of films at the same partial pressures in a conventional diode system, e.g. for a TCR of $-265$ ppm $°C^{-1}$, films deposited in the present equipment have a resistivity of $2.5 \times 10^3$ $\mu\Omega$ cm as opposed to a resistivity of $1.5 \times 10^3$ $\mu\Omega$ cm for films deposited in a conventional system [2]. This increased resistivity is expected to be due to the worm-like structure of the films, rather than due to differences in substrate temperature during deposition in the different systems since it has been shown [15] that for Ta films reactively sputtered in oxygen that the film resistivity for a given TCR is independent of substrate temperature, but depends mainly on the oxygen content of the films.

### 4.2. Effects of heat-treatment

The fact that the diffraction patterns which are obtained from non-heat-treated films are diffuse makes it difficult to identify the material present in the films on the basis of crystallographic structure. However, the time required for recrystallization to occur will give some information about the structure of the films since a given phase will possess a unique recrystallization time at a given temperature [16]. The 15 min period at 500°C which was required for the recrystallization of $Ta_2O_5$ in films deposited at a carousel rotation speed of 20 rpm agrees with that previously found for $Ta_2O_5$ in sputtered Ta films [2] and also in bulk form [17]. This indicates that amorphous $Ta_2O_5$ is present in films deposited during carousel rotation at 20 rpm. By the same argument, the longer recrystallization times for films deposited at other carousel rotation speeds indicate that these non-heat-treated films do not contain amorphous

$Ta_2O_5$. Since these latter films contain less oxygen than the former films, and, in addition contain crystalline $Ta_2O_5$ after a sufficiently long heat-treatment, it is suggested that the non-heat-treated films deposited at 0, 1, or 10 rpm may contain sub-oxides, as have been previously observed [2, 18] for sputtered Ta films. In the present case, these sub-oxides may undergo dispropination during heat-treatment.

In addition to $Ta_2O_5$, the recrystallized films contain $\beta$-Ta. The different recrystallization times indicate different crystallographic structures before heat-treatment, but due to the lack of knowledge of the recrystallization conditions for $\beta$-Ta, it is not possible to determine if $\beta$-Ta is present in any of the films prior to heat-treatment. The presence of $\beta$-Ta following heat-treatment was not observed in films sputtered in the same oxygen and nitrogen partial pressures in a conventional diode system [2]. It is difficult to establish a reason for this difference since it is not known whether $\beta$-Ta films are the result of deposition in a very clean vacuum system [19] or are the result of reactive sputtering [20], or whether $\beta$-Ta is a distinct crystallographic phase [6] or is a result of interstitial ordering [21] in what is basically a bcc lattice. However, since it has been shown [1] that the application of a negative substrate bias during sputtering will inhibit the formation of $\beta$-Ta, the lack of bias in the present case, contrasted with the use of bias in the conventional diode system [2], may account for the formation of $\beta$-Ta in the present case only.

The films which undergo a change of TCR during heat-treatment (Table I) correlate well with those films which undergo structural changes as observed by electron microscopy. The TCR of films deposited at a carousel rotation speed of 0 or 1 rpm is not changed by a 15 min heat-treatment at 500°C, nor is the structure of the films changed by such a heat-treatment. In contrast to this behaviour, both the structure and TCR of films deposited at 20 rpm are changed by this heat-treatment, indicating that the change in TCR is associated with recrystallization of the films.

In contrast to this behaviour of film TCR with heat-treatment, the resistivity of all films investigated increases during the 15 min heat-treatment, independently of whether or not changes were observed in the film structure. Further investigation of this effect shows that the time dependence of the change in film conductance depends on the carousel rotation speed (Fig. 6). For films deposited at a carousel rotation speed of 20 rpm, recrystallization occurs after 15 min at 500°C and the conductance change is a non-linear function of the heat-treatment time. For films deposited during carousel rotation at 1 rpm recrystallization occurs after 30 min of heat-treatment, and the conductance change is a linear function of the square root of the heat-treatment time for about 15 min, after which the relationship becomes non-linear. As opposed to this behaviour, films deposited onto a stationary carousel have not recrystallized after 35 min of heat-treatment and the conductance change is a linear function of the heat-treatment time for at least 150 min. This linear relationship between conductance change and the square root of the heat-treatment time suggests that surface oxidation [2] of the film is occurring. Evidence for a surface oxidation mechanism is obtained from the agreement of the activation energy of the process producing the conductance change (1.2 eV) with the activation energy of 1.3 eV for surface oxidation [2] of Ta films. The non-linearity in the conductance decrease as a function of the square root of the heat-treatment time for films deposited onto a rotating carousel is attributed to the recrystallization mechanism which increases the film conductance acting in conjunction with the surface oxidation mechanism which decreases the film conductance.

The greater conductance decrease which occurs during heat-treatment with an increasing carousel rotation speed, for a fixed film thickness (Fig. 6), indicates that the surface oxidation rate increases with increasing carousel rotation speed. These results are in agreement with the results of Werner and Worobey [22] who found that the stability of sputtered tantalum oxy-nitride films during heat-treatment decreased as the oxygen concentration increased and the nitrogen concentration decreased. Since the parabolic rate constant is directly related to a diffusion coefficient [23] it is suggested that the change in oxidation rate may be related either to the increased oxygen and decreased nitrogen concentrations with an increase in carousel rotation speed, or to differing structures in the films as indicated by different recrystallization times.

An Arrhenius plot of the film conductance (Fig. 2) indicates that electrical conduction in the films does not occur by a single mechanism. Since pure $\beta$-Ta films have a negative TCR of

$-150$ ppm $°C^{-1}$ [24] it is suggested that the two observed conduction components may be conduction within the $\beta$-Ta grains and conduction within the oxide regions. Conduction within the oxide regions is expected to have a large negative TCR [10], and will thus make the net film TCR more negative than that obtained for pure $\beta$-Ta films.

## 5. Conclusions

Ta thin film resistors have been d.c. diode sputtered in a system in which the substrates are mounted on a carousel in such a way that the substrates can rotate through the discharge. The films were sputtered in a partial pressure of $1.5 \times 10^{-5}$ Torr oyxgen and $1.5 \times 10^{-5}$ Torr nitrogen as a function of carousel rotation speed. For non-heat-treated films, the resistivity increases and the TCR becomes more negative as the rotation speed increases. Microprobe analysis demonstrates that an increase in the carousel rotation speed produces an increase in the oxygen content of the films and a decrease in the nitrogen content. Since it has been shown that oxygen has a greater influence on film properties than does nitrogen, this increase in oxygen content of the films may be responsible for the observed changes in electrical properties since an increase in oxygen content will produce an increase in resistivity and a more negative TCR. The increase in oxygen content with carousel rotation speed is attributed to the fact that the number of layers of freshly deposited Ta which are exposed to the oxygen environment is increased as the carousel rotation speed is increased. Since oxygen is more tightly bound to Ta than is nitrogen, the increase in adsorbed oxygen may displace some nitrogen which would otherwise be adsorbed, thereby reducing the nitrogen content of the film as the carousel rotation speed is increased. Transmission electron microscopy indicates that the physical structure of the films becomes elongated with an increase in carousel rotation speed, probably as a result of oblique incidence effects which occur during rotation of the substrate into and out of the discharge. These structural perturbations may be expected to be responsible for the fact that films produced in this system have a larger resistivity for a given TCR than do films sputtered in the same partial pressures of oxygen and nitrogen in a conventional diode system.

Heat-treatment of the films at 500°C produces recrystallization of the films, the time required for recrystallization depending on rotation speed. Recrystallized films consist of a mixture of $\beta$-Ta and $\beta$-$Ta_2O_5$. The film resistivity increases with heat-treatment time. For films which have not recrystallized, the resistance change during heat-treatment is shown to be due to surface oxidation of the films since the corresponding conductance change follows a parabolic time law and has an activation energy equal to that for oxidation of Ta. For films in which recrystallization does occur, a parabolic law is not observed for the conductance change during heat treatment, indicating that a conductance increase due to recrystallization occurs in conjunction with the conductance decrease produced by the surface oxidation mechanism.

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