

# Critical oxygen content in porous anodes of solid tantalum capacitors

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X-ray diffraction analysis of sintered porous anodes of solid tantalum capacitors and the current-voltage ( $I-V$ ) characteristics of  $Ta_2O_5$  amorphous layers formed on the anode surface have been performed. A strong correlation between a sharp increase of direct current in the  $I-V$  characteristics at some critical oxygen content and the creation of a saturated solid-phase solution of oxygen in tantalum was found. The appearance of a crystalline oxide  $Ta_2O_5$  phase was detected in porous anodes at oxygen contents above the critical oxygen level. The decrease of effective radius below  $1\ \mu m$  of Ta powder particles used in sintering leads to the size effect: the oxygen content in the porous anode after sintering exceeds the solubility limit. © 1998 Kluwer Academic Publishers

## 1. Introduction

Solid tantalum capacitors (STC) are widely used in modern electronic devices. Their advantage over other capacitors are high specific charge per unit volume or mass, low direct current and high reliability which are achieved due to unique structural and electrical properties of STC basic layers [1]. Porous anode sintered in vacuum from a fine tantalum powder provides a high anode surface area. Thin dielectric amorphous  $Ta_2O_5$  film, formed by electrochemical oxidation of the Ta anode, has high dielectric permeability and high dielectric strength. The semiconductor  $MnO_2$ , serving as a cathode, possesses a solid electrolyte property, providing long time stability of the capacitor electrical parameters. The major trend in STC fabrication is the reduction of the effective radius,  $r$ , of the Ta powder particles which results in the increase of the surface area of the porous anode and thereby a corresponding increase in specific charge of the capacitors.

An important parameter of STC is a direct current leakage (DCL) which characterizes the quality of a dielectric layer. It is a direct current through the capacitor when a d.c. voltage is applied. It is well known that DCL in STC is virtually independent of the oxygen content,  $C_o$ , below some critical value,  $C_{oc}$ , and sharply increases for  $C_o \approx C_{oc}$  [2, 3]. In the limit of very high oxygen content  $C_o \gg C_{oc}$ , DCL saturates.

Although the existence of the critical oxygen content and its possible interpretation were discussed

in previous reports [2, 3], evidence of the critical phenomenon connected to the observed behaviour of the DCL has never been provided experimentally. In the present work we report on a structural phase transition which occurs at the critical level of oxygen content in sintered anodes. We show that for  $C_o = C_{oc}$  the solid-phase solution of oxygen in Ta becomes saturated at room temperature and Ta oxide crystallites begin to form in the Ta anode leading to the degradation of anodic Ta oxide. Moreover, we found that for  $r$  smaller or of the order of  $1\ \mu m$  the oxygen content  $C_o$  in sintered anodes exceeds the critical level  $C_{oc}$ . This sets bounds for the utilization of very fine powders with submicrometre particles.

## 2. Experimental procedure

In our investigations we used Ta powder grades with different  $r$  values from  $1.2\ \mu m$  to  $4\ \mu m$ . The original oxygen content in the powder was from  $1.2 \times 10^4$  p.p.m. to  $1.6 \times 10^4$  p.p.m. The powders were sintered into porous pellets at temperatures in the range 1750–2000 K in a vacuum of  $\sim 1.3 \times 10^{-4}$ . The oxygen content in sintered anodes was in the range  $1.8$ – $5.0 \times 10^4$  p.p.m. depending on powder grade and sintering conditions. Oxygen content in sintered anodes was measured using a LECO EF-500 oxygen/nitrogen chemical analyser. In this technique Ta powder or Ta pellets are placed in carbon crucibles and heated in vacuum. The evaporated oxygen reacts

with carbon, and the formed carbon oxides are analysed by IR absorption spectra.

In our studies we performed X-ray diffraction (XRD) examination of porous anodes and analysis of current-voltage ( $I - V$ ) characteristics of  $Ta_2O_5$  layers formed on the anode surface. XRD characterization employed  $CuK_{\alpha}$  radiation on  $\alpha\theta:\theta$  powder diffractometer "Scintag", equipped with a Ge solid state detector cooled by liquid nitrogen. Amorphous  $Ta_2O_5$  films of  $0.13\ \mu m$  thickness were formed by electrochemical oxidation of sintered anodes in  $0.01\ M$  water solution of phosphoric acid at room temperature.  $I - V$  characteristics were measured in a galvanic cell with  $1\ M$  water solution of phosphoric acid and tantalum cathode.

### 3. Results and discussion

XRD profiles were obtained for eight Ta anodes with  $r = 2.1\ \mu m$  and different oxygen content. Fig. 1 shows the positions of (211) diffraction maxima for three different values of oxygen content. The shift in the positions of the peaks allowed us to determine the variation of the lattice spacings (211) in Ta and to estimate a lattice parameter for different oxygen content in the Ta anode. It was found that the Ta lattice parameter increased with increase of the oxygen content in the anode and reaches its maximum value at the critical oxygen content. Further increase of oxygen content does not affect the Ta lattice parameter.

We performed electrical measurements on nine samples in the same range of oxygen content as in anodes used for XRD studies.  $I - V$  characteristics for the same three samples as in Fig. 1 are shown in Fig. 2. As clearly seen from the plot, the  $I - V$  curve is highly non-linear which is typical for amorphous dielectrics in strong electrical fields. Defining a DCL as a value of

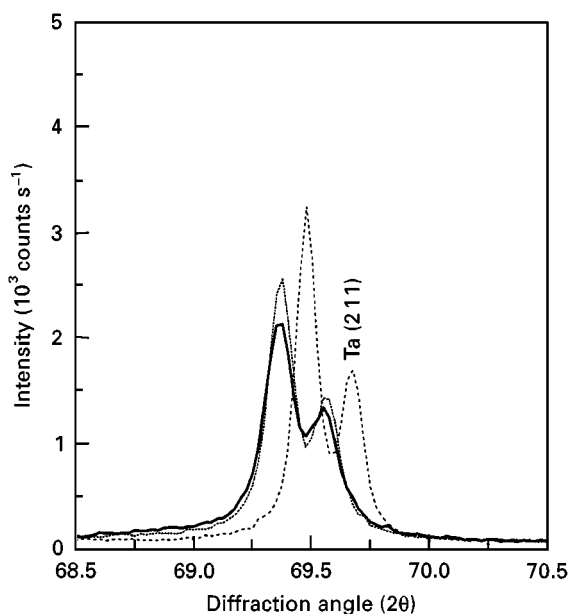


Figure 1 Tantalum (211) Bragg diffraction line obtained for anodes with effective particle radius of  $2.1\ \mu m$  and having different oxygen content, (---)  $3 \times 10^4$ , (—)  $3.4 \times 10^4$ , (-·-)  $3.6 \times 10^4$  p.p.m.

the current at  $50\ V$  we can plot DCL and lattice parameters versus oxygen content on the same graph for all our samples, see Fig. 3. The DCL curve (solid line) exhibits a sharp increase for oxygen content exceeding  $C_{oc} = 3.4 \times 10^4$  p.p.m. which defines an experimental value for critical oxygen content. The values of lattice parameter vary linearly with oxygen content for concentrations below  $C_{oc}$ . However, the saturation of the lattice parameter is clearly observed for  $C_o \geq C_{oc}$  at  $0.33166\ nm$ . Such a strong correlation in the behaviour of the DCL and lattice parameter at the  $C_{oc}$  cannot be accidental. Indeed, a careful XRD analysis of our samples with  $C_o > C_{oc}$  indicates the appearance of a crystalline phase of  $Ta_2O_5$  in Ta anode. Fig. 4 shows fragments of XRD profiles for two anodes, with oxygen content below and above  $C_{oc}$ , which clearly illustrate the peaks corresponding to the crystalline oxide  $Ta_2O_5$  phase for  $C_o > C_{oc}$ .

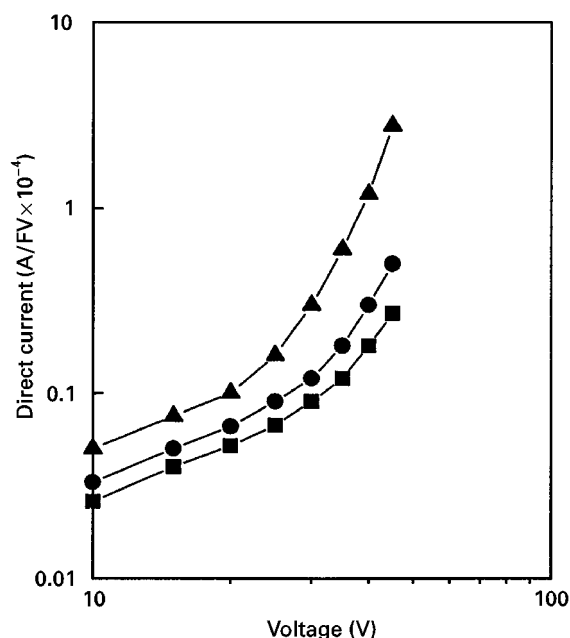


Figure 2 Dependence of the DCL on voltage for  $Ta_2O_5$  films formed on anodes with different oxygen content  $C_o$  (effective radius is  $2.1\ \mu m$ ), (■)  $3 \times 10^4$ , (●)  $3.4 \times 10^4$ , (▲)  $3.6 \times 10^4$  p.p.m.

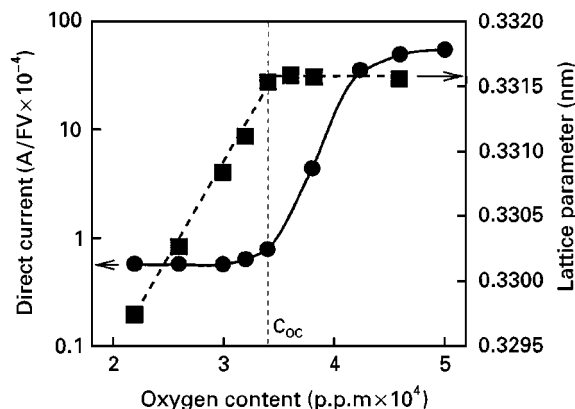


Figure 3 Dependences of the DCL (●) (at  $50\ V$ ) and the Ta lattice parameter (■) versus oxygen content in the porous anodes with effective particle radius of  $2.1\ \mu m$ .

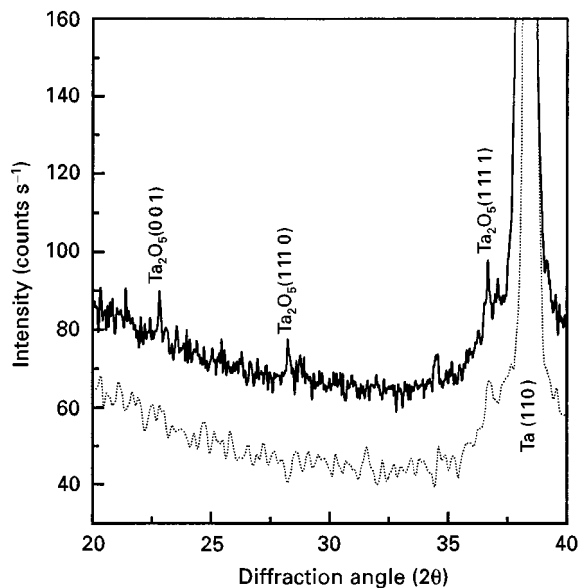


Figure 4 Fragments of XRD profiles for anodes with high (—)  $3.6 \times 10^4$  p.p.m.) and low (---)  $3 \times 10^4$  p.p.m.) oxygen contents and effective particle radius of 2.1  $\mu\text{m}$ .

Since the solubility limit of oxygen in Ta is much higher at the sintering temperature than at room temperature, precipitation of oxide phases from the solid solution of oxygen in tantalum may occur during the cooling stage.

The presence of the  $\text{Ta}_2\text{O}_5$  crystallites in the Ta anode obviously will affect the dielectric properties of the oxide layer formed by electrochemical oxidation of the anode. They will act as crystallization nuclei for the amorphous  $\text{Ta}_2\text{O}_5$  film, initiating the formation of crystalline  $\text{Ta}_2\text{O}_5$  inclusions in the dielectric layer. An electrical conductivity of these crystalline inclusions is higher than that of amorphous  $\text{Ta}_2\text{O}_5$  matrix because of the higher mobility of charge carriers. This explains why an appearance of crystalline inclusions in  $\text{Ta}_2\text{O}_5$  amorphous film causes the increase of DCL.

The difference in conductivity of amorphous and crystalline  $\text{Ta}_2\text{O}_5$  phases is most significant in a strong electrical field because of peculiarities of charge transport in disordered amorphous dielectrics [4]. This is why we chose to present DCL values in Fig. 3 for the highest voltages, namely 50 V.

Our measurements performed on anodes with different effective particle radii have shown that critical oxygen content,  $C_{oc}$  increases inversely proportional to  $r$ . However, this result does not imply that anodes containing smaller particles are less sensitive to oxygen. The observed dependence of  $C_{oc}$  has a trivial geometrical origin. Since oxygen content in anodes measured by the chemical oxygen analyser has contributions coming from the natural surface oxide and oxygen dissolved in the volume of the particles, we expect a  $1/r$  dependence of surface to volume ratio. Hence, for the same concentration of solid oxygen solution in the volume of Ta particles, we expect to have larger measured values of  $C_o$  as  $r$  becomes smaller. Our X-ray results on determination of the Ta

lattice parameter for anodes with critical oxygen content were the same for all  $r$ , which conforms to a saturated solid solution of oxygen in tantalum at room temperature.

Our  $I$ - $V$  tests of capacitors with  $r$  below 1  $\mu\text{m}$  show large DCL values which suggest that for such fine particles the oxygen content exceeds a critical level. We believe that it is a consequence of a technological process used in fabrication of fine particle capacitors. During powder sintering surface oxide is dissolved in the particles volume [5]. The additional bulk oxygen content in the Ta particles caused by this process is inversely proportional to  $r$ . For the small  $r$  values, the sintering temperature of the powder is chosen to be lower to prevent anode shrinkage. The low sintering temperature does not allow the oxygen re-evaporation from the Ta during the sintering process. These two factors, namely, the increase of surface/volume ratio and decrease of the sintering temperature, lead to the size effect for very fine Ta powders: cumulative oxygen content in the bulk of the Ta particles with  $r < 1 \mu\text{m}$  is close to or even exceeds the solubility limit at room temperature. This effect limits a further decrease of the particle radius in manufacturing of solid tantalum capacitors.

#### 4. Conclusions

In summary, we observed saturation of a solid solution of oxygen in Ta at a critical oxygen content  $C_{oc}$  and the structural phase transition in Ta porous anode at oxygen contents exceeding the critical value  $C_{oc}$ . The appearance of a new phase of crystalline  $\text{Ta}_2\text{O}_5$  at an oxygen concentration above the solubility limit causes the degradation of Ta anodic oxide and makes the use of Ta powders with fine particles,  $r < 1 \mu\text{m}$  questionable.

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