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Electrochemical study of anodic oxide layers of tantalum

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**Electrochemical study
of anodic oxide layers of tantalum**

DISSERTATION

submitted to the
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6. SUMMARY AND CONCLUSIONS

1. The anodic formation of tantalum oxide, used in modern electrolytic capacitors, has been studied by electrochemical methods. The work was focused on the initial stages of the anodization, i. e. on very thin layers and on low currents; both have received little attention in the literature so far. The experiments were carried out under galvanostatic (constant-current) or constant-voltage conditions. Both the steady and nonsteady states were investigated. In the steady-state galvanostatic anodization the potential increases continuously with time because of the growth of the oxide layer. The nonsteady-state conditions were realized by suddenly changing the voltage or the current.
2. It was found that the surface treatment prior to the application of the current strongly affects both the steady- and the nonsteady-state results. Chemically polished, sandpapered and "as received" Ta wires were used. The first ones gave the best oxide films (from the viewpoint of electrolytic capacitors). In this case at constant current the anodization potential V (and thus the film thickness) increased steadily with time t at a relatively high rate so that high anodization potentials can be reached even at current densities as low as $0,4 \mu\text{a}/\text{cm}^2$.
3. It was shown that two kinds of electric current can flow through the oxide, an ionic and an electronic current, the latter becoming relatively important (and sometimes quite predominant) at low currents. This applies particularly to the sandpapered and "as received" Ta wires. The existence of an electronic current and its characteristics are of importance in connection with the leakage current of electrolytic capacitors.

The following experimental evidence indicates that a change in the conduction mechanism (from ionic to electronic) takes place under certain conditions:

a/ The slope of the steady-state galvanostatic V - t lines decreases above a characteristic voltage indicating a decrease in the growth rate of the oxide and thus a decrease of the current efficiency of the oxide formation. This is best interpreted by assuming that electrons are now provided to the oxide layer by an electrochemical reaction taking place at the oxide/solution interface. The transport of these electrons through the oxide does not increase

the thickness of the layer in contrast to the transport of ions which necessarily corresponds to a growth of the layer in the absence of Ta dissolution.

b/ The potential at which the break in the V-t line occurs in a 1% H_3PO_4 solution corresponds indeed approximately to the oxygen evolution potential in this solution. The potential of the break can be shifted toward less positive values by adding to the electrolyte redox systems which make electrons available at less positive potentials: With ferro/ferricyanide it is lowered by ca. 1,4 v and with ferro/ferri sulphate by ca. 0,9 v. This is in good agreement with what to be expected on the basis of the redox potentials of these systems.

c/ Constant-voltage experiments were also carried out in which thick layers of about 1300 \AA were formed at 78 v (SCE) on chemically polished tantalum and afterwards the voltage was stepwise decreased to a few volts. The steady-state current first decreased more or less exponentially with the voltage (as it is expected for the ionic current) but became finally proportional to the current in a number of cases, i.e. Ohm's law holds at sufficiently low voltages. A calculation based on the usual theory of ion transport through anodic oxide layers shows that even at the lowest voltages used the validity of Ohm's law cannot be due to the fact that the backward current becomes comparable to the forward current (i.e. that one is approaching equilibrium) but rather speaks for a change in the conduction mechanism. The ohmic resistance of the film can be calculated from the slope of the linear part of I-V curve yielding about $10^9 \Omega \text{ cm}^2$ in a typical case. This represents probably the resistance to the electronic (not to the ionic) current. The value of this resistance as well as the length of the linear part of the curve appear to depend strongly on the quality of the film.

d/ If we regard in the galvanostatic experiments the slope of the V-t line as representative for the current efficiency, we can calculate from this slope the ratio of the ionic to the electronic current i/i_e after the break in the V-t lines (3.a/). In some cases (with the ferricyanide system) this ratio was as low as 10^{-3} . At a given anodization potential it increases, in general, with increasing current density. This is easily understood if the ionic current increases faster with voltage than the electronic current (for the thick films it seems indeed that the ionic current increases exponentially whereas the electronic current obeys Ohm's law as mentioned in 3.c/).

In the galvanostatic experiments involving very thin films low i/i_e ratios were obtained only with sandpapered and "as received" tantalum. However, even with the chemically polished metal there is a slight change in the slope of the galvanostatic V-t line at $0,4 \mu\text{a}/\text{cm}^2$ in the region of the oxygen evolution potential. This fact, as well as the results of the constant-voltage experiments summarized under 3.c/ suggest that even with the chemically polished metal the electronic current can become important provided the total current is sufficiently low.

e/ In the experiments carried out under nonsteady-state conditions it was found that the galvanostatic transients are modified in a characteristic manner in the region of the break of the V-t lines (see 4.e/). This also indicates that the conduction mechanism changes then.

4. a/ A set-up was constructed to change suddenly the current from one constant value to another one (galvanostatic transients) or from one constant voltage to another one (constant-voltage transients) and to record the corresponding change of potential (or current) with time. In the galvanostatic transients the potential goes through a maximum (i.e. overshoot), and a subsequent minimum before the new steady rate of potential increase is finally reached. The excess voltage EV (the difference between the anodization potential at the maximum and the steady-state potential extrapolated backward) and τ_2 (the elapsed time between the maximum and the minimum) were determined under various conditions as a function of steady-state anodization potential which represents the film thickness at a given current. The results were compared with Dewald's theory where the carriers of the ionic current are assumed to be interstitial Ta ions the concentration of which depends on the field (and thus on the current); its equilibrium value at the higher current is reached, however, relatively slowly, thus causing the overshoot. In the present work, a quantitative relationship between τ_2 and the thickness (i.e. anodization voltage) was derived from Dewald's equations.

b/ The excess voltage EV was found to increase linearly with the steady-state anodization potential V according to equation

$$EV = (2,68 \pm 0,06) \cdot 10^{-2} V + 2,3 \pm 1,3 \quad [31]$$

obtained by the least square method.

This indicates that the excess field does not depend on the film thickness. This is in agreement with Dewald's theory.

c/ The time of decay τ_2 was found to be also proportional to the anodization potential. This is in disagreement with the logarithmic relationship derived from Dewald's model. A possible explanation would be that Dewald's assumption of the absence of space charge in the oxide film does not hold for the very thin films studied here. It is to be noted, however, that the EV-V straight line does not show any break in the range of film thicknesses investigated (10 - 100 Å). This suggests that the situation in very thin films of the order of 10 - 20 Å is not essentially different from that in thicker films.

d/ Well developed overshoots were observed on oxide films already at 0 v (SCE) anodization potential, i.e. about 15 Å film thickness. Also, the prolongation of the EV-V straight line intersects the abscissa at a potential approximately 200 mv more positive than the reversible oxidation potential of tantalum. These tend to indicate that even in these very thin films the main resistance to the charge transport does not lie at the metal/oxide or oxide/electrolyte interface (as assumed in certain theories) but rather within the layer itself.

e/ The excess voltage and τ_2 decrease whenever the slope of the steady-state V-t line starts to decrease (3.a/). In some cases the overshoot and thus EV and τ_2 completely disappear. After the change in slope of V-t line the excess voltage may increase again but it remains small when the slope of the V-t line after the break is small, i.e. when the electronic current strongly dominates. This tends to indicate that only the ionic current exhibits overshoots in contrast to the electronic current. In principle overshoot measurements could thus be used to distinguish between ionic and electronic current. This does not mean, however, that the excess voltage is halved when the relative value of the ionic current decreases, e.g. from 100 to 50%, because the excess voltage depends only on the ratio of the ionic currents before and after the current step. This ratio does not necessarily have to decrease and can even increase when the i/i_e ratio is small (the applied current step being kept constant). When the electronic current becomes strongly predominant the overshoot, however, is more or less completely suppressed because the step

is no longer galvanostatic for the ionic current (although the applied current is still galvanostatic).

f/ In addition to the aforementioned galvanostatic transients constant-voltage transients were also studied. The transient behavior observed under various conditions is discussed.

7. ZUSAMMENFASSUNG

1. Die anodische Oxidation von Tantal, die bei der Herstellung von Elektrolytkondensatoren angewendet wird, wurde mittels elektrochemischen Methoden untersucht. Die Arbeit befasst sich in erster Linie mit dem Anfangsstadium der Oxidation bei kleinen Stromdichten, die bis jetzt wenig untersucht wurden. Die Versuche wurden bei konstantem Strom (galvanostatisch) oder bei konstanter Spannung unter stationären sowie auch nicht stationären Bedingungen ausgeführt. Es wurde eine Apparatur entwickelt, welche gestattet, den Strom oder die Spannung plötzlich zu verändern und die instationären Einstellvorgänge zu registrieren.
2. Es wurde gefunden, dass die Vorbehandlung der Metalloberfläche die stationären sowohl als die nicht stationären Ergebnisse wesentlich beeinflusst. Chemisch polierte Oberflächen ergaben die vom Standpunkt der Elektrolytkondensatoren besten Oxidschichten.
3. Es wurde gezeigt, dass zwei Arten von elektrischen Strömen durch das Oxid fließen können, ein elektronischer und ein Ionenstrom. Der erstere wird bei kleinen Strömen erheblich und überwiegt dann manchmal gänzlich. Die Existenz und die Eigenschaften des elektronischen Stroms sind in Zusammenhang mit den Verlustströmen der Kondensatoren von Bedeutung.

Es wurde aus 5 verschiedenen Arten von Ergebnissen auf eine unter bestimmten Bedingungen eintretenden Aenderung im Leitungsmechanismus, von ionisch zu elektronisch, geschlossen. Es zeigte sich u.A., dass oberhalb einer charakteristischen Spannung die Geschwindigkeit der Zunahme der Spannung mit der Zeit kleiner wird, was auf eine Verminderung der Stromausbeute der Oxidbildung und somit auf das Vorhandensein eines Elektronenstroms hindeutet. Die charakteristische Spannung liegt in einer Phosphorsäurelösung etwa beim Po-

tential der Sauerstoffentwicklung. Sie wird durch Zugabe von Redoxsystemen nach wenigen positiven Werten verschoben: Bei Zugabe von Ferri-Ferrosulfat und Ferri-Ferrocyanid verschiebt sich die charakteristische Spannung in beiden Fällen so wie es auf Grund der Normalpotentiale der beiden Redoxvorgänge zu erwarten ist. Der Elektronenstrom kann eben erst fließen, wenn Elektronen der Oxidschicht durch eine elektrochemische Reaktion zur Verfügung gestellt werden und das Potential, bei dem dies geschieht, ist durch das Normalpotential des Vorgangs gegeben.

4. Bei plötzlicher Erhöhung des Stromes überschwingt die Spannung und geht durch ein Maximum. Die Höhe des Maximums und die Abklingdauer der Ueberschwingung wurden für verschiedene Bedingungen in Abhängigkeit von der Grundspannung (bzw. von der Schichtdicke) gemessen und die Resultate statistisch ausgewertet. Die Ergebnisse werden in verschiedener Hinsicht diskutiert. Aus der Theorie von Dewald wird eine quantitative Beziehung für den Zusammenhang zwischen Abklingdauer der Ueberschwingung und Grundspannung abgeleitet. Die Abhängigkeit der Höhe des Maximums von der Grundspannung entspricht der Voraussage der Dewaldischen Theorie, die Abhängigkeit der Abklingdauer dagegen nicht.

Die Höhe des Maximums wird jeweils kleiner in dem Potentialbereich, in dem die Stromausbeute der Oxidbildung abnimmt. In gewissen Fällen verschwindet dann die Ueberschwingung ganz. Es wird sehr wahrscheinlich gemacht, dass das Ueberschwingen der Spannung nur beim Ionenstrom, nicht jedoch beim Elektronenstrom auftritt, woraus sich im Prinzip eine einfache experimentelle Möglichkeit ergibt zwischen den beiden Stromarten zu unterscheiden.

Eine ausführlichere Zusammenfassung findet sich im englischen Text S. 88.