Transient Behaviors at a Constant Current for the Tantalum Anodic Oxide Film

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In order to evaluate the tantalum anodic oxide film for the solid capacitor, a constant current of 300 μA was applied to the sintered tantalum pellet which has been anodized in dilute phosphoric acid solution (1.7 kΩ·cm/20°C).

The transient behavior for the specimen after heating (250°C, 10 min) was deviated from that expected from the Dewald’s equation based on the Frenkel defect model, which indicated the deterioration of the film by the heating. The deterioration, however, could be repaired by the subsequent flow of a constant current after the heating, then the transient curve after reheating gave the normal shape derived from the equation.

Both the plots of maximum voltage vs. logarithm of the annealing time and maximum voltage vs. reciprocal of the annealing temperature, gave the linear relationships as was expected from the equation providing that the film had no weak spots.

1 Introduction

When a constant current is applied to the tantalum anodic oxide film, the field shows so-called “overshooting”, i.e. the field goes through maximum. Such behavior has been explained by the “Frenkel defect model” proposed by Bean, Fisher and Vermilyea, and later Dewald derived an equation for formation kinetics of the defects, although some questions were asked by Vermilyea himself and Young.

The purpose of this study was to confirm the Dewald’s equation for the anodic tantalum oxide film and further to examine the deterioration of the film by heating using the equation. The heating process is inevitable in the production of the solid tantalum capacitor because manganese dioxide must be formed on the film by pyrolysis of manganese nitrate. Thus the heating process is important in controlling the film properties. The deterioration of the film in this process was partly reported in the previous paper.

2 Experimental

Sintered tantalum pellets were used as the specimen. The preparation, the dimensions and the anodizing process were the same as that described in the previous paper. A constant micro anodic current was applied to the anodized specimen in a dilute phosphoric acid solution (1.7 kΩ·cm/20°C) at 20°C with a counter electrode of stainless steel and the voltage-time curves were measured. The apparatus was also the same as that described in our previous paper.

3 Results and Discussions

3.1 Explanation of experimental results in terms of the Frenkel defect model

It was found in our previous paper that the anodic oxide film was deteriorated by heating, but it could be repaired by subsequent flow of a constant current. When the film after the first heating was repaired by this method, the second heating didn’t cause the film to deteriorate. Apparent difference between the films after the first and the second heating (not pyrolysis) at 250°C for 10 min was shown in Fig. 1, in which a constant micro-current (300 μA) was applied to each film.

In both curves maximum voltages are observed. The fundamental reason for this behavior is considered as follows. In the well-known Eqs. (1) and (2) for the ionic conduction within the oxide film, field increases not only with increase of current density but also with decrease of the concentration of the mobile ions (m) in the film, while m is not constant but depends on E.

\[
i = 2a_r m + \nu_2 \exp \left[ \left( -W_2 + qa_1 E \right) / kT \right] \quad (1)
\]

\[
E = (kT/qa_2) \left[ \ln \left( i/2a_2 \nu_2 \right) + W_2/kT - \ln m \right] \quad (2)
\]

where \(i\) is current density, \(E\) is field strength within
2. Reaches to a steady state field. This is the qualitative should depend on under a constant current. The record instead of field in this experiment. The Frenkel defect. Accordingly, the theory, the net rate of generation of the Frenkel defect serves as ionic moving was considered to be

\[
dm/dt = (N_n - m) \nu, \quad \cdot \exp \left[\frac{-W_1 + qaE}{kT} \right] - \text{i}m \quad (3)
\]

where \( \nu, W_1 \) and \( a \) are the same signs as before except that subscript \( 1 \) is for the transference process of ions from the lattice sites to the interstitial one. \( N_n \) and the concentration of the lattice sites, hence \( \langle N_n - m \rangle \) represents the concentration of ions in the lattice sites.

This is nearly equal to \( N_n \) because \( N_n > m \). A cross-section of the vacant lattice sites is given by sign \( \sigma \).

The first term on the right hand of Eq. 3 represents the rate of generation of the Frenkel defects and the second term shows the rate of capturing of the interstitial ions to the vacant cation sites.

We derived further equations from Eq. 3 as follows. Equation (4) was obtained by equating \( dm/dt \) of Eq. 3 with that derived from Eq. 1.

\[
dE/dt = -A \cdot \exp (BE) + C \quad (4)
\]

where \( A=(2N_0 \nu_x q/kT) \cdot \exp \left[\frac{-(W_1 + W_2)}{kT} \right], \quad B=q(a_1 + a_2)/kT, \quad C=kTq/a_2.
\]

Then \( E \) was found by integration to be

\[
E = (1/B) \ln \left[ \frac{C \cdot \exp (BCt + Q)}{A \cdot \exp (BCt + Q) - 1} \right] \quad (5)
\]

where \( Q \) is the integral constant.

Eq. 5 shows that \( E \) reaches to a constant, \((1/B) \ln (C/A)\), as the time \( t \) elapses so as to becomes \( A \cdot \exp (BCt + Q) \gg 1 \). Differentiating Eq. (5) with \( t \), we obtained Eq. (6) and (7).

\[
dE/dt = C \left[1 - A \cdot \exp (BCt + Q) \right] \quad (6)
\]

\[
d^2E/dt^2 = \left[ABC^2 \cdot \exp (BCt + Q) \right] \left[1 - A \cdot \exp (BCt + Q) \right] \quad (7)
\]

where \( [1 - A \cdot \exp (BCt + Q)] < 0 \) because \( E \) must be positive number in Eq. 5. This indicates that \( dE/dt \) and \( d^2E/dt^2 > 0 \). Therefore \( E \) should continuously decrease with \( t \) until the steady state value. The rate of decrease is also diminished with \( t \) and a point of inflection is absent. Such consideration was compatible with the curve B, while not with the curve A in Fig. 1. In the curve A, a point of inflection appears, which indicates the incompatibility with the Dewald’s equation. If the Dewald’s equation is assumed to be correct, the curve A must be abnormal transient behavior but the curve B is normal one. This is the confirmations of the deterioration of the film by the first heating, the repair of the film by the subsequent current flow after the first heating and no deterioration of the film by the second heating.

Fig. 2 shows voltage-time curves at constant current (300 \( \mu \)A) for a specimen after heating at 100°C for 30 min. In this case curves A (after the first heating) and B (after the second heating) are overlapped each other and show normal transient behaviors. This means no deterioration of the film at such a low tem-

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**Diagram: A: After heating the anodized specimen  
B: After reheating the specimen at point P on the curve A**

Fig. 1 Voltage-time curves at 300 \( \mu \)A for the specimen after the heating

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the oxide film, i.e. potential across the film divided by the thickness of the film, \( a_1 \) is activation distance, \( m \) and \( \nu_2 \) are concentration and frequency of the mobile ions respectively, \( W_2 \) is activation energy in the absence of applied field, \( q \) is charge on the mobile ions and \( k \) and \( T \) are the conventional signs. The subscript 2 is used to refer to the parameters for the mobility of the interstitial ions. From Eq. 2, \( E \) should depend on \( m \) under a constant current. Bean, et al.\textsuperscript{1)}, assumed that the vacant cation sites are immobile but the interstitial ions are mobile and \( m \) increases with increasing \( E \). When a constant current is applied to the film, the field increases fairly rapidly with the charging. The initial field just after the charging corresponds to the field for \( m \) at zero field because the rate of variation of \( m \) with the field is not so rapid as the charging rate. The field then decreases rather slowly with increase in \( m \) and finally reaches to a steady state field. This is the qualitative explanation for the maximum fields observed in the curves in Fig. 1. For convenience, cell voltage was recorded instead of field in this experiment. The cell voltage would be almost proportional to the field because the components of the cell voltage other than the field within the film would be relatively small under the high field adopted in the present experiment, besides the variations of their components with time would be negligibly small.

Although maximum voltages were observed in both curves in Fig. 1, considerable difference was found between the two, in which lower maximum voltage and slower rate of decrease of the voltage were found in the curve A. In this section the difference was examined by using the Dewald’s equation based on the Frenkel defect model. According to the theory, the net rate of generation of the Frenkel defect which
As will be reported in our following paper, we found from the transient behavior at a constant voltage that the first term on the right hand of Eq. 3 was incorrect and it had to be replaced by

\[ m(N_s - m_v) \exp \left[ - (W_i - qa_i E) / kT \right] \]

In our improved equation, however, the same results as \( \frac{dE}{dt} = 0 \) and \( \frac{d^2E}{dt^2} > 0 \) were also derived.

### 3.2 Confirmation of the term "iem" in the Dewald's equation

The next problem was to confirm the second term on the right in Eq. 3, i.e. \( iem \). For this purpose, the influences of annealing (heating) on the transient behavior were examined. The theoretical treatments were the same as that reported by D.A. Vermilyea\(^{15}\).

The outline is as follows. In the annealing, Eq. 3 can be rewritten as Eq. (8) because \( E \) is equal to zero.

\[
dm/dt = N_i v_i \exp \left[ - (W_i / kT) \right] - 2a_i m_{i} v_{i} \exp \left[ - (W_s / kT) \right] \tag{8}
\]

where \( T \) is annealing temperature. Neglecting the thermal rate of generation of the interstitial ions, i.e. the first term on the right,

\[
dm/dt = - 2a_i m_{i} v_{i} \exp \left[ - (W_s / kT) \right] \tag{9}
\]

The integration of Eq. 9 gives Eq. 10.

\[
m(t) = m_i (1 + m_i K) \tag{10}
\]

where \( K = 2v_i a_i \exp \left[ - (W_s / kT) \right], m_i \) and \( m(t) \) are the concentrations when the annealing time is zero and \( t \) respectively. The current \( i \) which flows in the film containing carriers concentration of \( m(t) \) after annealing in the electrolyte at temperature \( T' \), is

\[
i = 2a_i m(t) v_i \exp \left[ - (W_s / kT') \right] \exp \left[ qa_i E / kT' \right],
\]

so that

\[
E = \left( kT' / qa_0 \right) \ln \left( i / 2a_i m_i v_i \right) + W_s / kT' + \ln \left( 1 + m_i kT \right) \tag{11}
\]

This field represents the instantaneous one, i.e. maximum field, at a constant current because this field is to be given by the film in the condition produced by the preliminary annealing.

Eq. 11 shows that a plot of maximum field or voltage against log (time of annealing) for a given annealing temperature should give a straight line of slope \( kT' / qa_0 \), when \( 1 \leq m_i K_t \). The condition, \( 1 \leq m_i K_t \), may be fulfilled when \( m(t) \) becomes negligibly small against \( m \) as can be seen from Eq. 10. Fig. 3 shows this relationship for an annealing at 100°C. A straight line is observed after 5 min of the annealing although the plots are slightly scattered. Deviation from the straight line below 5 min may be reasonable because \( m(t) \) doesn’t become negligible against \( m \), besides the specimen may not be held at a given temperature owing to the short time of annealing. From the slope of the straight line, \( a_i \), was roughly estimated to be 2.5 Å providing that \( q \) is equal to +5e and the formation rate is 16 Å/V\(^t\).

In the annealing at 250°C, however, \( V_{max} - \log t \) relationship wasn’t linear but was badly scattered as shown in Fig. 4, curve A. The maximum voltages...
plotted on this curve corresponded to that of the curve A in Fig. 1, hence this was not the normal $V_{\text{max}}$ because the film was deteriorated at 250°C heating. When the $V_{\text{max}}$ corresponding to that on curve B in Fig. 1 were plotted against $\log t$, curve B in Fig. 4 could be obtained. Linearity appears in this curve though only in the limited range ($PQ$). After 15 min of annealing, it is not linear. This indicates that even by the current flow after the first annealing, the film can not sufficiently be repaired if the annealing time becomes long. Even if it could be completely repaired, the second annealing might deteriorate the film in the long time of annealing. From the slope of $PQ$, $a_1$ was estimated to be 1.6 Å, which would be a reasonable value since it gives the half distance of the lattice constants of the tantalum oxide.

Eq. 11 also derived another information that $V_{\text{max}} - 1/T$ relationship would be linear when the annealing time was held constant at the various temperature although Vermilyea didn't refer to this. In this case $K$ becomes variable instead of $t$ in Eq. 11 because $K$ contains term $1/T$. The linearity was obtained as shown in Fig. 5. The maximum voltages at a given temperature were taken from those on the curves corresponding to curve B in Fig. 1, in which the film after the first annealing had been repaired by the current flow prior to the second annealing. Only the point at 250°C was found to deviate from the straight line. This means imperfect repair of the film in such a high temperature as was already mentioned. When the $V_{\text{max}}$ after the first annealing was plotted against $1/T$, linearity could hardly be obtained due to the deterioration of the film.

![Graph](image)

**Fig. 5** Relationship between reciprocal of the annealing temperature and maximum voltage at 300 µA

### 4 Conclusion

Transient behavior at a constant current for anodic tantalum oxide film was reasonably explained by the Dewald's equation based on the Frenkel defect model providing that the film had no weak spots. By utilizing this equation, it was found that the film was deteriorated by the annealing at high temperature, but it could be repaired by the subsequent flow of a constant current except over 250°C annealing.

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**References:**