R 345 *Philips Res. Repts* **13**, 277-295, 1958

ON THE RELATION BETWEEN CURRENT AND FIELD DURING ANODIC OXIDATION

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541.138.2:537.311.3

Summary

Starting from the assumption that an anodic oxide layer on metals like Al and Ta has an amorphous structure, a relation between field and current during anodic oxidation is derived. It appears that this relation is somewhat different from the exponential one usually derived in literature (Verwey, Mott). With these formulae, it is possible to explain the various results obtained with our experiments presented in this paper. Probably they may explain the rather different numerical results mentioned in literature in the same way. The consequences of the amorphous structure on a more detailed picture of the oxidation process, as proposed earlier, have also been calculated. The results point to a frequency dependence of one of the parameters as was actually observed in our experiments. The observed agreement between theory and experiments has made it possible to calculate approximately the parameters introduced in this theory.

Résumé

En tenant compte du fait que les couches d'oxyde, formées par oxydation électrolytique sur l'Al et le Ta, ont une structure amorphe, on déduit, à l'aide des méthodes déjà connues (Verwey, Mott), une relation entre le courant et le champ électrique. En écrivant la nouvelle rélation dans la forme $i = \alpha \exp(\beta F)$, le paramètre β ne dépend pas seulement de la température mais aussi de l'intensité du champ F. A l'aide de cette relation, les expériences décrites dans cet article peuvent être expliquées, et en même temps la cause probable des différences entre les valeurs α et β, données dans la littérature, est indiquée. Il paraît que dans le cas d'un champ alternatif la valeur de β dépend aussi de la fréquence. Ceci est confirmé par l'expérience. On calcule les valeurs des paramètres d'après la relation modifiée, ce qui donne des résultats satisfaisants.

Zusammenfassung

Berücksichtigt man die Tatsache, daß die mittels elektrolytischer Oxydation angebrachten Oxydschichten auf Al und Ta amorpher Struktur sind, so kann man auf bekannte Weise (Verwey, Mott) eine Beziehung zwischen Strom und Spannung ableiten. Schreibt man die neue Beziehung in der Form $i = \alpha \exp(\beta F)$, so hängt der Parameter β nicht nur von der Temperatur, sondern auch von der Feldstärke F ab. Mit Hilfe der Beziehung werden die in diesem Artikel beschriebenen experimentellen Resultate erklärt und werden auch die möglichen Ursachen der Unterschiede zwischen den in der Literatur gegebenen Werten für α und β angegeben. Es zeigt sich auch, daß der Wert für β von der Frequenz des angelegten Feldes abhängt. Dies wird durch das Experiment bestätigt. Man berechnet die Werte der Parameter nach der abgeänderten Berechnung und erhält befriedigende Resultate.

1. Introduction

When metals like Al, Ta and others are oxidized anodically, the current through the oxide layer shows during and after formation a marke dependence on the applied field F across the layer. This is a well-know fact and it has been the subject of a number of calculations and corresponding experiments 1). It is also the subject of the present paper.

Most calculations lead in one way or another to an expression of the form

$$i = a \exp \beta F. \tag{1}$$

The interpretation of a and β may be different in different theories. On the other hand the many experiments to determine a and β have introduced into literature a number of different values for the same metal, although all investigators are necessarily using the same range of currents which corresponds to about the same range of fields.

Now the present paper, section 2, suggests a correction to the existing theories 2) leading to eq. (1). It is connected with the amorphous structure of these oxide layers, which point of view recently 3) has proved to be succesful in respect to the dielectric behaviour of these layers.

In section 3, the special model of the oxidation process, as proposed by Bean, Fisher and Vermilyea 4) and extended by Dewald 5), has been worked out in view of our present experiments.

In sections 4 and 5 these experiments, with Al oxide layers and Ta oxide layers respectively, are described and analysed on the basis of the formalism of section 3. Finally the conclusions are given in section 6.

2. Preliminary remark

2.1. The theories of anodic oxidation always involve moving ions in a "landscape" of potential valleys 2). Although the following considerations can also be applied to the case of one essential barrier existing at one of the interfaces, we shall give special attention to the models in which the bulk of the oxide plays the important role. The time during which an ion remains in a particular potential valley with a depth q can be given by

$$\tau = \tau_0 e^{q/kT}, \tag{2}$$

τ_0 being a proportionality constant. If we simplify the process to a one-dimensional one, an external field F will increase or decrease the value of q to $q \pm apF$, p being the charge of the ion and a the distance between a minimum and a maximum (fig. 1a). This implies that at a sufficiently high field nearly all jumps will be in the direction of the field and the well-known current-field relation is found to be

$$i = 2\, anp\nu\, e^{-q/kT}\, e^{apF/kT}, \tag{3}$$

in which n is the number of ions per cm^3 (n is supposed to be independent of F) and $\nu = 1/2\tau_0$. This is equivalent to eq. (1):

$$i = \alpha \exp \beta F, \quad \beta = ap/kT. \tag{4}$$

The value of β determines that of α; the value of α, with known values of ν and n, implies q.

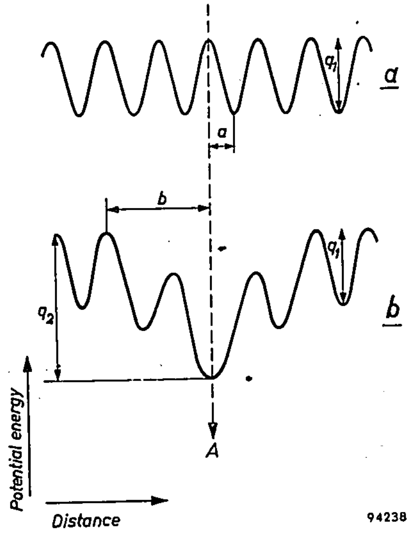

Fig. 1. The potential energy of an interstitial ion (a) in case of a periodic lattice; (b) in case the lattice ion at A of fig. a has left its position, creating a vacancy.

2.2. The first extension is introduced by assuming that the oxide is not a crystal but has an amorphous structure. This means that not only one exact q-value is present, but that we can define a function $G(q)$, such that $G(q)\mathrm{d}q$ is proportional to the number of valleys with q between q and $q + \mathrm{d}q$ with $\int G(q)\mathrm{d}q = 1$. The consequences of this picture on the a.c. impedances of the layer were described in a recent paper and were found to be in agreement with experiments ³). It is quite reasonable therefore to introduce this physical picture in connection with the present experiments too.

The analogue of eq. (3) is now given by

$$i = \int_0^\infty 2anp\nu G(q) e^{-q/kT} e^{apF/kT} \, \mathrm{d}q = 2anp\nu \, [\int_0^\infty G(q) e^{-q/kT} \, \mathrm{d}q] \, e^{apF/kT}, \tag{5}$$

which is again equivalent to eq. (1), leading to the same value of β as in eq. (4).

2.3. However, it is not correct to assume different q values without assuming also a and ν to be dependent on q. Introducing this into eq. (5) one obtains

$$i = 2pn \int_0^\infty a(q)\,\nu(q)\,G(q)\,e^{-q/kT}\,e^{a(q)\,pF/kT}\,\mathrm{d}q \equiv 2pn\,H(F)\,. \qquad (6)$$

In first approximation $H(F)$ will be of exponential shape, but writing

$$i = \alpha \exp \beta F, \quad \alpha = \text{const.},$$

one will observe that β — being proportional to d ln $H(F)/\mathrm{d}F$ — is still a function of F. In fact, β is likely to increase with F as a result of the increasing influence of large a values with increasing F.

2.4. The influence of small changes of F can be calculated by differentiating eq. (6). By interchanging integration and differentiation one obtains

$$\frac{\mathrm{d}i}{\mathrm{d}F} = 2pn \int_0^\infty a(q)\,\nu(q)\,G(q)\,e^{-q/kT}\,e^{a(q)\,pF/kT}\,\frac{a(q)p}{kT}\,\mathrm{d}q\,. \qquad (7)$$

Assuming $a(q)$ to be not too strongly dependent on q, one can approximate eq. (7) by writing $a(q) = \bar{a}$, except when $a(q)$ occurs in the exponent, where its influence is relatively much stronger. This yields

$$\frac{\mathrm{d}i}{\mathrm{d}F} = 2pn\,\frac{\bar{a}p}{kT}\,H(F)\,. \qquad (8)$$

This equation may be simplified if one makes the following experimental arrangement. During oxidation with constant current i_0, determined by eq. (6), a small a.c. voltage is superimposed on the d.c. voltage. This will not influence the oxidation, and eq. (8) yields

$$\left(\frac{\partial i}{\partial V}\right)_{d=\text{const.}} = 2pn\,\frac{\bar{a}p}{kT}\,\frac{H(F)}{d},$$

d being the thickness of the layer. If we assume that at each moment d is proportional to the total number of coulombs passed during the oxidation, we may write $d = k'i_0t$ and we obtain

$$R_p = \left(\frac{\partial V}{\partial i}\right)_{d=\text{const.}} = \frac{k'}{\beta_1}\,t\,, \qquad \beta_1 = \frac{\bar{a}p}{kT}\,. \qquad (9)$$

This result is of course also obtained by starting from the simple eq. (3). The result of this calculation shows that it remains valid if the generalized form of eq. (6) is used. It suggests that if the equivalent parallel resistance (which is the R_p defined by eq. (9)) is measured with an a.c. bridge during formation, the rate of increase of R_p with time will be approximately a constant which is also independent of current density *).

3. Analysis of a special model of the oxidation process

3.1. Let us return for a moment to the simplified model of a crystal with one constant $q = q_1$, in order to consider the process of ionic movement in more detail. Further, we assume that during the oxidation the metal ions move whereas the oxygen ions stand still. This has also been proved experimentally by Vermilyea [6]).

Now, one might start from the idea that the lattice metal ions in the oxide are strongly bound to their lattice sites, i.e. that the depth of the potential valley at a lattice site is too large to give the ion a measurable chance to escape. This implies that each new metal ion coming from the metal has to pass the whole layer via interstitial lattice sites in order to occupy an empty lattice site on the electrolytic side. The value of q_1 in this process is apparently the depth of the interstitial potential valley (fig. 1*a*). However, we reject this picture for reasons which will be published separately.

We prefer the picture given by Bean et al. [4]) in which a definite chance exists for a metal ion to move out of its lattice site into an interstitial position, thereby creating a vacancy. From the interstitial position the ion can move like an interstitial ion until it is captured by one of the vacancies. The mean free path can vary from one to several lattice distances. Thus a mechanism of creation and annihilation determines the number of interstitial ions. An increase of the field strength during oxidation will not only increase the "velocity" of the moving ions as in section 2; it will also increase both the number of ions and the number of vacancies until a new equilibrium is reached. But this mechanism implies that another $q = q_2$ enters into the calculations, being related to the energy required to create an interstitial ion-vacancy pair (fig. 1*b*). Obviously, q_2 is larger than q_1. For this special model, the derivation of the $i(F)$-relation runs as follows.

3.2. If the concentration of interstitial ions in a given situation is n, we still have eq. (3):

$$i = 2anp\nu_1\, e^{-q_1/kT}\, e^{apF/kT}, \tag{3}$$

which we can interpret as

$$i = n p v, \tag{10}$$

in which v is the effective velocity of the interstitial ions in the crystal.

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*) It may be mentioned that, starting from eq. (1) with $\beta = \beta(F)$, one may derive $\beta_1 = \beta(F) + F\partial\beta(F)/\partial F$. So in the approximation of eqs (8) and (9), i.e. $\beta_1 =$ constant, one may write $\beta(F) = \beta_0 - \beta'/F$.

In this case n is not a constant but is itself determined by a jump process. In general, the change of n is determined by the difference between creation and capture, which can be written as has been done by Dewald [5])

$$\frac{\mathrm{d}n}{\mathrm{d}t} = N_0\, \nu_2\, e^{-q_2/kT}\, e^{bpF/kT} - \frac{i\sigma n}{p}, \tag{11}$$

in which

$2b$ = the width of the potential valley with depth q_2 as defined by fig. 1b;
N_0 = the total concentration of lattice sites, being approximately the concentration of lattice ions;
ν_2 = the jump frequency of the lattice ions, not necessarily equal to ν_1, the jump frequency of the interstitial ions, and
σ = a capture cross-section.

Substituting eq. (3) in eq. (11), one obtains for the stationary state ($\mathrm{d}n/\mathrm{d}t=0$)

$$n = (N_0\nu_2/2\sigma\nu_1 a)^{\frac12} \exp\left[\tfrac12(-q_2 + q_1)/kT\right] \exp\left[\tfrac12(bp - ap)F/kT\right]. \tag{12}$$

Using again eq. (3) or eq. (10):

$$i = (2a\nu_1\nu_2N_0/\sigma)^{\frac12}\, p \exp\left[-\tfrac12(q_1 + q_2)/kT\right] \exp\left[\tfrac12 Fp(a + b)/kT\right], \tag{13}$$

which is equivalent to eq. (1): $i = \alpha \exp \beta F$.

Equation (13) is also given by Dewald [5]), with the difference that he assumed $\nu_1 = \nu_2$. If eq. (13) is valid, β gives the average of a and b, and α the average of q_1 and q_2 if the values of ν_1, ν_2 and σ are known.

3.3. Introducing now the amorphous structure of the oxide as was supposed in section 2.2, we have to define a distribution function $G(q_1, q_2)$, such that $G(q_1, q_2)\mathrm{d}q_1\mathrm{d}q_2$ is proportional to the number of lattice sites in the oxide where the interstitial valley depth has a value between q_1 and $q_1 + \mathrm{d}q_1$, and where the creation of an ion-vacancy pair at that position would require an energy between q_2 and $q_2 + \mathrm{d}q_2$. In fact $G(q_1, q_2)$ will show a (possibly flat) maximum as a function of q_1 (with constant q_2) as well as a maximum as a function of q_2 (with constant q_1). The two values of q for these maxima will differ (corresponding to $q_2 > q_1$ in section 3.1).

Just as in the case of section 2.2, the result is $i = \alpha \exp \beta F$, α now containing a double integral and β being a constant.

3.4. If we now assume, as in section 2.3, that the functions $a(q_1)$, $\nu_1(q_1)$, $b(q_2)$, $\nu_2(q_2)$ and $\sigma(q_2)$ are not constants, the result is

$$\begin{aligned} i = (2N_0p^2)^{\frac12} \iint G(q_1, q_2) \left\}a(q_1)\nu_1(q_1)\nu_2(q_2)/\sigma(q_2)\right\{^{\frac12} \exp\left[-\tfrac12\,(q_1 + q_2)/kT\right] \times \\ \exp\left[\tfrac12 Fp \left\}a(q_1) + b(q_2)\right\{/kT\right] \mathrm{d}q_1\mathrm{d}q_2 \equiv (2N_0p^2)^{\frac12} H_2(F). \end{aligned} \tag{14}$$

By writing $i = \alpha \exp \beta F$, evidently β is again not a constant but depends on F.

3.5. In accordance with section 2.4, one obtains for small changes of F by differentiating eq. (14) with respect to F

$$\frac{\mathrm{d}i}{\mathrm{d}F} = (2N_0p^2)^{\frac{1}{2}} \frac{p(\overline{a+b})}{2\,kT} H_2(F), \tag{15}$$

which yields

$$R_p \equiv \left(\frac{\partial V}{\partial i}\right)_{d=\mathrm{const.}} = \frac{k'}{\beta_2} t, \qquad \beta_2 = \frac{\overline{a+b}}{2} \frac{p}{kT}. \tag{16}$$

The shape of all these formulae has not changed, either by introducing the two q values q_1 and q_2, or by generalizing this mechanism into a "diffuse-double-q-process", but we find other interpretations of observed β values, with respect also to their dependence on F.

3.6. There still remains one remark to be made about the mechanism with respect to a.c. measurements. According to eq. (11), a sudden change of the field F will change $\mathrm{d}n/\mathrm{d}t$ abruptly from zero to a definite value, different from zero. As a response to this, n will start to change, until — owing to the factor n of the second term of eq. (11) — $\mathrm{d}n/\mathrm{d}t$ is zero again and a stationary state with a new equilibrium value of n is realized. Apparently a finite time $\tau'(= p/i\sigma)$ is necessary for completing this process. But this means that if the frequency f of any small a.c. field (superimposed on the large constant d.c. field) is such that $f > 1/\tau'$, this process cannot take place at all, and in fact one measures a system with a constant number of interstitial ions, being the number corresponding to the average constant field. This is precisely the situation of section 2 in which only q_1 was considered.

Also when q_1 and q_2 are distributed according to the partition function $G(q_1, q_2)$, we will find this effect of excluding a part of the jump mechanism by increasing the frequency. Although this relaxation phenomenon causes β_2 to depend also on frequency *), it provides in principle the possibility of separating the processes of section 2 and of section 3, i.e. to determine $\bar{a}$ and $\overline{a+b}$ separately.

3.7. One may conclude that, if all these complications are present in fact, no definite α and β values can be given which are valid in all circumstances. This is also the conclusion from our experiments. Nevertheless, on the basis of the considerations given in these sections a number of numerical results can be obtained from the measurements.

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*) From eqs (3) and (11) one may derive

$$\beta_2 = \frac{\bar{a}p}{kT} \frac{(1+\bar{b}/\bar{a}) + j\omega\tau'}{2 + j\omega\tau'}, \tag{17}$$

with $j = \sqrt{-1}$, $\omega = 2\pi f$ and $\tau' = p/\sigma i_0$ (i_0 = d.c. current). This yields for small ω: $\beta_2 = \frac{1}{2}(\bar{a} + \bar{b})p/kT$, which is eq. (16), whereas for large ω we find $\beta_2 = \bar{a}p/kT$, which is eq. (9).

4. Experimental results with aluminium, and discussion

4.1. The experiments were carried out with aluminium which was cleaned by a treatment with chromic acid. This implies a surface increase by a factor 1·07. After this it was oxidized anodically in an aqueous solution of borax + boric acid (5 + 20 g/l). A platinum electrode was used as cathode. During the oxidation the current i through the oxide layer and the voltage V across this layer were measured. The thickness of the layer will increase as a function of time t.

Before going into the detailed experiments, we will consider one particular problem connected with many experiments. It is often necessary to calculate the thickness d of the layer by equating

$$d = k' \int i\,\mathrm{d}t \doteq k'\bar{i}\,t \tag{18}$$

and the problem arises as to how to determine the constant k'. The most simple (and often realized) way is to assume a 100% efficiency of the oxidation from which, using the specific density and assuming stoichiometric composition, a value of k' can be calculated. This can be checked by separate measurements, e.g. by weighing the Al plate before and after oxidation or by an optical method. It is found that the 100% efficiency is obtained in many cases; however, at low current densities (and temperatures well above room temperature) a lower efficiency has been found. Some results are given in fig. 2, which are obtained by averaging the data from the weighing method and the optical method.

The reason for a lower efficiency than 100% must be the fact that some of the oxygen ions arriving at the oxide - electrolyte interface are not used as lattice ions, but are discharged. The corresponding electrons will travel through the layer, contributing to the total current measured in the outer circuit. Now this implies that the total observed current has to be corrected on the basis of fig. 2 and that these corrected i values (as being the real

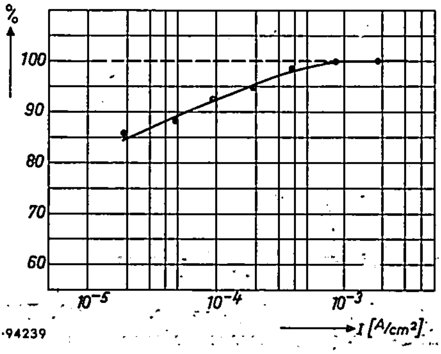

Fig. 2. The electrical output of anodic oxidation as a function of current density.

ionic currents to which the formalism applies) must be used throughout the calculations and not only in eq. (18).

There remains then the question whether (and how) the electron current influences the ionic current and whether these two currents can be handled separately. Owing to this uncertainty the experiments with $i < 0{\cdot}4$ mA/cm² remain doubtful. Hence the range of i values in our experiments is limited. We will return to these questions in the next sections.

4.2. During oxidation with constant current the thickness of the layer will increase linearly with time. Because constant current implies a constant field, one measures in fact a linear increase of voltage V with time t (constant "speed").

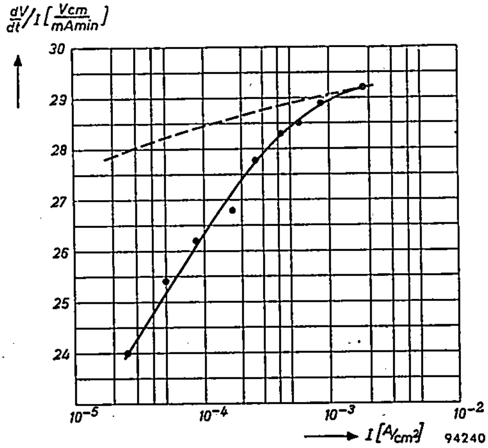

Fig. 3. The "speed of oxidation" as a function of the current density.

Starting from eq. (1) and calculating the thickness d with eq. (18) we obtain

$$\frac{1}{i}\,\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{k'}{\beta}\ln\,(i/a)\,. \tag{19}$$

On the basis of this eq. (19), the experimental results of these "speed" measurements are given in fig. 3, where $\mathrm{d}V/i\mathrm{d}t$ is plotted as a function of $\ln i$, in which i is the observed current. It appears that a linear relationship is not realized in fact. On the basis of eq. (19) this implies that the value of k'/β decreases, i.e. β increases with the field F (fig. 4).

However, as has been suggested in section 4.1, it seems advisable to correct the observed i values on the basis of fig. 2, i.e. using only the ionic part of the current. This is a correction both for ordinate and abscissa, as can be seen in fig. 3. The result is indicated by the dotted line, which implies a less pronounced, but still existing dependence of β on the field F (fig. 4), the range of observed fields now being very small. As these results are very strongly dependent on the applied correction, one should not lay too much emphasis on the numerical results.

An explanation why β is not a constant is given in sections 2.3 and 3.4. It does not seem possible, therefore, to correlate these observed values with any microscopic parameter. These results also illustrate how easily large fluctuations of β (and accordingly of $\ln \alpha$) can occur.

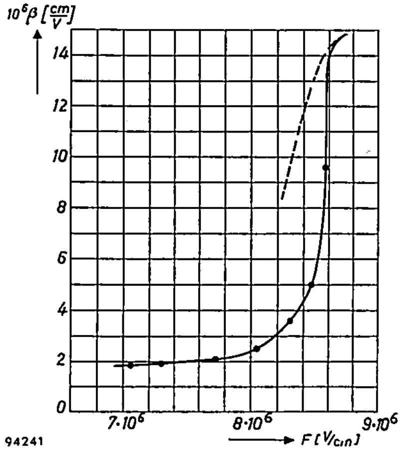

Fig. 4. The value of β (eq. (19)) as a function of the field F.

4.3. Another approach to the problem of the $i(V)$-relation is given by the following experiments.

During oxidation with constant average current, a voltage of the type shown in fig. 5 is superimposed regularly on the direct voltage. This is done with the experimental set-up shown in fig. 6. The d.c. voltage is supplied by the potentiometer A, which can be so adjusted as to produce a

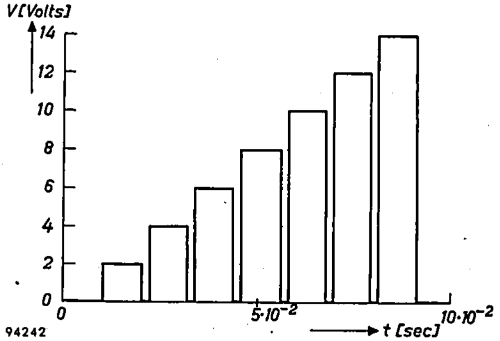

Fig. 5. The extra voltage pattern, superimposed on the d.c. voltage during oxidation.

constant average current through the oxide layer C_e. By means of a rotating contact B, the superimposed voltage of fig. 5 is obtained. The resistance r is introduced in order to effect short-circuiting when B does not touch any contact.

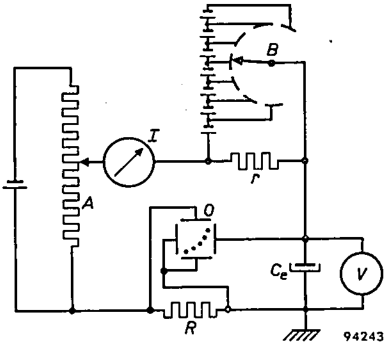

Fig. 6. The experimental arrangement of the experiments of section 4.3.

The response of the current to these field variations can be measured as the voltage across the resistance R. This response is conducted to the vertical plates of an oscilloscope O, while the voltage variations are applied to the horizontal plates (fig. 6). The dependence of di (the change in the current) as a function of dV (the voltage change) is now visualized, an example being given in fig. 7. Now during the first minutes of the oxidation (i.e. small thickness of the layer) the voltage variations imply high field variations, i.e. high current variations, whereas when the layers are thicker, the voltage variations imply relatively small field and current fluctuations. This fact has two consequences.

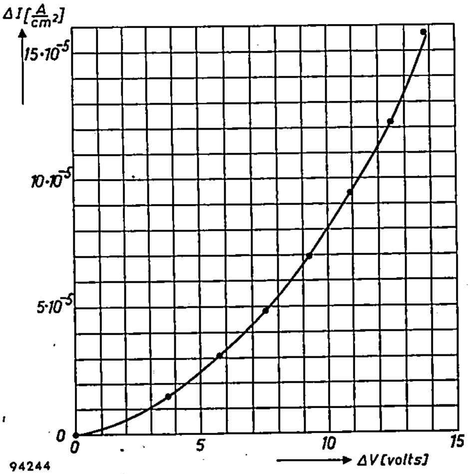

Fig. 7. The current response Δi as a function of the voltage changes ΔV during anodic oxidation.

Firstly, during the oxidation one has to increase the constant d.c. current on which the fluctuating current is superimposed in order to obtain a constant average current. This constant average current can be controlled by observing the $V(t)$-curve, which will be linear in that case.

Secondly, the relatively high current fluctuations at small thickness imply that a large part of the $i(F)$-characteristic is described each time the set of voltage changes is applied. At larger thickness only the tangent at "one point" of the $i(F)$-characteristic is described as only small variations are realized. Without going into details, we may say that the analysis of these experimental results can easily lead to a fictitious β depending on thickness if one assumes the constant β of eq. (1). This was actually found in our experiments but it is of no use to reproduce these data here. One can only say that the value of β, found in this way with the largest thickness, must not be in contradiction to the β found in section 4.2 at the corresponding current density. This is in fact the case in our experiments, where these β values also increase with increasing current density.

As in section 4.2, it does not seem possible to correlate these observed values with any microscopic parameter.

4.4. The results of the previous sections are somewhat ambiguous as a result of the dependence of β on F. As has been pointed out in the theoretical sections 2 and 3, this dependence is eliminated approximately if we would be able to measure during the oxidation *small* current fluctuations as a result of small voltage variations, superimposed on the d.c. voltage which increases during oxidation. This section will deal with this type of experiments.

The measuring set-up is shown in fig. 8. C_e is the electrolytic system, S a constant d.c. current supply, by which the Al plate of C_e is oxidized. This current is measured by the ammeter mA, the voltage across the layer is read on the electrostatic voltmeter V.

The generator G supplies the a.c. voltage to the bridge. The branch $R_s - C_pR_p$ is used to compensate the impedance of C_e, C_1 and C_2 being constant capacities. An oscilloscope O is used as the zero indicator.

In the $R_s - C_pR_p$-branch, the resistance R_s is meant to compensate the resistance of the electrolyte, which is about constant throughout one measurement. The parallel C_p and R_p are supposed to compensate the oxide layer. This R_p then is exactly the R_p defined in eqs (9) and (16).

The experiment now runs as follows. An Al plate is oxidized by the current from the source S. During the oxidation the voltage V across the layer and the values of R_p and C_p are measured as a function of time.

In first instance, we measured with a generator frequency $f = 24$ c/s. In fig. 9 an example is given of R_p as a function of time, the constant current of oxidation being 0·43 mA/cm^2.

As can be seen, R_p increases linearly with time in accordance with eqs (9) and (16). The slope γ of this curve is given in table I, which also gives the values of γ observed with several other current densities.

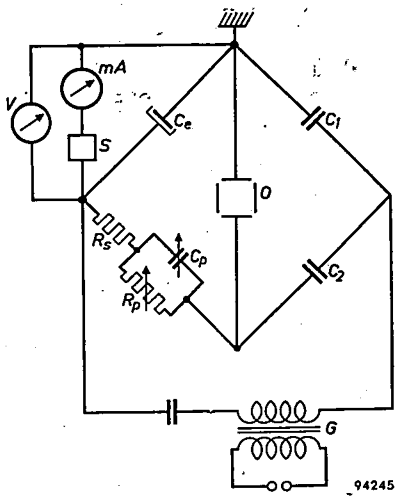

Fig. 8. The experimental arrangement of the experiments of section 4.4.

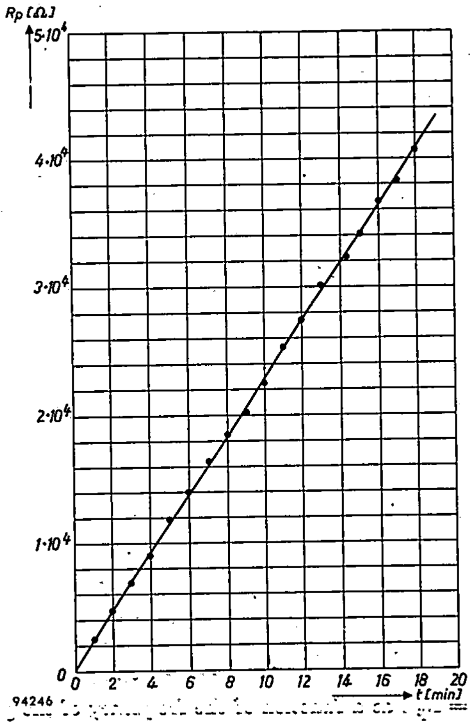

Fig. 9. The linear increase of the equivalent parallel resistance R_p during anodic oxidation.

TABLE I

Slope γ of R_p vs time at various current densities i

i[mA/cm²]	γ[Ω/min]
0·425	2230
0·51	2210
0·68	2150
0·765	2190
0·85	2210
0·935	2190
1·02	2220

It can be seen that these values are indeed independent of the current density, being also in agreement with the considerations in sections 2 and 3.

In order to avoid ambiguity, we consider only current densities giving an efficiency of 100% (cf. section 4.1, fig. 2). This is also the reason why it is difficult to give these γ values as a function of temperature.

The next information is obtained by measuring R_p as a function of the frequency of the generator. The results are given in fig. 10 in which $\gamma = R_p/t$ is plotted as a function of ln f. Although apparently this γ is also a constant as a function of frequency when $f > 10$ c/s, a definitely lower γ value is observed at lower frequencies. A qualitative explanation for this behaviour is given in section 3.6.

Summarizing this results of the R_p measurements, we can state that when $f > 10$ c/s, a constant γ value is observed, independent of time, current density or frequency. It seems justified to identify this γ with k'/β, given in eqs (9) and (16). This gives $\beta = 1{\cdot}55.10^{-6}$, independent of the current density, i.e. of the field. Apparently, this method of determining the value of β seems to be successful.

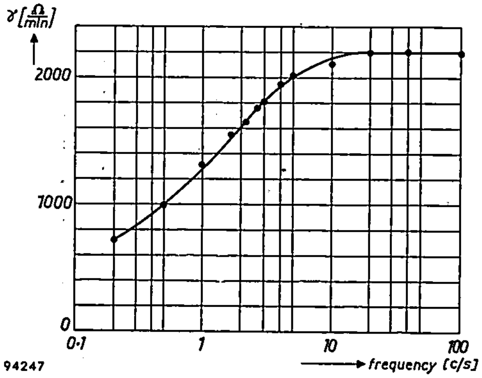

Fig. 10. The value of $\gamma = R_p/t$ as a function of the frequency of the generator in case of Al-oxide layers.

Now we are able to correlate this γ value with the microscopic quantities of eq. (9) or eq. (16). This yields (with $p = 3e$) $\bar{a} = 1{\cdot}3$ Å or $\frac{1}{2}\,(\overline{a+b}) = 1{\cdot}3$ Å. To decide between the two possibilities, we consider fig. 10 again. If the decrease in γ with decreasing frequency is indeed caused by the effect suggested in section 3.6, this would imply

$$\bar{a} = 1{\cdot}3 \text{ Å}. \tag{I}$$

This would be the only exact value which can be derived from our experiments. If, however, we were to be content for a moment with the approximations of eqs (10)-(13), just in order to get an impression of "some average value" of the different parameters (denoted by $\bar{q}_1$, $\bar{q}_2$, etc.), it is possible to calculate more details of the mechanism. For it is also seen from fig. 10 that the time τ' defined in section 3.6 is of the order of 1 second. But this is the time which an interstitial ion will need to find a lattice site. If the mean free path of an ion is l,

$$\tau' \approx l/v\,, \tag{20}$$

v being the velocity which — with the large fields under consideration — is only directed in the field direction. According to eqs (10) and (3),

$$v = 2\,\bar{a}\,\bar{\nu}_1\,e^{-\bar{q}_1/kT}\,e^{\bar{a}pF/kT}.$$

Now with respect to the mean free path l, we a priori suppose l to be of the order of 10 atomic distances $2\bar{a}$, with which we mean $l/2\bar{a} > 1$ and $l/2\bar{a} < 100$. For both $l/2\bar{a} = 1$ and $l/2\bar{a} = 100$ would correspond to a special and extreme oxidation process. It should also be mentioned that l will not be independent of the number of vacancies, i.e. l will depend on the field F (eq. (12)).

With $l/2\bar{a} = 10$, eq. (20) yields

$$\nu_1 \approx 10\,e^{(\bar{q}_1-\bar{a}pF)/kT}.$$

With $\bar{\nu}_1 = 5{\cdot}10^{12}$ sec^{-1}, $kT = 1/40$ eV, one obtains $\bar{q}_1 - \bar{a}pF = 0{\cdot}67$ eV, which value is not very dependent on the exact values of l, $\bar{\nu}_1$ and τ'.

Using result (I) and substituting $F = 8{\cdot}7.10^6$ V/cm (being the observed field for $i = 10^{-3}$ A/cm^2), we find $\bar{a}pF = 0{\cdot}34$ eV, which yields

$$\bar{q}_1 = 1{\cdot}0 \text{ eV}. \tag{II}$$

This value, being essentially some average value, is in close agreement with other values of q_1 given in the literature. An attractive feature of this value is that it is here deduced from the frequency dependence of the γ values, which is a new approach to its determination.

The value of v is found from eq. (20); with the numerical assumptions concerning l and τ', this yields

$$v \approx 20\bar{a}/\tau' \approx 25\ \text{Å/sec}, \tag{III}$$

which depends strongly on the values of l and τ'.

With these results we can go further. From eq. 10 one obtains the value of n, the concentration of moving interstitial ions. With the current density $i = 10^{-3}$ A/cm^2 (belonging to the field $F = 8{\cdot}7.10^6$ V/cm used above) it is found that

$$n = i/pv \approx 0{\cdot}8.10^{22}\ \text{cm}^{-3}. \tag{IV}$$

As this is linearly dependent on the value of v, i.e. of τ' and l, we can only consider this number as an order of magnitude. With respect to the total number N_0 of Al lattice sites (which is 3.10^{22} on the basis of a specific density 3·1), it means that n is of the order of 10% of N_0. This rather high result will be discussed subsequently.

Using this value of n, we can calculate more parameters on the basis of eq. (12). Substituting the values of N_0, $\bar{a}$ and n and assuming $\sigma \approx (4\bar{a})^2$ and $\nu_1 \approx \nu_2$, one obtains

$$(-\bar{q}_2 + \bar{q}_1) + (\bar{b}p - \bar{a}p)F \approx 0, \tag{V}$$

this result being not very dependent on the exact values of all parameters used. Now $\bar{b} > \bar{a}$ and if one may adopt a picture as given by Bean et al.[5]), $\bar{b}$ is about $3\bar{a}$ or even $5\bar{a}$. Substituting $\bar{b} \geqslant 3\bar{a}$ in result (V), we obtain $q_2 - q_1 \geqslant 0{\cdot}7$ eV. With (II) this yields

$$\bar{q}_2 \geqslant 1{\cdot}7\ \text{eV}. \tag{VI}$$

We have now found a consistent set of parameters. Although some substituted values are not exact ones, this does not influence the values of $\bar{q}_1$ and $\bar{q}_2$ very much. The value of n/N_0 is in any case an order of magnitude. This high value is in agreement with the fact that $\bar{q}_1 - \bar{a}pF$ is about equal to $\bar{q}_2 - \bar{b}pF$ (result (V)). For this implies that the energy for creating a new interstitial is not much higher than the energy of moving this interstitial. The influence of the field, however, remains very different in both cases as a result of $\bar{b} > \bar{a}$.

The value $\bar{b} \geqslant 3\bar{a}$ is also in agreement with the result of fig. 10. For it is observed that $\gamma_{(f=0)} < \frac{1}{2}\gamma_{(f>10)}$ in which $\gamma_{(f=0)}$ determines $\frac{1}{2}(\overline{a+b})$. Figure 10 would even suggest $\bar{b} \geqslant 5\bar{a}$, which would imply $\bar{q}_2 \geqslant 2{\cdot}4$ eV.

It may be mentioned that for $f > 100$ c/s the γ values of fig. 10 show a tendency to decrease again, although at 300 c/s this decrease is only 15%. It is also observed that the time τ' decreases with increasing temperature in accordance with eqs (20) and (10).

5. Experimental results with tantalum, and discussion

The experimental findings with aluminium, as described above, have shown that only the "R_p measurements" (section 4.4) gave useful results.

With respect to tantalum, therefore, we have carried out only R_p measurements.

The results are qualitatively the same with tantalum as with aluminium. R_p increases linearly with time at constant current density during the oxidation and the slope γ is independent of these current densities. The value of γ as a function of frequency is given in fig. 11. The same behaviour is observed as was found with Al (fig. 10). This means that we can give the same numerical details as in section 4.4.

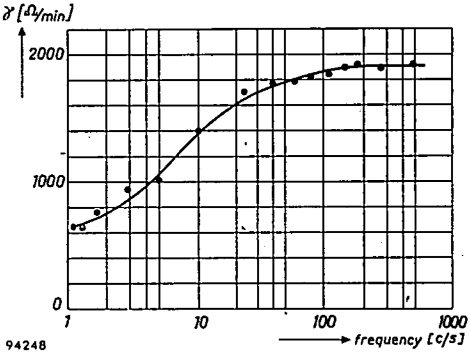

Fig. 11. The value of $\gamma = R_p/t$ as a function of the frequency of the generator in case of Ta-oxide layers.

From the saturation value (at $f > 150$ c/s) of $\gamma = 1900\ \Omega/\mathrm{min}$, it follows that $\beta = 1\cdot 80.10^{-6}$ cm/V. This yields (with $p = 5e$)

$$\bar{a} = 0\cdot 9\ \text{Å}. \tag{I}$$

The time τ' is an order of magnitude lower than was observed with Al: $\tau' \approx 0\cdot 1$ sec. Under the same conditions as mentioned in section 4.4, one obtains $\bar{q}_1 - \bar{a}\,p\,F = 0\cdot 61$ eV. With $F = 6.10^6$ V/cm (when $i = 10^{-3}$ A/cm^2), this yields

$$\bar{q}_1 = 0\cdot 9\ \text{eV}. \tag{II}$$

Also we find

$$v \approx 200\ \text{Å/sec}, \tag{III}$$

which gives

$$n \approx 0\cdot 06.10^{22}\ \text{cm}^{-3}. \tag{IV}$$

The value of N_0 can be calculated as 2.10^{22} (assuming the specific density $\varrho = 8$), which implies $n/N_0 \approx 3\%$. On the basis of eq. (12), one obtains

$$(-\bar{q}_2 + \bar{q}_1) + (\bar{b}p - \bar{a}p)\,F = -0\cdot 2\ \text{eV}. \tag{V}$$

Again assuming $b \geqslant 3a$, the result is

$$\bar{q}_2 \geqslant 1{\cdot}8 \text{ eV}.$$

Once more we find a consistent set of results. Some of the substituted values are not exact values, but this does not particularly influence the values of $\bar{q}_1$ and $\bar{q}_2$. The assumption $\bar{b} \geqslant 3\bar{a}$ is also in agreement with the result of fig. 11.

6. Conclusion

In the present paper attention is given to the amorphous structure of the oxide layer. For, if one considers the movement of ions in such a layer, it is very unlikely that the depth q of a potential valley will be exactly the same for all ions. This implies that one has to define some distribution function $G(q)$ such that $G(q)\mathrm{d}q$ is proportional to the number of ions which are present in a valley with q between q and $q + \mathrm{d}q$. This point of view has been applied with success to amorphous dielectric layers, and recently also to the present oxide layers with respect to their impedance.

Working out this idea, we obtain a relation between current and field during anodic oxidation, which is not of purely exponential shape. The consequences of this fact have clarified the situation with respect to our experimental results, which were different with different methods if the simple exponential law was assumed. The often quite different data, found in literature, may probably also be connected with this fact. As a result of our calculations we prefer one experimental method, being the "R_p measurement". This R_p-value is the equivalent parallel resistance measured in an a.c. bridge by a small a.c. field which is superimposed on the d.c. field that causes the oxidation.

A second part of our calculations was based on a closer examination of the ionic movement. The idea of Bean et al. [5]) concerning the creation and annihilation of interstitially moving ions was worked out for the case of the amorphous structure. It appeared that this does not alter our relations between current and field, but the interpretation of the observed parameters is different. Moreover, it can explain why the results of the R_p measurements are found to depend on the frequency of the applied a.c. field.

The R_p measurements were carried out on aluminium-oxide and tantalum-oxide layers. In fact, these results are qualitatively in agreement with the theoretical considerations given. From these results, numerical details of the proposed model are calculated, some of them however only approximately. It is of special interest to point out that we used the observed frequency dependence of figs 10 and 11 as independent data in these calculations.

The authors express their thanks especially to Mr B. C. Bouma who was the first to propose and perform measurements where small voltage variations were superimposed on the applied voltage during oxidation and who also executed several experiments which were of great help to them in writing this article. The authors are also indebted to Mr K. Compaan for discussions on the subject of this paper.

Eindhoven, January 1958

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