CHAPTER I

Anodic Oxide Films and Related Aspects—Present State of the Art.
The field of oxide films on metals/semiconductors have a wide range of applications in industrial products and processes such as batteries, capacitors, thin films devices, nuclear technology, energy conversion, storage system and related technologies, dielectric and insulating materials. Thin oxide films on metals act as protective and decorative coatings. Anodic oxide films are considered to be a special class of reaction films which are intentionally produced in electrolytic solutions. The sustained growth of oxide films on metals through anodic oxidation requires the transport of material through the phases involved and across the interfaces. The transport of metal up to the metal-oxide interface and of oxidizing agent up to the film environment interface will not be rate controlling once the metal surface is covered with a film. The Kinetics of the growth of oxide films display a very wide range of behaviour.\textsuperscript{1–32} The growth of porous or cracked films is related to transport phenomenon in very much more complicated fashion than is the growth of a continuous film of essentially uniform thickness.\textsuperscript{1,2} The rate controlling reactions presumably occur, therefore, at the metal-electrolyte interface, with the only transport processes being those with in the electrolyte phase, that is transport of oxidizing species up to, and in some instances one or more of the products away from the electrode surface.

The principal characteristics of valve-metal anodic oxidation behaviour is the requirement of a very high overfield
that is of the order of $10^8$ V m$^{-1}$ or larger. Second characteristics is the formation of an oxide film of essentially fixed stoichiometry, to the exclusion of other processes, such as metal dissolution and oxygen evolution. The metals that come the closest to exhibiting this behaviour are tantalum, niobium and aluminium in some electrolytes. However, a large number of metals, semiconductors and alloys approach this behaviour of metals under certain conditions. No metal, when anodically oxidized, satisfies the second characteristics precisely, since film dissolution and/or oxygen evolution will inevitably occur, even if only to a small extent. For purposes of much of the discussion, the second condition relating to film dissolution and oxygen evolution may be relaxed and all systems characterized by a high overfield and a film of essentially fixed stoichiometry may be included in valve metal category.

Typical members of the valve metal group are Ta, Al, Nb, Zr, Hf, W, Sb, and Bi. Some of these show group characteristics, while others do so only in a few electrolytes or with in a limited range of pH. Other elements, such as Mg, Sn, Be, Si, Ti and Ge are sometimes included in the classification because they also form oxide films on anodic polarization under certain conditions. The name valve electrode implies the rectifying action of the oxide film rather than the more fundamental characteristics of the group, which is the tendency to form a protective high resistance oxide film excluding all other electrodes processes in anodization. Tantalum is the extreme
example of this behaviour. Thermodynamically, all these metals are reactive in the most natural environments like air and water and should tend to form oxide. These reactions often fail to occur at any appreciable rate and tantalum finds use for the protection of equipment whose survival in very corrosive environments must be assured. The reason being that the oxide formed acts as a barrier between the metal and atmospheric oxygen. Further reaction can occur only by diffusion or migration of ions through the oxide film. If this oxide coated metal is made the anode of an electrolytic cell, the applied external force (Current) sets up an electrostatic field or increases the field already present in it which results in the continuous growth of the film by causing the metal or oxygen ions to be pulled through the film. It is unlikely that ion transport through thin films at high field strengths would be controlled within the film. Hence we can say that the growth of anodic oxide films is essentially a problem of ionic conduction at high field strengths complicated by the presence of oxide bulk and its boundaries-metal/oxide and oxide/electrolyte interface at which transport process must occur. The rate controlling step, possibly being anion net work-defect injection into the oxide, must occur. Other anodic processes such as oxygen evolution and film dissolution are almost inhibited even though there may be a potential difference of some hundreds of volts across the film,
provided the metal surface is smooth and not contaminated with other metals and free from inclusions. Over the range of potential in which the current is very small, the oxide acts as the dielectric of a capacitor, provided the film is pore free and/or flawless. The thickness of the oxide film can be estimated by applying a simple equation for a parallel capacitor. Apart from such obvious considerations as insolubility and stability as regards hydration, it is altogether not clear why some metals fail to grow oxide film at low voltages while others give films of very high thickness. There is also great controversy about the dominant conduction mechanism in the metal oxide films. The majority of the work refers to the system metal/metal oxide/metal; the system metal/metal oxide/electrolyte has received comparably less attention. Basically, there are three methods of film preparation, evaporation, thermal oxidation and electrochemical method. In the present investigations, the electrochemical method for the production of films is used.

Theories of Ionic Conduction

In attempting to understand the mechanism of high field ionic conduction in anodic oxide films on metals like Nb, Al, and Ta one of the key characteristics which must be considered is that the ionic current produced by a given electrostatic field in the oxide depends very strongly on the history of the film. Ionic conduction process is
affected by the method, a film is made. The "latent ionic conductivity" (ionic conductivity which would be observed on reapplying a field) changes with in milliseconds and continues to change for hours at room temperature at zero field after halting film growth. On reapplying a constant field, a steady state is eventually obtained after an initial transient, and the ionic current density is then constant for a given field \( E \) independent of thickness. The ionic charge transport depends on the electric field strength across the oxide film. In case of cation mobile system, the ionic conduction taking place, can be either at high field or at a low field. In case of high field conduction, it is assumed that the electric field strength is high enough to prevent movement of cations against the field direction whereas in low field conduction studies it can no longer be assumed that movement of cations against the field direction is negligible. In the following theories, high field strengths of the order of \( 10^8 \) to \( 10^9 \text{V/m} \) required for film production are operative in ionic conduction mechanism. The range of field strength is sufficient to prevent ionic motion against the field direction. Under high field conditions, Guntherschulze and Betz\(^5\) established that average field strength \( E \) and ionic current density \( i \) under steady state conditions are related by the equation

\[
i = A \exp BE \quad (1)
\]

where \( A \) and \( B \) are constants involving parameters of ionic transport. For simple electrochemical reactions, charge
transport is controlled by the step which has the highest potential energy with respect to the rate determining step. For deriving equation (1) for the ionic current, it is further assumed that one ion or vacancy is not blocking the path of another. The fundamental equation is derived by taking an idealized situation of a charged particle which has acquired sufficient energy from thermal agitation plus the applied field, hopping from the position of one potential to reach the next site after travelling a distance '2b' and a barrier height 'ϕ' (Fig. 1). For a symmetrical barrier, the maximum of the barrier is located at a distance 'b' from barrier minimum. The interstitial ions are considered to be vibrating in simple harmonic motion with a frequency.\(\nu\). If the average scattering length is '1' of the charged particle and \(b<1<3b\), then the charged particle can cross the barrier after travelling a distance '2b' and attain the thermal energy equal to or greater than the barrier height(\(\phi\)).

In the absence of field, the proportion of charged particle which will possess at any moment sufficient energy 'ϕ' to jump the barrier will be given as \(\exp(-\frac{\phi}{kT})\). Since an energy exceeding 'ϕ' is a necessary condition from the stand point of classical mechanics for the charged particle, the hopping frequency of the particle to cross the barrier of height ϕ is given by the product\(\nu \exp(-\frac{\phi}{kT})\) by assuming that the charged particle has \(\nu\) chances per second to jump the barrier if it has sufficient energy. This equilibrium
FIG. 1. Potential energy (P.E.) of mobile ions vs distance with and without an applied field.
barrier model is an approximation to the real state of affairs. Nevertheless, this picture has a measure of validity for thermally activated transport processes and the measure of particle current in solids. The relationship between this equilibrium barrier model and the actual solid state diffusion and conduction forms the basis of various current theories of anodic oxide film growth.

Ionic conduction takes place through the movement of defects in the lattice and it depends on the electric field strength and the concentration gradient. The field E is assumed to reduce the height of the barrier from $\Phi$ to $\Phi - qbE$ for the charged particles moving with the field (where q is the charge on the particle and 'b' is the distance from minimal to maximum potential barrier). When the charged particles move against the field then the barrier height increases from $\Phi$ to $\Phi + qbE$. For the sake of simplicity, it is assumed that the barrier is symmetrical for which 'b' is half the separation of successive sites. Hence 'b' can also be termed as half barrier width or activation distance or the half jump distance.

By taking into account the effect of field in reducing the height of the barrier, the current density $i$ could be written as

$$i = 2bn \exp - \left\{ (\Phi - qbE)/kT \right\} \quad (2)$$
(2)
(regarded as forward current)

For the ions moving against the field, the equation for current density is given by

$$i = 2b \left\{ n + 2b \frac{2n}{3x} \right\} \exp - \left\{ (\Phi + qbE)/kT \right\} \quad (3)$$
(3)
(regarded as backward current)
where \( n \) is the number of mobile ions per unit volume, \( x \) is the distance through the oxide and \( \psi \), the chemical activation energy. The term \( \left\{ n+2b \left( \frac{3n}{3n+2b} \right) \right\} \) represents the effect of the concentration gradient. The field applied is sufficiently high to ensure that very small amount of ions are moving against the electric field direction i.e. backward current is negligible, so that the observed current is directly given by equation 2. This situation is known as high field approximation and it is typical for the oxide films on most of the valve metals. Mott, Cabrera and Verwey have suggested that the overall current shows an exponential dependence on the field as in equation 1. This equation is termed as the fundamental equation for high field ionic conduction and is a key equation in the theory of anodic film growth. However, it can be modified suitably taking into account the rate determining step in ionic conduction. Comparing Eqn.(2) with Eqn. (1), it can be seen that

\[
A=nq\exp \left( \frac{-\psi}{kT} \right) \quad \text{and} \quad B = \frac{bq}{kT}
\]

The constant \( B \) is also equal to \( \frac{d\ln I}{dE} \) which is also the reciprocal of Tafel slope. From the values of constant \( B \), we get the expression for the effect of temperature with Tafel slope and it is given as

\[
\frac{d\ln I}{dE} = \frac{bq}{kT}
\]

Verwey's model suggests that the limiting factor is the rate at which ions move from one interstitial position to another. He considered the energy barrier for ion movement.
through the oxide bulk to be in a state of electrical neutrality and taken as the rate determining step. The equations he suggested for ionic current density are similar to those of Cabrera and Mott, the identification of the parameters being now related to the bulk oxide properties instead of metal/oxide interface properties. Hence the Cabrera-Mott and Verwey theories can be considered to be the limiting cases of one single barrier theory, Cabrera and Mott holding for thin films and Verwey for thick films where electrical neutrality exists in the bulk oxide. Verwey noted that the value of $B$ in the empirical equation

$$i = A \exp BE$$

for $Al^{3+}$ gave an estimate of the half jump distance $b'$ using the relation

$$\frac{dE}{d\ln i} = \frac{1}{b} = \frac{kT}{bq},$$

which was considered to be larger than expected on this basis. Verwey did not elaborate this discrepancy, only suggesting that it was due to imperfections in the oxygen lattice which made the ionic movement easier. In the model of Mott and Cabrera, crossing of the metal/metal oxide interface is considered to be the rate determining step. According to this theory, taking space charge to be negligible, the current over entrance barrier is given by the fundamental equation with the vital difference that the concentration of ions on the surface say $N_s$ replaces $2bn$ (eqn. 2), where $N_s$ is assumed to be constant i.e. independent of $E$. Hence the current density across the entrance barrier is given by

$$i = N_s \sqrt{s} q \exp \left\{ \left( \phi - qbE \right)/kT \right\}$$

(5)

$\phi$ being the entrance barrier energy, $b$ is the distance from an equilibrium site in the metal to an equilibrium site in
the oxide film or half jump distance of the entrance barrier, \( \sqrt{s} \) is the vibrational frequency normal to the barrier. This theory predicts a temperature dependent Tafel slope — a result common to any theory based on current control by a single barrier where no limit is placed on the concentration of ions before the barrier. Number of workers have examined this theory and reasonable values of \( A \) and \( B \) have been obtained taking 
\[ A = N_s \sqrt{s} q e^{-\Phi/kT} \] (from equations (1) & (5)). The value of 'b' deduced was rather high. The views expressed about the Tafel slope are at variance. The discrepancies in the magnitudes of Tafel slope may be due to taking values of fields (E) same at the interface as in the bulk oxide. It is also not necessarily valid to assume that the oxide formed is amorphous and not crystalline, and every ion which escapes from the metal is pulled right across the film can also not be concluded from this theory. The data of Young showed the field dependance of Tafel slope. This dependence was accounted for quantitatively, over a range of temperatures, by an empirical equation of the form 
\[ i = i_0 \exp \left[ - \left( Q - \kappa E + \gamma E^2 \right) kT \right] \] (6)
where \( Q, \kappa, \) and \( \gamma \) are all positive constants. At the time this equation was postulated, no theoretical justification for the quadratic term in the field, \( \gamma E^2 \), was offered. Dignam showed that a quadratic term of precisely the correct magnitude arises from ions transfer processes at high field strengths. He calculated the probability of an ion transfer process in the
The presence of a very high field assuming a form for the interaction potential between the ionic species and its immediate surroundings.

The existence of two controlling barriers should lead to the setting up of a space charge in the oxide has been reported by a number of workers$^{33-39}$. It was suggested that if there was a barrier controlling the current within the oxide, ions must have entered the oxide from the metal at a rate either higher than or less than the rate at which they diffused through the oxide barrier which was supposed to be the escape of interstitial ions from vacancies. The entrance current would be equal to the migration in the initial non-steady state only at one field and temperature. Further, if the entrance rate was less than the migration rate the current was controlled by the entrance barrier; if the entrance rate exceeded the diffusion rate, ions must be piled up within the oxide and constitute a space charge. This space charge reduces the field across the metal oxide boundary until the rate at which the ions entered the oxide was adjusted to that at which they could escape through it and react at the solution interface. Any barrier exercising control within the oxide, before which the number of ions were not allowed to increase without limit, must lead to a space charge and dual barrier control. It was possible that the generated vacancies diffused to the metal at a rate equal to that at which the interstitial ions migrated to the solution.
interface but this seemed unlikely on general grounds and was rejected by Dewald in his application of Vermilyea theory to transient currents. According to Diggle and Vijh, the space charge caused the rate-limiting step for transport to change from an interface barrier to conduction within the anodic film so that the Tafel slope underwent a corresponding transient with different hopping distance assumed for each of these limits. Dewald, following some of the qualitative ideas of Haring discussed the possibility of an increase in the activation distance as resulting from a change in the rate-determining energy barrier from the metal/oxide interface to the oxide bulk. He considered the oxide as an ionic lattice of stoichiometric composition through which excess metal ions can move under the influence of field from an interstitial site to the next. It was assumed that when an ion traverses the film, it may experience deactivating collisions with the lattice and requires reactivation before proceeding. As a first approximation, deactivation occurs immediately after each activation. Dewald's theory is able to account for all of Vermilyea's data and in particular, can predict a temperature independent slope for a wide range of experimental data. The values of jump distances 'a' and 'b' seemed to be rather high. This has also proved the invalidity of Vermilyea's rejection of the existence of any substantial space charge because his measurements showed no dependence of field E on thickness.
Dewald's theory also justified the reported evidence of Young about the presence of space charge in films formed anodically. Lobushkin et al. and other workers also noted that a space charge exists when films are grown on valve metals by anodic oxidation. They also came to the conclusion that the value of the space charge is dependent upon the thickness of the coating. Experimental measurements have also shown a relation between the thickness coating and electrical discharge properties.

These observations led to examine the above theories and the mechanism of ionic conduction through anodic oxide films rather more critically, to study the space charge effects in the oxide film and to find out the exact nature of Tafel slope with the variation of temperature (Chapters II and III).

**Breakdown Phenomenon**

Since the studies of Guntherschulze and Betz, electrical breakdown during the anodization of valve metals has been the subject of many investigators. Recent reviews found difficulties both in the definition of breakdown and in the interpretation of the processes. Several mechanisms were proposed to explain breakdown, such as fissure formation in the oxide or local crystallization in the amorphous insulator. Evidence was not found, however in support of these mechanisms and it was shown that crystallization does not precede breakdown but is a effect caused by local heating.
It has been suggested $^{48}$ that breakdown during anodization is connected with electronic impact ionization and avalanching. This view has also been shared by other investigators $^{48,54,55}$. Van Geel et al. $^{56}$ observed (in aluminum oxide) that the intensity of electroluminescence accompanying anodization increases as some exponential function of oxide thickness. The nature of this increase was interpreted with the assumption of electronic avalanche formation. Fritsch $^{57}$ investigated the rate of oxide growth and current transients during the anodic growth of silicon dioxide, also interpreting observations with avalanche formation. It has been more difficult to obtain experimental evidence for avalanche mechanisms from breakdown observations. This may in part be due to the fact that even the definition of breakdown is subject to discussion $^{50,51}$. Since the electric field is constant during anodization, breakdown has been defined by some voltage value. As such, various voltages are proposed, the voltage at which sparking starts, the maximum voltage which can be reached on anodization or the voltage at which a deflection from linearity arises in the voltage versus time curve. These voltages describe more or less important aspects related to breakdown during anodic growth. They do not account, however for individual observations of numerous breakdown events. To provide this information, new approaches were proposed for the description of breakdown properties during anodization $^{52-96}$. These are based on the measurement of the total number of
breakdowns as a function on anodization voltage in the work of Orlav et al.\textsuperscript{58} and Albella et al.\textsuperscript{59} and on the determination of the rate of breakdown as a function of thickness by Kadary and Klein\textsuperscript{60,61}.

A systematization of the variety of anodic films on Al and of their breakdown phenomenon was recently made by Tajima in a comprehensive review\textsuperscript{62}. Many are the factors which influence these phenomenon with different types of films. With barrier-type (non-porous) anodic films, however, which are widely used in the capacitor industry, only a few factors are known to affect the electrical breakdown. The effect of current density\textsuperscript{63-68}, temperature\textsuperscript{63,67-71}, topography and method of pretreatment of the electrode surface\textsuperscript{72}, stirring conditions of the electrolyte\textsuperscript{73,83,84} and history of anodic film formation anodized metal and the composition and concentration of the electrolyte\textsuperscript{63,66,69,74-79}, has been the subject matter of study of a number of workers. However, contradictions existed in the data on the form and the extent of influence of the above factors on breakdown voltage. The presence of an electrolyte contact makes the breakdown features very peculiar and quite different from those of 'dry' electrics, including metal/anodic film/metal systems\textsuperscript{12,80-82}.

It is evident from the literature that the identification of the breakdown mechanism is usually a complex problem. Difficulties arise for experimental and also for theoretical reasons. Therefore, attempt has been made to develop a theory of breakdown during anodization aiming to explain the features of the phenomenon (Chapter IV). The theory is limited only
to the cases where the anodization of the valve metal follows usually the kinetics of barrier anodic film formation \[1,2,12,75\] namely where the side reactions are eliminated and/or seems not to influence the anodization process.

Ikonopisov and Elenkov\(^{97}\) observed that when a barrier oxide film is formed by galvanostatic anodization to a given voltage \((U_v)\) which is then held constant, the growth of the film causes a rapid decreasing of the current, the latter attaining asymptotically to a constant value after prolonged anodization. If the voltage is then reduced by 25\% the film growth stops. The current \((i)\) through the film becomes entirely electronic \((i_e)\) that is why the application of lower \((U)\) potentials permits the investigation of electronic conductivity through a dielectric in contact with an electrolyte. This undoubtedly is of an academic interest as it has a direct technological significance as well. The range \(U<0.75 U_v\) corresponds to the operational voltages of the electrolytic capacitors, and \(i_e\), usually called 'leakage current' is one of their basic characteristics. Recently Albella et al. have extended the model of breakdown caused by the avalanche of electrons injected at the electrolyte/oxide interface during anodization put forward by Ikonopisov\(^{55}\) in anodization experiments. The electronic current \((i_e)\) through a given anodic film was found to depend on both the composition and the conductivity of the contact electrolyte at constant field strength \((E)\) and temperature \((T)\)\(^{97,99}\). The dependence
Thus found was a positive indication that electronic injection from the electrolyte controlled $i_e$ at the electrolyte/oxide interface. However the question of the kinetics and the mechanism of the electronic conduction through barrier oxide is far from settled. This stimulated the present investigation (Chapter V) of the dependence of $i_e(E)$ and $i_e(T)$ with tantalum oxide films using different contact electrolytes.

Related Properties

Certain other important aspects of ionic conduction through anodic oxide thin films such as rectification studies, dielectric measurements, effect of added ions, current efficiency, mobility of ions, heat treatment, formation characteristics in the presence of UV radiations, have also received attention. However, in several cases, the mechanisms have not been properly understood and the conclusions arrived at by different workers have, often, been at variance with one another. This is partly, due to different metals being used by different workers. Even when the same metal is used, the problem is also complicated on account of varying surface conditions, current densities and contacting electrolytes. Therefore, the present work includes a systematic study of these aspects of ionic conduction using the same conditions of surface, current density, electrolyte and the metal (Chapters VI and VII).
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