

Dielectric breakdown processes in anodic Ta₂O₅ and related oxides

A review

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The dielectric breakdown properties during the anodic oxidation of valve metals (Ta, Nb, Al, etc.) are reviewed. First, the theories developed for insulating films flanked by metal electrodes are analysed. The major emphasis is placed on the avalanche models since they give the best account of the experimental facts observed with electrolytic contacts, i.e. during the anodization. Some hints to increase the breakdown potential are finally given.

1. Introduction

Anodic oxide films have received a lot of attention in the last decades due to their good insulating properties. For this reason they have been successfully used in a large variety of applications, such as electrolytic capacitors [1], thin film transistors and MOS structures [2, 3], corrosion protection films, decorative coatings [4], etc. Perhaps, one of their main characteristics is the possibility to grow the oxides at low temperatures (below 90 °C), which is an attractive alternative to thermal oxidation, usually carried out at much higher temperatures.

The anodic oxides show very peculiar characteristics. They are grown electrolytically from certain metals (Al, Ta, Nb, Zr, etc.) and semiconductors (Si, AsGa, etc.) at very high electric fields ($\sim 10^6$ V cm⁻¹), so that the films are also able to withstand high fields under anodic polarization. Usually, they are obtained in galvanostatic conditions, i.e. by applying a constant current to the anodizing cell. In these circumstances, the charge passed makes the thickness of the film increase linearly with time. In the same way, the applied voltage increases linearly as well, in order to keep the electric field constant during the process. Under these apparent steady-state conditions (i.e. with a constant field), the voltage finally reaches a value at which some light sparks start to appear. They are frequently accompanied by voltage and current pulses, as well as copious gas evolution and other phenomena. This is the so-called electrolytic breakdown or scintillation, which limits the oxide growth in a natural manner.

This limitation has attracted a lot of research in order to gain insight into the basic breakdown mechanism, and thus improve the breakdown characteristics. In fact, the breakdown in a similar system,

insulator films flanked by metallic contacts, is an old problem which has been widely investigated. However, no definite mechanism which is able to explain the large variety of experimental facts can be given. This can be attributed to the inherent difficulty of the problem, related to the microscopic character of the breakdown phenomena, appearing in the film randomly both in space and time. The case treated here about the breakdown during anodization, i.e. with a liquid contact, is even more complex and the existing theories have been extracted from those applied to metallic contacts, without taking into account the intrinsic peculiarities of the problem. For this reason, in this review we first describe the microscopic mechanisms of the anodic oxide growth, since they are the ultimate factors determining the oxide properties (Section 2). We then look into the main breakdown characteristics, highlighting some well established experimental facts (Section 3). The general theories of breakdown in insulating films with metallic contacts will finally be reviewed in order to check the limits of their applicability to the breakdown in anodic oxides (Section 4). The paper will end with a critical review of the specific models proposed for this problem, i.e. the breakdown during the anodic oxidation (Section 5).

2. Properties of anodic oxides related to breakdown during anodization

The anodic films are usually grown under galvanostatic conditions. In that way the thickness, x , of the films is proportional to the amount of charge, Q , consumed during a certain time, t , i.e. $x = KQ = Kjt$, where K is the charge to mass (thickness) conversion ratio. The constant current, j , requires a constant electric field, F , to drive the ionic species, namely

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oxygen and metal ions, through the already formed oxide. Both magnitudes, F and j , are related by the classical equation for ionic movement, which in its simpler form is given by

$$j = j_0 \exp[-(W - qaF)/kT] \quad (1)$$

where j_0 is related to the concentration and mobility of the moving species; W is the energy barrier for the ions; a is half the activation distance; q , the charge transported by the ions; k , the Boltzmann constant; and T , the absolute temperature [5]. For most of the metals treated in this review the oxide formation takes place at both the electrolyte/oxide and oxide/metal interfaces [6], at a rate which depends on the anion and cation transport numbers.

In parallel with the oxide formation there are other reactions taking place mostly at the electrolyte/oxide interface. These reactions lead to oxygen evolution, oxide dissolution and incorporation of electrolyte species into the oxide.

The incorporation of electrolyte species into the oxide plays an important role in determining many of the parameters of the oxidation process. The incorporation process was firstly investigated by Randall *et al.* [7] and Draper [8] in tantalum and niobium oxides using radiotracer techniques, and latterly by many other researchers [9, 10]. As a consequence of the incorporation, the resulting oxide may present a duplex layer structure as in the case of Ta_2O_5 or Al_2O_3 formed in phosphoric acid. In these oxides the inner layer can be considered pure and stoichiometric since it is the product of the oxidation reaction at the oxide/metal interface. On the contrary, the outer layer incorporates electrolyte anions up to 15% at. for the films obtained in the more concentrated electrolytes [7].

The presence of electrolyte species incorporated into the oxide seriously affects the properties of the final oxide. This is easily understood because the foreign atoms have a different mass, a different binding energy with the host atoms and, consequently, a different polarizability. So it is reasonable to expect a variation of the properties of the anodic oxides obtained in electrolytes with different concentration, thus giving different doping content. It has been shown for Ta_2O_5 formed in phosphoric acid electrolytes a large decrease in the density as the anodization is performed in electrolytes of increasing concentration. This produces a corresponding decrease of the relative permittivity and refractive index [11–15]. Similar trends have been also found in Al_2O_3 and Nb_2O_5 , although quantitative results for these oxides are rather scarce [16].

The dielectric properties of the anodic oxides, mainly Ta_2O_5 , Al_2O_3 and Nb_2O_3 , have been extensively investigated because of their relation with the electrolytic capacitors. Most of these properties have been studied from the point of view of d.c. conduction through the system metal/anodic oxide/electrolyte. Quite surprisingly, this system shows asymmetric conduction or rectification in the sense that the easy conduction or forward direction is found when the metal is polarized negatively. Similar phenomena were

also found in anodic oxides flanked by metallic evaporated contacts. Early theories to explain these results were based on assuming for the system a *p-i-n* structure [17] with an oxygen-rich layer at the oxide/metal interface. In fact, the good electron-injecting characteristics of the metal interface have been attributed to the gradual variation of the stoichiometry of the oxide across this interface, since these injecting characteristics disappear when the anodic oxide is substituted by evaporated or sputtered oxide [18]. The rectification has also been explained in terms of the presence of flaws or weak points in the oxide [19], because of the observed influence of the contacting electrolyte on the conductivity of the whole system.

There is still great controversy about the mechanism of the electronic conduction under reverse polarization. This is in part due to the difference in the experimental results, sometimes contradictory, and also to the inherent difficulties on the measurements of the electronic current in insulators. In this regard, it is very common to find hysteresis effects and other problems associated with the polarization mechanisms and trapped charges which distort the measured signal. In any case, three zones in the I–V characteristics are generally found in the case of anodic oxides with wet contacts [20, 21]. At low voltages, below $\sim 10\%$ of the formation voltage, the characteristic is ohmic-type, dominated either by the conductivity of the contacting electrolyte [21] (as a consequence of the presence of flaws), or by the injection of electrons from the interface through some electrochemical reaction [20, 22]. At intermediate voltages, up to $\sim 85\%$ of the formation voltage, the current-voltage curves follow a field dependence of the type, $j_e^\alpha \exp(\beta F^{1/2})$, with β constant, which is characteristic of a Schottky or Poole–Frenkel emission [21, 23]. At higher voltages, when the applied field approaches the anodization field, the current has obviously a marked ionic character, varying exponentially with the applied voltage.

For the intermediate voltage range, Ikonopisov has found a rather striking dependence of the electronic current, j_e , on the conductivity of the contacting electrolyte, σ , according to a power law of the type [24]:

$$j_e = m\sigma^n \quad (2)$$

with m and n constants. Christov has speculated on this dependence by considering the electrolyte as an injecting electrode with semiconductor properties [25]; however no quantitative proof of the model was given. As we shall see later, Ikonopisov used the above empirical equation to explain the observed dependence of the breakdown voltage on the logarithm of the electrolyte resistivity. It is interesting to note that Equation 2 rules out the possibility of a Poole–Frenkel mechanism based on the ionization of the impurity centres in the bulk of the oxide, postulated by some authors including Ikonopisov himself [21, 23], the impurity centres being associated in this case with electrolyte species incorporated into the oxide [26]. At present, no systematic study has been made in order to assess the influence of these species on the electronic conductivity of the anodic oxides. From our point of view, the measurement of the conduction character-

istics in oxides grown in electrolytes with different concentrations (thus giving a different doping content) are indeed necessary, since they would provide more information about the source of electrons in these insulating films.

One of the most characteristic phenomena associated with the anodization process is the electroluminescence, i.e. the emission of visible light. Among the metals, aluminium is perhaps the one giving the most intense glow and for this reason it has been thoroughly studied. Van Geel *et al.* [27] were the first to observe an exponential dependence of the intensity of light, L , on the oxide thickness, x , in galvanostatic conditions, according to:

$$L = a[\exp(bx) - 1] \quad (3)$$

with a and b constants. Ikonopisov *et al.* also confirmed this dependence for different electrolytes, organic and inorganic, although they observed a departure from the above equation in the range of large thickness [28]. The electroluminescence was also found to be nearly proportional to the anodization current density, and strongly dependent on the electrolyte nature, state of the metal surface, purity, etc. but with little or no dependence on the electrolyte concentration. All these facts led Shimizu and Tajima to hypothesize the electroluminescence as a local phenomenon associated with the existence of flaws and impurities in the anodic oxide [29], instead of being uniform all over the oxide surface. Although this behaviour still needs further clarification, the evidence presented on the exponential variation of the brightness with thickness, Equation 3, strongly supports the idea of an electron avalanche model to explain the light emission, as has been generally suggested [30, 31].

3. Characteristics of the breakdown phenomena during anodic oxidation

The dielectric breakdown of anodic oxides during their electrolytic growth is a very old phenomenon, known for a long time [32]. The problem is complex because there is a variety of processes participating during anodization and breakdown. Due to this complexity, in what follows we will refer to the ideal or quasi-ideal systems, such as tantalum or niobium anodic oxides which, under a broad range of experimental conditions, show near 100% current efficiency with no lateral reactions, e.g. oxygen evolution, dissolution, hydration, etc. Aluminium anodization in some cases may also meet these requirements. Perhaps, the more comprehensive review of the problem was that given by Ikonopisov in 1977, and to our knowledge no other review has been published since then [33].

The main features of the breakdown phenomena can be summarized as follows:

i) The breakdown voltage, V_B , is determined fundamentally by the nature of the anodized metal and the composition of the electrolyte. Nowadays, it is generally accepted that the interface between the electro-

lyte and the growing oxide is what controls the breakdown characteristics [34].

ii) For a given oxide and electrolyte, it is widely documented that the breakdown voltage increases linearly with the logarithm of the resistivity of the electrolyte, ρ , i.e.

$$V_B = A + B \log \rho \quad (4)$$

with A and B constants, characteristic of the electrolyte and the oxide. To cite only a few examples of this behaviour, the reader is referred to the classical reviews of Vermilyea [35], Young [16], Burger *et al.* [36] and Yahalom [37]. In relation to Equation 4, some authors state that V_B is, in the case of aluminium oxide, specially dependent on the anion concentration of the electrolyte and not upon the acidity [38, 39]. However this point needs further testing in other oxides.

iii) The breakdown voltage is also strongly dependent on the state of the surface of the parent metal, i.e. the purity, presence of flaws, mechanical and thermal treatments, etc. Generally speaking, the presence of defects at the metal surface produces an unavoidable decrease of the breakdown potential with the occurrence of sparks just at these defects.

iv) The breakdown voltage is almost independent of the current density, temperature and other anodization conditions [40]. The independence of the temperature excludes Joule heating effects as a direct cause of the breakdown. In this regard, contradictory results between different authors can be often found. This is explained if one takes into account the complex influence of the current density and temperature on the anodization characteristics, i.e. electric field of formation, electrolyte uptake by the oxide, rate of growth, final thickness, etc. In any case, V_B is quite reproducible for a given set of anodization conditions in repetitive experiments.

v) The appearance of the breakdown is generally accompanied by a rapid succession of pulses in the voltage-time curves, as well as by visible sparks at some definite points randomly distributed across the surface and by gas evolution. In some cases, these effects are preceded by a sudden decrease of the voltage [41]. As a consequence of the breakdown process, the oxide presents crystalline spots, cracks and microfissures which can permanently degrade the dielectric properties if the oxide is held under prolonged breakdown conditions [42]. Mechanical stresses and cracks may also precede the breakdown, thus producing additional deviations of linearity in the voltage-time curve when the anodization process is carried out under galvanostatic conditions [43].

vi) Usually, it is established that the breakdown appears whenever a critical thickness is reached during the anodization [37]. This emphasizes the fact that during anodization the thickness of the oxide is increasing whereas the electric field is constant, in opposition to the breakdown tests in insulator films flanked by metallic contacts, where a ramp voltage is applied. In this case, the thickness is constant and the field is increasing during the experiments up to some critical value, F_B , at which the breakdown starts.

Unfortunately, in the electrolytic breakdown no assessment of the critical oxide thickness has yet been made.

vii) Successive anodization processes applied on the same sample, only differing in the electrolyte concentration, show that the breakdown voltage attained in each electrolyte is determined exclusively by the anodization electrolyte at that moment, regardless of the previous state of the oxide.

Due to the complex dependence of the breakdown voltage on the anodization conditions, it is difficult to assign a specific value for a given oxide. Ikonopisov *et al.* have reported a broad variation, between about 150 V to ~ 800 V, in the breakdown voltage for the series of metal oxides Ta, Nb, Al and Zr when anodized in solutions of ammonium salicylate in dimethyl formamide of increasing resistivities, at a current density of 0.01 A cm^{-2} [31]. Some authors argue that the breakdown properties should reflect some intrinsic property of the oxide. Without underestimating this assumption, it is obvious from the above related features that the breakdown processes are strongly dependent on the experimental conditions. Then, any attempt to account for the breakdown voltage should keep in mind the influence of the anodization conditions on the elementary processes causing the breakdown.

4. Breakdown theories in thin insulating films

The majority of the models proposed for the breakdown during anodization have been taken from the existing theories for breakdown in insulating films flanked by metallic electrodes. Many of these theories were, in their turn, extracted from the concepts applied to bulk insulators and semiconductors. So it is pertinent first to have a general look at the mechanisms suggested for dielectric breakdown. There are several reviews on this problem [44–47] which show a good deal of progress in this field of research, though it still remains an open subject. In this paper we shall be concerned mainly with the electronic theories of breakdown since they are more developed than others but alternate proposals, such as thermal or ionic models also related with the electrolytic breakdown will be considered as well.

4.1. Avalanche theories

The early theories of breakdown by Von Hippel and Fröhlich were based on the behaviour of free electrons which were supposed to be accelerated by the electric field, the breakdown appearing when the rate of the energy provided by the field was larger than the energy lost in collisions with the lattice atoms [48, 49]. As a consequence of this energy imbalance the accelerated electrons produce avalanches by impact ionization giving rise to current runaway and thermal destruction. The effect of the impact ionization on the rate of energy loss was taken into account by Seitz in the so-called 'forty generation theory' [50]. Following the avalanche breakdown model in gases, an initial

electron in the conduction band of the dielectric can gain enough energy from the electric field to release a bound electron from an atom of the lattice by a mechanism of impact ionization. Next, by the same mechanism the two electrons can result in four and so on, giving rise to an avalanche of electrons. The most important aspect of the above model is the prediction of the logarithmic decrease of the breakdown field with the interelectrode distance, in agreement with the experimental results in many insulators. The model also relies on the idea of a 'critical size' of the avalanche or equivalently a 'critical thickness' needed for breakdown. This fruitful idea has been sustained in many well-established breakdown theories.

Experimentally it has been found that the breakdown voltage in insulator films is affected by the nature of the contacting electrodes. This effect was explicitly considered by Forlani and Minnaja by assuming that the electrodes constitute the main source of the primary electrons for the avalanche [51, 52]. These primary electrons are supposed to be injected into the insulator either by tunnelling or thermal excitation through the energy barrier at the metal contact–insulator interface, yielding an electronic current, j_e , at the cathode (Fowler–Nordheim and Schottky mechanisms, respectively). The electrons are then accelerated and multiplied in avalanche in their travel to the anode, so that the current, $j_e(x)$, at a distance, x , from the cathode can be expressed under certain simplifying conditions by

$$j_e(x) \cong j_e \exp(rqFx/E_i) \quad (5)$$

valid for distances x much less than the recombination distance of the electron. In the above expression, E_i represents approximately the impact ionization energy; q , the electron charge; and r , a recombination constant ($r \cong 1$). When the expression for j_e is introduced in Equation 5, the condition that the exponent of the resulting equation should be kept close to zero to avoid an irreversible damage led to Forlani and Minnaja to calculate the electric field for breakdown. In the case of a Schottky mechanism of injection, an inverse dependence between the electric field for breakdown, F_B , and the insulator thickness, d , can be found. This inverse dependence seems quite natural in an avalanche theory since the smaller the interelectrode distance, the less the probability of forming avalanches of the proper size. Such inverse relations, usually of the type $F_B \propto d^{-1/2}$, have been observed by Budenstein and Hayes [53].

An important objection to Seitz's theory and to other avalanche theories, which do not account for the space charge effects, concerns the positive charge (or holes) left behind by the electrons in their ionizing collisions. Later, O'Dwyer took into account the effect of the positive charge and calculated the enhancement of the field at the cathode due to the accumulation of positive charge near this interface [54–56]. As a consequence of the field enhancement an increase in the injected current is originated, giving rise to a negative slope in the current–voltage characteristics. The instability, and therefore the breakdown, arises for the

critical electric field at the points of the I-V curves where the negative resistance appears.

The same basic assumptions were also used by DiStefano and Shatzkes [57], to calculate the breakdown field in wide gap insulators, as in SiO_2 with a band gap, E_i , about 9.0 eV. In such cases the O'Dwyer model is unsatisfactory, since it predicts very low ionization rates, insufficient to cause a negative resistance type of instability. To obtain a negative resistance they introduce a nonlocal ionization rate, based on the energy distribution of the electrons in their scattering with the lattice. Due to this distribution in energy, only a small fraction of the electrons, those in the high energy tail with an energy higher than the ionization energy, E_i , are able to produce ionizing collisions (Fig. 1). Although no analytical expression is derived for the dependence of the breakdown field, F_B , on the oxide thickness, the model predicts continuous increase of F_B when the thickness is reduced, in accordance with the experimental observations for SiO_2 .

In a latter development, Klein and Solomon treated the problem more generally by allowing the possibility that the effect of the positive charges can be opposed by recombination processes with the avalanche electrons (IR model), instead of the drift of the holes assumed by O'Dwyer (ID model) [58, 59]. The local character of the avalanches was previously taken into account by Klein, who assumed that a single avalanche by itself cannot lead to breakdown [60]. However, due to the random character of the avalanches, it might happen by chance that one new injected electron hits an already progressing avalanche, thus producing new ionizations and a further increase of the field near the cathode. This in turn, increases the probability of electron injection at this point, giving rise to a greater current until final destruction by Joule heating occurs (Fig. 2). This model explains the statist-

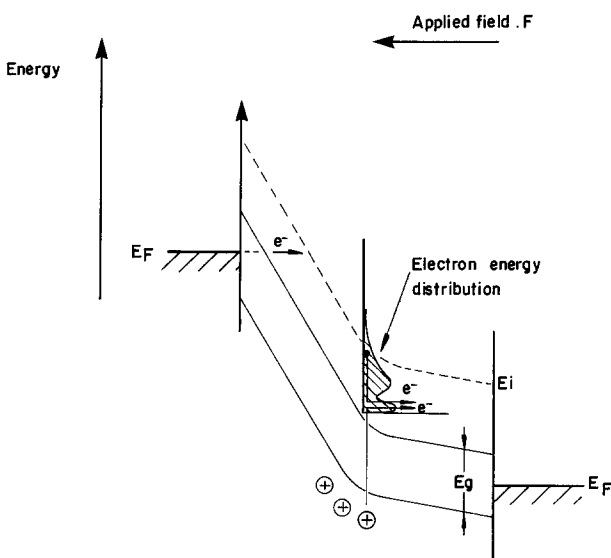


Figure 1 Impact ionization model for a dielectric film flanked by blocking contacts according to DiStefano and Shatzkes model. The scheme shows the band bending due to the enhancement of the electric field at the cathode, caused by the relatively immobile holes generated in the avalanches (adapted from [57]).

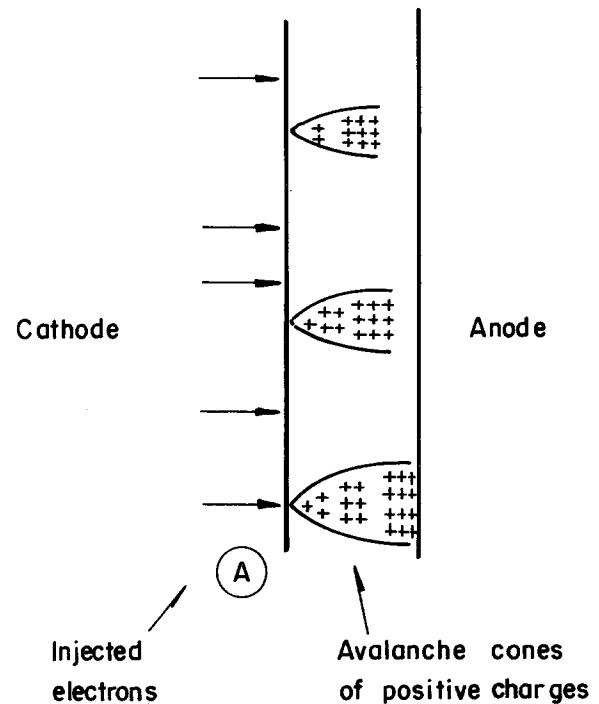


Figure 2 Schematic diagram of the breakdown processes in insulator films caused when an injected electron hits, by chance, the atoms in an already existing avalanche, point A (adapted from Klein [60]).

ical behaviour, both in space and time, usually observed for the breakdown events in the form of sparks or small bursts distributed across the sample surface. Implicit in the model is the cumulative character of the avalanches for the breakdown condition. This is a basic hypothesis used in many other non avalanche models, as well. Tacitly, the model also presumes a local distortion of the electric field, i.e. only affecting those points where the avalanches occur, and not influencing the rest of the sample surface.

4.2. Other breakdown models

To complete the picture of the breakdown models we shall mention some other models, not directly related with the avalanches, which have been proposed as alternatives to explain the breakdown processes. Many of these models have been put forward in the form of qualitative descriptions of the mechanism of breakdown, so that it is difficult to contrast them with appropriate experiments. In the so-called thermal breakdown this is produced by Joule heating of the dielectric [61]. Ridley has considered the thermal breakdown as a reasonable alternative in large band-gap insulators, like silicon dioxide, where the estimated electric field for avalanche breakdown may be an order of magnitude higher than observed [62].

The cumulative character of the breakdown processes along with their random distribution has been explicitly considered in several approaches [63-67]. In the first one, by Jonscher and Lacoste, certain defects coalesce in clusters by the passage of current until a stage is reached at higher voltages where the carriers gain enough energy to produce a rapid growth of current in a narrow channel [63]. In a similar ap-

proach, Volters and Van der Schoot made a formulation of the breakdown based on the damage produced by the carriers on the material either when they become trapped at the existing defects or when they reach the anode [64]. Through a detailed calculation for SiO₂ films they showed that the energy per unit volume dissipated in these two processes is much higher than that dissipated in the collisions with the phonons which are distributed through the entire lattice [65]. As in the Jonscher and Lacoste model, the presence of positive and negative trapping centres exerts a channelling effect on the current. The cumulative effect of the charge passing through these defects increases the damage and the possibility of a further channelling effect [66].

A common characteristic of the majority of these nonavalanche models is their inability to quantify the breakdown. In addition, they contain in some cases a great deal of speculation. Typically, the breakdown is attributed either to the presence or to the propagation of some type of defects whose nature is not clearly identified.

5. The breakdown during anodic oxidation

In the previous section we were concerned with the breakdown processes in insulators flanked by metallic contacts. This problem has many characteristics in common with the breakdown during anodic oxidation, such as the statistical behaviour of the breakdown events, the breakdown damage in the form of pores and microfissures, the emission of light sparks, etc. This indicates that the breakdown processes could be very similar in both cases, or even could be the same. However, the systems under study are in many aspects very unlike. Firstly, in the anodization system the cathode or injecting electrode is a liquid electrolyte, which implies that the injection of electrons into the growing oxide should be carried out through some redox electrochemical reaction at the outer interface, either between the electrolyte and the oxide or between the electrolyte species themselves. Secondly, the interfaces between the oxide and the contacting electrodes are not in a fixed position, since fresh new oxide layers are continuously being formed at one or both interfaces. Moreover, there is a permanent flux of ions arriving and reacting at these interfaces. In the third place, the atoms of the lattice are not at rest either, since during the oxide growth the positive and negative ions are moving in opposite directions. In addition, along with the oxygen negative ions there is always a certain fraction of anion electrolyte species either travelling or staying at fixed positions in the lattice. And finally, the anodization electric field under galvanostatic conditions (as is usually the case) can be considered constant and determined by the ionic current (Equation 1). All these aspects make the anodization system behave with its peculiar breakdown characteristics, as it was already pointed out, in Section 3. Therefore, any breakdown theory during anodization should be based on these differences with respect to the metallic contact system, and in addition

the proposed mechanism should account for the particular processes observed in the electrolytic breakdown.

The early theories of breakdown during anodization recognized the importance of the electrolyte/oxide interface in the initiation and control of the discharge [32, 68]. This was based on the observed influence of the breakdown voltage on the nature and concentration of the contacting electrolyte, Equation 4, as well as on the solid state properties of the oxide itself [69]. The above said idea of a 'critical thickness' for breakdown (see Section 3) led many authors to postulate the avalanches as a basic mechanism for breakdown [68, 70]. Within this framework the electrons were supposed to be injected into the oxide from the electrolyte through some electrochemical reaction at the interface, taking place mostly when a certain critical thickness has been reached [37, 70]. The primary electrons then develop into large sustained avalanches which give rise to the final breakdown by Joule heating. In these first qualitative models no precise equations for the influence of the anodization parameters on the breakdown voltage were given.

In a series of papers, Yahalom and Zahavi [34, 42] and Yahalom and Hoar [38] assessed the effect of some lateral processes taking place during anodization such as the temperature rise, the crystallization at some specific spots in the oxide, or the inclusion of the electrolyte anions in the outer oxide layer, and even the internal stresses in the film generated during formation, but no definite answer which ascertained the exact nature of the breakdown processes could be established.

5.1 Avalanche theories

Perhaps, the first attempt to rationalize the experimental results and give a quantitative account of the main breakdown characteristics during the anodization process was put forward by Ikonopisov [33]. The model basically follows the lines of Forlani and Minnaja theory [52], i.e. the direct injection of primary electrons, in this case from the electrolyte, into the oxide conduction band either by a Fowler-Nordheim or Schottky mechanism. The primary electrons then grow in avalanche across the thickness, as determined by Equation 5, until the avalanche current reaches a critical value at which Joule heating effects give rise to breakdown. Thus, by introducing in Equation 5 the value for the critical current for breakdown, j_B , and using the relation

$$V_B = d_B F \quad (6)$$

d_B being the oxide thickness at breakdown, and F , the anodization field, a general expression for the breakdown voltage, V_B , was obtained:

$$V_B = \frac{E_i}{r q} \ln(j_B/j_e) \quad (7)$$

The above equation contains the dependence of V_B on the anodization parameters, namely the solid-state properties of the growing oxide (through the constants E_i , r , and j_B) and the electron-injection properties of

the electrolyte (through the variable j_e). These electron-injecting properties of the electrolyte are also dependent on the anodization electric field, F , and for a given F they are determined by the nature and concentration of the electrolyte. As was mentioned earlier in the description of the conduction mechanism (Section 2), Ikonopisov used the empirical equation 2 to relate the electronic current injected in the oxide with the conductivity of the electrolyte. Thus, by substitution of Equation 2 in Equation 7 for j_e , he was able to demonstrate the well-known dependence of the breakdown voltage on the electrolyte resistivity, Equation 4. Obviously, the validity of this law does not prove the correctness of the derivation, since it relies on the use of an empirical equation (Equation 2), whose own validity still remains somewhat uncertain. The electron injection properties assigned to the electrolyte in this model, just as if it were a metal contact, should be also questioned unless some specific electrochemical reaction at the interface is disclosed.

A similar model based on the discrete character of the avalanches was put forward by Klein *et al.* for tantalum oxide [71] and aluminium oxide [72]. In these papers, they measured the rate of breakdown events in the form of light sparks and current pulses for different anodization fields. Through a complex analysis of the breakdown rate curves, they were able to obtain the parameters which determine the formation of the avalanches, namely the ionization coefficient, the mean free path for electron-phonon collisions, the size of the avalanches, etc. showing a reasonable fit with the expected values. The ionization coefficients are in the range of $1.2\text{--}1.5 \times 10^5 \text{ cm}^{-1}$ in Ta_2O_5 and somewhat higher in Al_2O_3 for typical values of the anodization current. The model used for these calculations is the same as that established by Klein for insulators flanked by metallic contacts [60]. Although the description of the instabilities caused by a succession of avalanches and the effect of the positive charge seems to be quite realistic, this model also fails in considering the electrolyte as a metal electrode, injecting the primary electrons by a Fowler-Nordheim mechanism. Thus, the specific properties of the electrolyte are not considered, and no relations for the breakdown voltage and its dependence on the electrolyte characteristics were given.

In a later paper, Kadary and Klein measured the light emission by electroluminescence during anodization experiments of tantalum in citric acid electrolytes with different concentrations and current densities [73]. Their findings were essentially the same as those previously encountered by Van Geel *et al.* [27] and Ikonopisov *et al.* [28] for aluminium anodization, i.e. a nearly exponential increase of the emitted light with the oxide thickness, with a larger intensity for higher anodization currents and near independence of the electrolyte resistivity. The electroluminescence was supposed to be due to electron-hole recombination processes, between the carriers originated in the avalanche mechanisms present during anodization. By using first-order kinetics for these recombination processes, Kadary and Klein were able to demonstrate the empirical Equation 3, the constant b being identi-

fied with the ionization coefficient α and a , a parameter directly related to the primary electron current injected by the cathode j_e . The values of α obtained through a fitting of the experimental curves with the theoretical equations were in good agreement with those obtained through the counting of the breakdown pulses [71]. Although the independence of the light intensity with the electrolyte concentration still remains unexplained, nevertheless these electroluminescence observations constitute, for some authors, the best experimental evidence supporting the hypothesis of the existence of avalanche processes during anodization.

One of the failures of the Ikonopisov and Klein models was their inability to give an adequate explanation of the electrolyte influence on the breakdown characteristics. This effect was explicitly considered by Albella *et al.* [74, 75] by assuming that the primary electrons for the avalanches are originated at the electrolyte oxide interface, from the electrons released from the electrolyte species once they get incorporated into the oxide. As we saw earlier, the electrolyte species behave as impurity centres close to the oxide conduction band, so that they can act as a source of electrons, which can be released from these centres in a field-assisted Poole-Frenkel mechanism. The electrons are then accelerated by the high anodization field and multiplied in avalanche until they reach the anode. The breakdown appears when the avalanche current, $j_e(x)$, reaches a critical size (just a certain fraction of the anodization current, j), since at the anode the ionization rate cannot be larger than the formation rate. In this and the above avalanche models the continuity of the current throughout the oxide is implicitly ensured by one or both of the following mechanisms: electron-hole recombination with extra electrons injected at the electrolyte interface; or hole drift towards the cathode and discharge at this interface. In both cases oxygen evolution at the cathode would be the most likely lateral reaction. The first process would in addition explain the concurrent emission of light. The field distortions originated by the positive space-charge left behind by the avalanche electrons (see Section 3.1) are not considered in a first approach, since in the initial stages of anodization, i.e. for low thickness, they are supposed to be negligible. In the advanced stages, they probably would affect only local areas, where the avalanches develop in larger sizes.

Within this model, the set of equations derived by Albella *et al.* predicted a small continuous decrease of the slope of the voltage-time curves under galvanostatic conditions, in agreement with the results found for tantalum oxide [76]. The breakdown voltage is given by the relation

$$V_B = \frac{F}{\alpha} \ln\left(\frac{z}{\gamma\eta}\right) \quad (8)$$

where z is a constant, and γ and η are parameters determined respectively by the concentration of the electrolyte species in the oxide and by their ability to donate electrons (see Equation 7). Typical values for these parameters, and for α and F , give the correct

order of magnitude for the experimental breakdown voltages found for Ta₂O₅ [75]. Furthermore, from the observed correlation between the parameter, γ , and the anion concentration in the electrolyte it follows from the above equation that there will be a linear decrease of the breakdown voltage with the logarithm of the anion concentration in the electrolyte, in accordance with the experimental observations [38, 39]. Other dependences of the breakdown voltage on the anodization conditions, i.e. formation current and temperature are also contained in Equation 8, although the interdependence between the variables F , α and γ may obscure the final variation of the breakdown voltage.

The model also predicts a relation between the electronic current and the total current during the anodization process of the type:

$$\frac{j_e(V)}{j} = \frac{\gamma\eta \exp[(\alpha/F)V]}{1 + \gamma + \gamma\eta \exp[(\alpha/F)V]} \quad (9)$$

When the values of the parameters γ , η , α , and F typically found in tantalum anodization are substituted, the above equation shows a nearly exponential variation of $j_e(V)/j$ with V in a range of voltages lower than V_B . At higher voltages the curve approaches asymptotically the unity. This behaviour is qualitatively very close to that found for the electroluminescence curves [28], which supports the hypothesis about the origin of the light emission from the avalanche current. As a final point of this model, it is worth mentioning its ability to explain the variation of V_B in successive anodization experiments just changing the electrolyte concentration, as described above (Section 3, vii) [37, 77, 78]. A thorough analysis of these experiments can be found elsewhere [75, 77].

From the preceding discussion in this section, it follows that the combined action of the electrolyte anion incorporation and avalanche electron multiplication can give a reasonable explanation of the major features of the breakdown problem, i.e. the critical thickness for breakdown, the appearance of electroluminescence and breakdown sparks, the variation of the breakdown voltage with the electrolyte concentration and the successive anodization experiments changing the electrolyte concentration. The parameters of the avalanche, mainly the ionization coefficient obtained in different and independent experiments, are also consistent with the model.

Recently, Di Quarto *et al.*, while maintaining the general basis of the Ikonopisov model [79], have proposed an alternative mechanism for the injection of the primary electrons of the avalanche injected from the electrolyte into the oxide. According to these authors these electrons are released in the oxidation reaction of the hydroxyl groups adsorbed on the oxide surface in contact with the electrolyte. In this reaction, the electrolyte concentration, C , influences the primary electronic current, j_e , following a power law (see Equation 2), which finally results in a logarithmic dependence of V_B with C . An important objection to this model (which also concerns the Ikonopisov model) is the difficulty in finding a limit for the exponential

growth of the electronic current predicted in a simple avalanche model. Successive anodization experiments, as described in Section 3 are also hardly substantiated on the basis of this model.

5.2. Other models

As in the case of insulators flanked by metal contacts, the presence of some local defects in the initial metal surface has been claimed by some authors as one of the causes which triggers the breakdown during anodization. This idea is supported by the observation of the localized nature of the breakdown spots, as well as by the reducing effect on the breakdown voltage when some impurities and defects are present in the starting material [80]. The presence of small defects or flaws in the metal surface has been seen also to promote the electroluminescence at these localized spots [30, 81]. The flaw generation in the oxide as well as its influence in the oxide growth kinetics in the surrounding areas has been studied in detail by Vermilyea [82] and more recently by Thompson *et al.* [83, 84]. These investigations have led the last authors to postulate that the breakdown in Al₂O₃ is a local phenomenon started at the flaws in the films [85]. Some sort of instability, including the possibility of electron avalanches, forms conduction channels with the concurrent heat generation which further contributes to the extension and multiplication of the damaged areas until final breakdown. The phenomenological description of the breakdown events offered by this group of researchers does not include the effect of the contacting electrolyte [85]. However their ideas are not contradictory with this effect if the flaws are thought to enhance the anodization electric field at these sites. The field enhancement will then promote the development of avalanches (greater in size than in other more perfect areas), with the primary electrons released from the incorporated electrolyte anions.

Other alternatives for breakdown, based on the mechanical stresses generated in the oxide during the anodic oxidation, have been proposed. The intrinsic stresses in aluminium oxide have been studied in detail by Bradhurst and Leach [86] and by Wüthrich [87]. Its influence on the morphology (glassy or crystalline) of the growing oxides has been recently considered by Leach and Pearson [88]. According to Di Quarto *et al.* [43, 79], the mechanical failure observed in zirconium and tungsten dioxides at some specific voltage may be caused by an increase of the internal stresses, of compressive type, originated in the film during its formation.

Sato distinguishes four different contributions to the overall mechanical stresses in anodic oxides: i) interfacial tension of the film, ii) electrostriction pressure resulting from the presence of the anodizing field, iii) internal stresses caused by changes in the volume ratios and iv) local stresses caused by impurities. In addition, hydration or dehydration reactions, when present, may also contribute [89]. Sato calculated the compressive stress originated only by the first two contributions since they were considered the most important for breakdown in those anodic films under-

going a change from a passive to a dissolution state during anodization. According to this model, there is a limiting thickness, d_B , above which the compression on the film may exceed the critical stress for breakdown. Since the adsorption of the electrolyte anions decreases the surface tension, a lower breakdown voltage is expected in electrolytes having higher concentrations. The above mechanism has been used by Kato *et al.* to explain the breakdown characteristics of aluminium oxide [39, 90]. However, the model should be regarded cautiously since the electrostriction effects apply mostly in the static case, i.e. in the already-formed oxide. Apart from that, it has been observed that, in opposition to common expectations, the electric field pressure on the surface produces a positive strain, i.e. an enlargement of the oxide thickness [91].

The dissolution effects typically found in some anodic oxides, for instance in the case of aluminium anodized in acid media, may play also a decisive role in explaining the initiation of the breakdown processes. In this respect, Parkhutik *et al.* have developed a model by assuming that the dissolution rate of the film increases exponentially with the surface potential, and hence with the oxide thickness [92]. The breakdown is postulated when a critical thickness is reached at which the dissolution rate may exceed a given value. The presence of the incorporated electrolyte species increases the surface potential, and therefore diminishes the critical thickness for breakdown. This plausible mechanism may act in conjunction with others, already explained, to give an account of the observed breakdown characteristics.

6. Concluding remarks

Now, it is pertinent to review the progress made in the understanding of the breakdown processes during the anodic growth of Ta_2O_5 and related oxides. As we saw above, one of the crucial points in the avalanche theories concerns the origin of the injected current at the electrolyte/oxide interface. While the older theories consider the electrolyte to behave as a metal which is able to inject electrons through a Schottky or tunnel mechanism, recent theories recognize the need of some electrochemical reaction at the oxide surface in parallel with the main oxidation reaction. At present, neither of the mechanisms proposed, i.e. hydroxyl oxidation [79] or incorporation of electrolyte species [76], has been unquestionably proven. This point is of the utmost importance since it is also directly linked to the question about which is the dominant conduction mechanism in the electrolyte/oxide/metal system under anodic bias. From the measurements made in the range of low and intermediate voltages, interface and bulk control has been postulated [21, 23, 93]. However the results cannot be extrapolated to the higher voltage range (i.e. at the anodization voltage) where ionic conduction under high electric fields is prevailing. Future research on this problem should clarify these points. Importantly, electroluminescence experiments under varying anodization conditions, particularly in different types of electrolytes (with low and high incorporation rates) and in a wide range of

anodization voltages, should be also carried out in order to shed light on the elementary electronic processes during anodization. Recent results on anodization experiments of tantalum under UV illumination have shown a decrease of V_B with respect to values obtained in the dark [94], which points at the electronic mechanisms as the main cause of breakdown.

From the discussion of the last section it follows that there is a general acceptance of the direct influence of the incorporated electrolyte anions on the mechanisms initiating the breakdown. There is also certain unanimity in considering the presence of defects and flaws in the oxide as the sites where the breakdown is started. As stated above, both effects are compatible and it is likely that their combined action is the main cause of the instability. The subsequent mechanisms are still not clear, although there is some evidence (electroluminescence and successive anodization experiments) supporting the hypothesis of an electronic current growing in avalanche across the oxide thickness. The avalanches, which can be present even in the earlier stages of the anodization, would be triggered with more intensity at those specific sites (e.g. local impurities, protuberances, flaws, etc.) where the electric field may be higher. In this regard, it is worthwhile to emphasize the important role played by the anodization electric field in the origin and further development of the avalanches. High electric fields give rise to an increase both in the amount of the incorporated species and in their probability of ionization if the Poole-Frenkel mechanism is the dominating process. Hence, the primary electron current would be enhanced by the presence of these high fields. Besides, the avalanche coefficient will increase by the effect of the field. Therefore, all these effects considered together contribute positively to diminish the critical thickness for breakdown, d_B . This fact does not necessarily imply a low breakdown voltage, V_B , since V_B is determined by the product between the electric field and the critical thickness, Equation 6.

As a general rule, for a given material one can expect good breakdown characteristics if the anodization electric field is kept as low as possible, i.e. if the anodization is carried out at low currents and high temperatures (see Equation 1). In addition, it would be very convenient to use electrolytes giving low anion incorporation rates. Sometimes, both conditions are not compatible and a trade off should be made. Interestingly, basic pH electrolytes, such as sodium and potassium hydroxide solutions, have been recently reported to result in very pure oxide films and high breakdown voltages during aluminium anodization [95]. In this respect, there is still some controversy about the main electrolyte characteristics (i.e. anion concentration, electrolyte pH, resistivity, etc.) which determine the final breakdown voltage. Kato has analysed the influence of these factors in the case of aluminium oxide [39]. However no systematic studies for different oxides in a broad range of electrolytes have been made. Moreover, the incorporation mechanism of the electrolyte species and the variables which control it (anion charge, atomic radii, etc.) are not known, either. For this reason it is very difficult to

predict a priori from the chemical composition which type of electrolyte would result in good breakdown properties. Furthermore, no assessment has been made about the influence of the amount of the incorporated species on the electrical characteristics of the final oxides. Future research along these lines would be necessary in order to get more insight into the breakdown problem.

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