Anodic Oxide Films

C. J. DELL'OCA, D. L. PULFREY, AND L. YOUNG

University of British Columbia Vancouver, Canada

I.	Introduction				2
II.	Introductory Survey of Some General Features of Anodization				3
	1. Overfield				3
	2. Substrates				3
	3. Preparative Techniques: Constant Current Formation				5
	4. Variable Instantaneous Ionic Conductivity: Transients				8
	5. Constant Voltage Formation				10
	6. Thermal Recrystallization of Tantalum and Niobium Pentoxide F	ilms			12
	7. Photostimulated Growth				13
III.	Theories of the Ionic Conduction Process				13
	1. Introduction				13
	2. Classical Work			ġ	13
	3. Tafel Slope Anomaly and Dewald's Theory			Ż	14
	4. Transients: Field Creation of Frenkel Defects				15
	5. Dignam's Effective Field, Slow Polarization Theory of Con	nstar	nt Fi	eld	
	Transients				16
	6. Two-Valued Activation Distance				18
	7. Amorphous Oxide; Mutability and Range of Site Parameters .				19
	8. Nonlinear Dependence of log J on E				19
	9. Explanations of Nonlinear Dependence of $\log J$ on E				22
	10. Evidence That Both Ions Are Mobile				24
	11. Ellipsometric Evidence of Two Layers				27
	12. Theories of the Mobility of Both Ions				29
	13. Reinterpretation of Ionic Conduction Data on the Two-Layer M	lode	1.		30
	14. Summary of Some Principal Facts as Regards Ionic Conduction				34
	15. Limitations of Classical Model and Need for Normal Mode Tre	atme	ent.		34
	16. Electronic Effect on Ionic Conduction				36
IV.	Gaseous Anodization				36
	1. Introduction				36
	2. Methods of Producing the Plasma				37
	3. Comments on Experimental Technique				43
	4. Results				45
	5. Possible Mechanisms of Oxide Growth				49
V.	Dielectric Properties				51
	1. Introduction				51
	2. Polarization Processes				52
	3. DC Electronic Conduction				63
	4. Dielectric Breakdown			•	66
	References				73

I. Introduction

The term "anodic oxide film" is used to denote films which are grown, as shown schematically in Fig. 1, by applying a voltage between an anode

.

FIG. 1.

and a cathode immersed in an electrolyte solution which may be aqueous, nonaqueous, or fused salt. A gaseous oxygen plasma and even some solid ionic conductors may be substituted for the solution. The principle is that the transport of metal or oxygen ions through the film, which must occur for the film to grow, is aided by the electric field which is established in the film by the applied voltage. Oxide films have been made to grow faster in un-ionized gas by applying a field across the oxide using a porous metal counterelectrode deposited on the surface of the oxide (1). Films may also be grown using oxygen dissolved in a metal counterelectrode (2). However, these are not quite the same process. It is well known that anodic oxide films may be grown under some circumstances on most metals and on group IV and III-V semiconductors. Among their varied uses applications in electronic devices are of increasing importance. In this review we consider the dielectric properties and the new technique of plasma anodization which are relevant to this application. We also attempt to summarize the present position as regards theory and experiment on the high field ionic conduction process involved in the growth of the films. This is the fundamental aspect most unique to these films. The emphasis is on tantalum and niobium. An introductory section is included describing preparatory techniques and some of the principal features of the growth process.

A fairly comprehensive account of the behavior of many materials was published in 1961 (3) and a survey of ionic and electronic conduction processes in 1966 (4). Bardina (5) published a review in 1964 (available in translation). Vermilyea (6) has published some review articles and Diggle *et al.* have recently covered anodic films on aluminum (7). Extended abstracts (and the texts of some of the papers dealing with rectification by oxide films) are available from two recent symposia (8, 9).

II: Introductory Survey of Some General Features of Anodization

1. OVERFIELD

Since the question of relating the measured voltage to the field in the oxide is not free from difficulties, a brief note will be given here. The simplest way of expressing experimental results is in terms of "overfield" defined by analogy with overpotential (3, 10). Thus, the metal-oxide-solution has theoretically a metal-solution potential difference corresponding to equilibrium. A slight increase or decrease, respectively, would cause oxide to grow or disappear if the reaction proceeded reversibly and if it only occurred when charge crossed the interfaces. The metal-solution potential differences cannot be measured, but one can calculate the equilibrium voltage with respect to some suitable equilibrium reference electrode, say Pt-H, in the same solution. The excess of the cell voltage over the theoretical reversible value, corrected for any ohmic potential differences in the solution, defines overpotential. Overpotential divided by thickness defines overfield. The overfield is not quite the field in the oxide since it includes possibilities of, e.g., thickness independent potential differences across metal-oxide or oxidesolution interfaces and also a contribution from metal or oxygen ion concentration gradients across the oxide. Because of the latter possible contribution. the field strength in the oxide need not be zero when the overfield is zero. However, in practice, with films thicker than a few hundred angstroms and perhaps up to several thousand angstroms, such as have been used mostly in studies of the growth process, the practice of taking overfield to mean actual electrostatic field intensity in the oxide seems to work well.

As regards the question of concentration gradients and of diffusion under conditions of high field ionic conduction, Fromhold and Cook (11) and Dignam (12) have recently pointed out various difficulties in the theory and have proposed some suggested solutions, which we shall not discuss, since there are few data with which they may be compared.

2. SUBSTRATES

With chemically polished or electropolished tantalum and niobium substrates, the ionic conduction is extremely reproducible. Successive films may be produced with the same average thickness to 0.1% provided that the electrical control of formation is adequate. Electronic conductivity and dielectric strength and dielectric losses at low frequencies are typically more difficult to reproduce, presumably because of the effects of flaws in the oxide.

Metallurgically polished surfaces are in general less satisfactory, and buffed surfaces give abnormal behavior when anodized above a certain thickness (3, 12a). The question seems to be one of mechanical failure of the growing oxide as surface asperities are smoothed, despite the extraordinary plasticity of the film on tantalum (3). Dunn (13) has recently shown that if anodized tantalum is put through a rolling mill, the thickness of the oxide is reduced uniformly without appreciable cracking. The ductility has also been investigated by Bubar and Vermilyea (14). Another extraordinary effect is that the films on chemically polished tantalum, but not on mechanically polished or rolled surfaces, or on chemically polished surfaces which have not been leached in hot water, may be detached whole with great ease in large sections. In this connection, methods have recently been developed for making "windows" of tantalum oxide (supported by a frame of metal) by dissolving the metal from the back (15). Similar windows of aluminum oxide have been used for some time in various technical applications.

There is evidence that no difference occurs in the thickness of films grown under equivalent conditions on different crystal faces of bulk tantalum. Differences with InSb were reported by Dewald but may occur due to some change in mechanism when a certain thickness is reached (16). With tantalum and niobium, single-crystal substrates are convenient where an electropolished surface is required since grain boundaries tend to produce steps during electropolishing in the normal method (10% vol. HF + H₂SO₄, about 100 mA cm⁻² depending on temperature and stirring). Tantalum and niobium films are normally prepared by sputtering (17), but electron bombardment evaporation is also used. The films vary in structure according to the details of the method. Field recrystallization in which the amorphous oxide is displaced by crystalline oxide during prolonged anodization is apparently less liable to occur with sputtered films than with bulk [e.g., Patterson and White (18)].

There is some evidence that the oxide grows at slightly different rates on film substrates as compared to bulk (19), but this might, a priori, be due to impurities in the sputtered films. Klerer (20), using surface profile measurements made with a Talysurf to obtain the thickness, reported that the oxide on sputtered films has a rather low dielectric constant. However, Mills *et al.* (19), and later Sitarik (21) and Muth (21a), using ellipsometry found the oxide on two types of sputtered film (β and BCC) to have essentially the same dielectric constant as that on bulk. It would seem that the optical thickness measurements are more reliable, in particular since no assumptions about densities are required. Incidentally, there is some confusion in the literature about the thickness of films on bulk tantalum. Thicknesses reported by Vermilyea are based (22) on an assumed density of 8.74 g cm⁻³ which later work showed to be about 10% too high (23, 24). If a correction is made to Vermilyea's data for this, good agreement is obtained with Young's thicknesses, based on optical data (23). The value of the dielectric constant of 25,

ANODIC OXIDE FILMS

often attributed to Vermilyea, if it was based on the above density, would agree after correction with that of Young [27.6 for the conditions stated (23)].* The dielectric constant is very appreciably reduced if films are formed in H_3PO_4 , as is discussed later, so that it is necessary to state the formation conditions. We make these points to urge that it would save confusion if the basis of values of the various parameters used to describe experimental results were stated in publications. This applies also to "anodization constants" (defined below). It is hardly sensible, for example, to compare data on sputtered films anodized at constant voltage to low current densities in the microampere range with data on bulk metal anodized at 10 mA cm⁻² in a different electrolyte. It is unfortunate that the very high degree of reproducibility of the ionic current growth process tends to be obscured in the literature by reason of such practices.

3. PREPARATIVE TECHNIQUES: CONSTANT CURRENT FORMATION

In many applications the aim is to grow a film of predetermined metric thickness or, perhaps more usually, optical thickness, or capacitance per unit area. Thus, in tantalum RC thin film integrated circuits (17) the capacitance must be controlled, though admittedly it is apparently standard practice to tune RC filters by adjusting the resistors (rather than the capacitors). This is done by anodizing away metal using a viscous electrolyte placed where required on the circuit which consists of tantalum sputtered in argon onto glass and shaped by photolithography. Anodic films have not been used much in optical applications except as protective coatings on aluminum though their use as electro-optic modulators has been investigated recently (see Section III,8). The film may require other properties to be optimized, such as de conductance, ac dielectric losses, drift of capacitance under temperature cycling. In the recent use of anodic oxide films in MOS transistors (25) the questions of semipermanent dipole moment of the dielectric which may drift under dc bias and of net charge and sensitivity to ionizing radiation are important.

Those engaged on using films for device applications often refer to the "anodization constant," normally given in units of angstroms per volt. This constant sometimes means the reciprocal of the field strength at the end of the formation process. However, this is not strictly a correct interpretation if it is derived from plots of thickness versus voltage for formation at constant voltage for a fixed time independent of voltage (cf. Section II,5 on constant voltage formation).

* The Ta_2O_5 films are definitely less dense than the crystalline oxides (24). The 8.74 g cm⁻³ value is based on a Handbook value of 8.735 g cm⁻³ but an extensive literature search and correspondence with the Handbook failed to reveal its origin. This value is still occasionally quoted for "bulk oxide."

The simplest method, which is nevertheless rarely adopted for applications, is to grow the oxide at a constant current density until an amount of charge corresponding to the desired thickness has been passed through the interface. In forming an oxide of formula M_xO_y whose density is ρ we might expect a thickness

$$D = QM\eta / A2yF\rho \tag{1}$$

where Q is the charge passed, A is the area, M is the molecular weight, F is the Faraday, and η is the current efficiency, i.e., the proportion of charge not used on other reactions. In many uses, particularly with more concentrated solutions (e.g., of H_2SO_4 or H_3PO_4), η defined as above works out as greater than unity for films of supposed Ta_2O_5 on Ta (26). Tracer (27, 28) and activation studies (29) have shown that the reason is that quite considerable quantities of electrolyte species may be incorporated—enough, as Amsel et al. (29) remark, to require the films to be properly described as merely anodic and not anodic oxide. Even in quite dilute solutions appreciable amounts of electrolyte are built into the oxide and appreciably affect their properties. The reason such effects of the electrolyte in *dilute* solutions were overlooked, until the work of Randall et al. (27), is that the capacitance C for formation at a given current density J and temperature to a given potential V tends to be such that VC is a constant independent of electrolyte. This parallelism between permittivity and ionic conduction is discussed in Section III,13 and is evidently of importance for the theory.

Values of current efficiency less than unity imply loss of current to side reactions. This may be oxygen evolution or may involve oxidation of other electrolyte ions. With tantalum it is normally a symptom of scratches or inclusions. Amsel *et al.* (29) have recently confirmed that loss of current to side reactions is normally <0.1%. This was done using a $Fe^{2+/3+}$ redox system with a reversible Pt electrode to detect oxidation. Except for thin films through which tunneling occurs in the presence of a redox system, it is believed not to have much effect. In earlier work (30), using polarography and also chemical analysis methods, oxygen gas evolution was found to be negligible. Inclusion of anions in the film may involve charge transfer through the film. Effects thought to be due to proton movements in the oxide are important if the film is subjected to cathodic polarization (31–33).

Some data are shown in Fig. 2 which illustrate how the charge required to form a given optical thickness of oxide on tantalum is only slightly (<1%) dependent on temperature and current density in dilute sulfuric acid, whereas in more concentrated acid, the included electrolyte not only causes a higher field to be required for a given J, but causes considerably less charge to be required to reach a given optical thickness (34).



FIG. 2. Charge per unit area to grow film on tantalum to thickness giving second order interference at 3500 Å: *top*, for concentrations of H_2SO_4 shown; *bottom*, for 0.2 N H_2SO_4 . [After Young (34)].

Since the film depends on the electrolyte even in quite dilute solutions of some electrolytes, it becomes a matter of importance in practical applications to choose the best electrolyte, even though tantalum is much less sensitive than aluminum in this respect. Little published data are available and much of the work has been done on sputtered films which are subject to variations. Dilute citric acid is commonly used for tantalum RC circuits (17, 20) as well as dilute phosphoric acid [e.g., Patterson and White (18)]. The latter electrolyte might be anticipated to have advantages with tantalum in MOS devices, since it reduces ionic conductivity (27). With aluminum, it reduces hydration effects (27). In Ta-Ta₂O₅-"electroless" Ni capacitors using bulk, chemically polished tantalum, hot 40% H₂SO₄ was found to be better than cold dilute acid presumably because of solvent action (35).

At constant current density the voltage increases linearly with the thickness: there is still no evidence with tantalum that the mean field intensity E in the film changes with increasing thickness at constant J and T, and the accuracy of some of the data is very high (23, 35a). The rate of rise of voltage is

$$(dV/dt)_{J,T} = (dV/dD)_{J,T} (dD/dt)_{J,T} = EJ\eta\chi$$
⁽²⁾

where χ is a "constant" whose value follows from (1). Since E depends on

J to a first approximation as $E = (1/B) \log (J/J_0)$ the rate of rise of voltage is primarily dependent on (almost proportional to) J. With tantalum (36), niobium (37) and some other metals the value of E and hence of D for given V may be calculated for known J and T, for electrolytes which are not strongly taken up by the film, from published data; some data are available on more concentrated sulfuric acid (34) and phosphoric acid.

Because the transport number of metal ions and the amount of electrolyte species built into the film depend to some extent on field or current density, the structure of a film formed in electrolytic solutions from which electrolyte inclusion is important must be expected to depend on the history of current densities to which it has been subjected. It is not known how mobile are the electrolyte species built into the films, and so it is not clear whether a sufficiently long formation at a final current tends to bring a film into the same condition as formation completely at that current. This can be important in investigating film kinetics because to form films completely at very low current densities is very time consuming. The effect was not detected in work with dilute H_2SO_4 (34) but may be seen in the data in Table I for dilute H_3PO_4 .

TABLE I

Comparison of Two Formation Sequences Ending at 9.5 μA cm^- 2 and 115.85 V on Ta in 0.07 M H_3PO_4 at 25°Ca

Assum	ed refractiv	e indices	Outer film	lm Apparent total thickness (Å)		
Outer film	Inner film Metal		divided by total thickness	Formation (1) ^b	Formation (2) ^c	
2.22	2.22	3.3-j2.3	Single film	1989	2077	
2.14	2.21	3.3-j2.26	0.56	2040	2135	
2.14	2.21	3.3-j2.26	0.51	2038	2133	

^a C. J. Dell'Oca and L. Young, J. Electrochem. Soc. 117, 1548 (1970).

^b Formation (1). 10 mA cm⁻² to 136 V followed by 9.5 μ A cm⁻² (for about 7 V) to V_F ($\Delta = 300.16^\circ$, $\psi = 41.60^\circ$).

^c Formation (2). Constant 9.5 μ A cm⁻² to $V_{\rm F}$ ($\Delta = 280.28^{\circ}, \psi = 32.75^{\circ}$).

4. VARIABLE INSTANTANEOUS IONIC CONDUCTIVITY: TRANSIENTS

A much more striking variation between the films produced at different current densities is seen in the "instantaneous" ionic current density produced on reapplying a field. For an arbitrary field, applied immediately, the current density is approximately proportional to the current density which was flowing immediately previously (36, 37). If the film is held at zero field for a time t after ceasing formation at a constant current density J, and

hence constant field strength E, and the original field is then reapplied, the "instantaneous" ionic current J' (as determined by extrapolation back to the time of reapplication of the field) decreases with increasing t (38, 39). The decrease is detectably nonlinear on a J' versus log t plot. If the decrease in J' is considered as a superposition of exponential decays $[\exp(-t/\tau)]$, then there is a wide range of τ . An example is shown in Fig. 3. The capacitance



FIG. 3. The quantity R is the instantaneous ionic current on reapplying a field after t at zero field divided by the steady state current for the same field. This is plotted for initial ion current densities shown. [After Young (39).]

and losses also decay during the period of zero field (40). The process is thermally activated. The process involved was thought to be the recombination of Frenkel defects (interstitial ions plus vacancies), but it may prove to be some more subtle change in the structure of the films. Lukovtsev has reported the related effect on niobium using formation with superposed ac and dc (41). Also related to the above effect is the fact that on increasing the current from one constant value to another the field goes through a maximum. Dewald (42) showed that the "excess" field (above the steady state value) is reached after a certain charge is passed and is independent of thickness. On decreasing the current, the field goes through a minimum. Such effects are clearly qualitatively what would be expected if the concentration of some mobile species such as Frenkel defects or Schottky defects varied with field but changed sluggishly on changing the field (cf. Section III,4). If a film is formed at low final ionic current density and perhaps annealed at 100° C to further reduce its instantaneous ionic conductivity the build-up of current on applying a large field is quite striking and shows some interesting features (Fig. 4) (37). After an initial decay of total current (which is



FIG. 4. Constant field transient: development of J with time at constant field. Films were originally formed at 100 V for 3–5 h giving 2040 Å of oxide and annealed in boiling water for 5 min. 130.9 V was then applied at 0°C after various pretreatments: (a) and (b) no previous voltage application subsequent to annealing, (c) 115.3 V for 1 min; (d) 115.3 V for 5 min; and (e) 94.9 V for 15 min. (These pretreatments give no appreciable change in thickness.) [After Young (37).]

probably due to long relaxation time dielectric processes), the current may be arranged to build up by a factor of a hundred or more over a few minutes period and the rate is well described by $dJ/dt \propto J^2$. This experiment is discussed later, but it evidently shows that if Frenkel or Schottky defects are being produced, then their production is not a purely field-assisted thermal activation process.

5. CONSTANT VOLTAGE FORMATION

The common way of making films for applications is to hold the film at fixed voltage, usually for some hours, after this voltage has been reached by ANODIC OXIDE FILMS

formation at constant current. The field decreases as the film grows and hence the current density also falls. In dilute H₂SO₄ and HNO₃, the E versus log J, T relation during this process is the same (within 1% of E) as for formation at constant J (42a). However, previous remarks about the history of the film apply in the case of solutions of electrolytes which are incorporated into the film. The motivation for this method of making films is that the leakage current of films so produced is believed to be smaller. Whether this is true with well-prepared surfaces is perhaps not well established, but it is probably so with more imperfect surfaces. In any case it is quicker than formation all the way at a low current; furthermore, formation at low J with imperfect surfaces seems to lead to inferior films. In the older work by Güntherschulze and Betz (43), films formed for a long period were known as "voll-formierte" perhaps referring to the structural solidity which gave lower J for a given E suddenly applied. It is commonly believed that weak places (such as cracks) may be patched during the process. This process would seem most credible when the electrolyte has some solvent action on the film.

During formation at constant voltage, the specimen may be represented by a point which descends a nearly linear $\log J$ versus E plot with decreasing velocity. There is, however, no limiting thickness and hence field. A simple relation may be derived between J and t at constant voltage (44).

We have, approximately, $J = J_0 \exp(BV/D)$, where J_0 is a constant. Hence,

$$(dJ/dt)_v = -(JBV/D^2) dD/dt = -J^2 \chi BV/D^2$$

where χ is defined by $J\chi = dD/dt$. Treating D as constant,

$$1/J = \text{constant} + (DV\chi/D^2)t \tag{3}$$

Plots of reciprocal total current density are linear against t until such time as the current has fallen to the stage where it is dominated by leakage (nonfilm forming) current (Fig. 5). Dignam and Goad (45) stated that if the more accurate form

$$J = J_0 \exp[(\alpha E - \beta E^2)/kT]$$

is used, the quadratic term partly cancels the error due to taking D constant in the integration so that the fit is better than might be expected. We have found that this method of plotting 1/J versus t is useful for checking that the formation is proceeding properly. Clearly, formation for fixed time at different V does not give the same final J, and the Å/V ratio for equal time has in theory no exact simple meaning as a reciprocal field, and a plot of thickness against voltage for formation for fixed time should not go through the origin. The current may eventually increase and go through a maximum due to field recrystallization (46).



FIG. 5. Reciprocal current as function of time during formation at constant voltage. [After Dreiner (44).]

6. THERMAL RECRYSTALLIZATION OF TANTALUM AND NIOBIUM PENTOXIDE FILMS

It is interesting to speculate that studies of the development of crystalline structure during heating at 500 to 800°C of anodic oxide films may possibly throw light upon the original structure of the amorphous material. A common technique has been to observe detached flakes of oxide which are sufficiently thin (about 500 Å) to be transparent in an electron microscope. Recrystallization may be done by external heating or internally by the use of the electron beam or of a hot stage. Following earlier work by Vermilyea (47), Harvey and Willman (48), Calvert and Draper (49), and Pawel and Campbell (50), it has been found recently by Spyridelis, Delavignette, and Amelinckx (51, 52) that both a superstructure and the lattice rows themselves may be directly resolved. The recrystallized oxide is thought to consist of a basic structure separated into long narrow strips of material by shear planes. In the diffraction patterns, extra spots appear due to the superstructure.

It has been found that the rates and temperatures of thermal recrystallization depend on the electrolyte used in forming the film, and, in particular, is slower for films formed in dilute phosphoric acid as compared to dilute sulfuric acid (52a). This would be expected in view of the effect of phosphate in reducing ionic conductivity in the growth process. It perhaps accounts for some of the spread in recrystallization temperature reported in the literature. Field recrystallization is also sensitive to the electrolyte (46).

ANODIC OXIDE FILMS

7. PHOTOSTIMULATED GROWTH

The films on tantalum and on several related materials show photovoltaic and photoconductive effects of some interest both academically and technically (e.g., Ta-Ta₂O₅-Au provides a useful UV photocell) (53). In addition, as has long been known, a process of photostimulated growth occurs with tantalum, tungsten, indium antimonide, and other materials (3, 54-56). This process, which is not understood, is mentioned here in that it is clearly an important hurdle to be taken in explaining the mechanism of ionic conduction. Little work has been done recently though it has been confirmed by ellipsometry that the photogrown material has optical properties very different from those of the normal oxide (52a).

III. Theories of the Ionic Conduction Process

1. INTRODUCTION

Since no model has been published which explains (even qualitatively) the facts as presently established, we resort to a partially historical survey of the theory of the ionic conduction: there is still use in considering models which have been shown not to work for films on Ta, Nb, and Al since, with the diversity of materials on which anodic oxides grow, some of these models may apply well to films on materials on which little or no data are presently available. Developments before 1961 are treated very briefly since a detailed review is available.

2. CLASSICAL WORK

Güntherschulze and Betz in describing the mechanism of anodic oxide growth, referred to the two lattices of metal and oxygen ions slipping through each other (43, 57). A similar phrase was used by Dignam (58) at a recent symposium in discussing Pringle et al.'s tracer work on the conduction process but, at the time it was first used, the advances being made in the understanding of low-field (i.e., ohmic) ionic conduction were all on the basis of the idea that only defects (i.e., interstitial ions or vacant lattice sites) are mobile. In the classical picture of ionic conduction the interaction between the potentially mobile ion and the lattice is taken to be a periodic time-independent function of the coordinates of the ion. This idea has become so ingrained that one forgets how unrealistic a concept it is. The applied field E (the macroscopic field in the dielectric) is supposed to add a term -Eqx, where x is the coordinate of the ion resolved in the direction of E and q the charge on the ion (Fig. 6). In a first approximation, therefore, if a is the distance between the positions of minima and maxima of the potential energy of the ion, the energy above the minimum needed to jump from one side to the next



FIG. 6. Supposed potential energy of ion versus distance with and without an applied field.

is W - qaE. The ion is treated as a nearly independent harmonic oscillator whose loose coupling to the lattice at temperature T causes it to have a chance of having energy W - qaE equal to $\exp -[(W - qaE)/kT]$. The ionic current density, at fields high enough to make jumps against the field unlikely, is then

$$J = q2anv \exp -\left[(W - qaE)/kT\right]$$
(4)

where *n* is the concentration of defects and v is the frequency of the ion's vibrations about its mean position.

The first application of this theory to anodic oxide films was that of Verwey (59) whose model for anodic films on aluminum was $\gamma' - Al_2O_3$ in which the empty metal ion sites in the spinel $\gamma - Al_2O_3$ were randomly distributed.

Mott and Cabrera (60, 61), however, considered that the first barrier opposing metal ions traversing the film, i.e., the barrier at the metal-oxide interface, would be the largest and would define the rate. The equations are essentially the same, but the implications are different in that one would expect a difference between different crystal faces of the metal.

3. TAFEL SLOPE ANOMALY AND DEWALD'S THEORY

Later investigations have shown that the equation $J = J_0 \exp[-(W - qaE)/kT]$ is inadequate and, furthermore, that one has to distinguish between steady state conditions (constant J) and various kinds of transient response. The form of the deviations has only gradually and partially been clarified and cognizance of the two-layer nature of the films due to both ions moving has only very recently been taken. The first anomalies (22, 31) were that the

Tafel slope $\partial E/\partial \log J$ did not behave correctly with temperature. The first proposal was due to Vermilyea (22) and was based on the idea that $\log J$ was linear in E, but that the temperature dependence of $\partial E/\partial \log J$ was not as predicted (kT/qa), but in fact was absent. The limiting value of the current efficiency reported by Güntherschulze and Betz (43) was shown to be due to an underestimate of film thicknesses.

Dewald (62) at this time proposed a theory which was nearly but not quite based on a mix of the models of Verwey and Mott. The mobile ions in the oxide were taken as in excess of electroneutrality. As the film grows, a transition was predicted to occur between Mott's theory of interface control to a kind of space charge limited current where the bulk parameters controlled the current. A more exact mix of Verwey's and Mott's models was later published (63) in which the neutral oxide contained a definite nonzero concentration of mobile ions. A simple transition from interface to bulk control then occurs as the thickness becomes sufficient to accommodate a space charge layer producing the requisite change in field from interface to bulk. To get a fit with the experimental data the transition has to occur in such a way that as T increases a process with bigger a takes over. The parameters are constrained to have certain values, which is improbable in itself and the fact that niobium behaves much like tantalum would seem excessively improbable (64). On the other hand, the transition from interface to bulk control with increasing thickness seems intrinsically probable but may occur at very low thickness (<100 Å).

4. TRANSIENTS: FIELD CREATION OF FRENKEL DEFECTS

The idea of the creation of Frenkel defects by field-assisted thermal activation of ions from lattice sites into interstitial sites was introduced by Bean, Fisher, and Vermilyea (65). This gives a mechanism which causes a delayed change in the concentration of carriers on changing the field. A similar theory could be constructed for Schottky defects, i.e., metal and oxygen defects. The steady state concentration is obtained by a balance between the above process and a capture cross-section recombination process

$$dn'/dt = Nv' \exp - \left[(W' - qa'E)/kT \right] - J\sigma n'$$
(5)

where n' is the concentration of vacant lattice sites, N is the concentration of lattice sites, W', v', and a' are the corresponding quantities to W, v, and a for high field conductions, σ is the capture cross section of a stationary vacant site for the mobile interstitial ions contributing the current density J. An essential point was made by Dewald (42). This is that a bulk situation is assumed: the bulk of the oxide is taken as electrically neutral. The concentration of mobile ions in transit adjusts to give zero net space charge, thus canceling the negative charge supposed to be associated with each vacant lattice site. This gives a field which is independent of thickness. Pairs of vacancies and interstitials were supposed to destroy each other with no external field applied due to the local fields between the nearby components of a Frenkel defect. This provides a plausible model to explain the decay of instantaneous ionic conductivity at zero field, discussed in an earlier section. The range of relaxation times does not need any postulate of variability due to an amorphous structure for its explanation, since the variable separation between the components provides the necessary effect (38). The faster change for films formed at higher current densities can be explained in terms of more defects and hence smaller average separation (39).

The accelerating nature of the development of the ionic current when a field is applied to a film which, on this theory, has a low concentration of defects was found by Young (37) and it was pointed out that Eq. (5) would predict exactly the opposite effect: the current should increase rapidly at first and then more slowly since the first term is defined by E and the second increases as n' increases. This effect was taken as evidence for some kind of momentum transfer process in which ions pick up energy from their motion in the field and in turn dislodge other ions from lattice positions: a sort of ionic avalanche. In the classical theory the ion was supposed to halt at each minimum in the potential energy plot and wait till it acquired W - qaE by random fluctuations from the lattice. Perhaps this is not so; the ion may conceivably break loose and then have a considerable mean free path. Such a process would be more likely to occur in amorphous materials such as those at issue. A theory involving the concurrence of two focused collision packets was advanced to account for the $dJ/dt \propto J^2$ law, Section II.4. The only other postulated explanation was provided by Dignam (66) and is discussed in the next section.

5. DIGNAM'S EFFECTIVE FIELD, SLOW POLARIZATION THEORY OF CONSTANT FIELD TRANSIENTS

A new theory of ionic conduction, which actually was proposed by Dignam somewhat later than developments described in sections below, is brought in here since it bears on the constant field transients described in the previous section. The original treatment is detailed and involves some complicated equations. Also Dignam has recently modified his theory (58). For our present purposes, however, the essential features are as follows. First, the field causing ion motion was taken as an effective field (3, 30), i.e., the macroscopic E in the dielectric plus a contribution $P\delta/\varepsilon_0$ from the polarization where δ is a numerical factor. Second, it was supposed that the oxide is a mosaic structure of molecular groupings. An ion jumping into such a grouping was considered to contribute kinetic energy which accelerated the rate of approach of the polarization toward its static value for the existing field. The rate of approach was supposed to be proportional to the current density. Thus, Eq. (30) in (66) contains among other terms, the following:

$$dP/dt = BJ(\varepsilon_0 \,\chi_s E - P) \tag{6}$$

where B is a constant, χ_s the static relative permittivity for this process. This is of the form required to fit the observed $dJ/dt \propto J^2$ result though the physical basis is not compelling. Dell'Oca and Young (67) showed that this result may be derived phenomenologically as follows. Suppose, as an approximation, that $J = J_0 \exp[-(W - \alpha E_{\text{eff}})/kT]$, where $E_{\text{eff}} = E + P\delta/\varepsilon_0$, then, at constant E and T, any variation in J must be due to variation in E_{eff} (assuming J_0 and W are constants). Thus,

$$(\partial J/\partial t)_E = J\alpha/kT(dE_{\rm eff}/dt)_E = (J\alpha/kT)(\delta/\varepsilon_0)(dP/dt)_E$$

so that $(dP/dt)_E$ must be proportional to J, at least to fit the initial part of the transient. Dignam and Ryan (68) claimed an unambiguous decision in favor of the above theory as against the Frenkel defect theory. The argument was in fact the same as that already given by Young for the invalidity of the original Frenkel theory and, of course, did not disprove the Frenkel theory as refurbished by the ionic avalanche feature.

The form of Eq. (6) is that of a single Debye-type process in which the relaxation time τ is inversely proportional to J. Dell'Oca and Young (67) noted that the observed audiofrequency dependence of the permittivity is such as to require a superposition of a range of τ , as discussed in Section V,2 of this review. If we assume that this range of τ exists because of a physical mechanism which is the same for all τ values, but for which τ is distributed because of the amorphous nature of the material, then we expect, on the logic of Dignam's theory, that all these processes will have their relaxation times shortened as J increases. Hence, in an experiment with superposed ac and dc fields, the ac response should build up as J builds up, since progressively more processes should contribute as their τ 's decrease with increase in J. This was not observed (Fig. 7).

It is interesting to note that on this slow polarization theory the process of change in the films at zero field, which reduces the current seen on reapplying a field (Section II,4), must be the decay of polarization. The nonlinearity of the step-response (Section V,2,b) would have to be related with this effect. This has not been tested.

Perhaps the main objection to Dignam's theory is the unreasonably large amount of slow polarization that must be postulated to account for the large increase in current in the constant field transients. Thus, for a relative permittivity of about 27.6 at 1 kHz (with $n^2 = 2.2^2$ giving the ultraviolet contribution) and say 0.7% fall in capacitance per decade of frequency in the audio range, which we may perhaps suppose continues to hold for 7



FIG. 7. (a) Current density; (b) percentage change in series equivalent capacitance during application of 125 V at 0° C to film made at 100 V for 24 h at room temperature and annealed at 100°C for 5 min. [After Dell'Oca and Young (67).]

decades, we get about 5% slow processes in the 27.6 and we expect only another 3.5% or so increase in ε_r out to f = 0.01 Hz.

6. Two-Valued Activation Distance

Another feature of the theory involving Frenkel defects as proposed by Bean, Fisher, and Vermilyea was that the activation distance a' for the production of Frenkel defects had one of two values, depending on the field strength. Thus, at high fields the second hump of a periodic potential energy curve formed an absolute maximum, whereas at low fields the first hump seen by an ion leaving a lattice site was supposed to be rate-controlling. Vermilyea reported that his second investigation of the steady state kinetics fitted this model, i.e., the quantity a' had two values (69). The other parameters had then to be supposed to vary in a rather complicated fashion to fit the data.

7. Amorphous Oxide: Mutability and Range of Site Parameters

On Bean, Fisher, and Vermilyea's Frenkel defect theory, if the field is suddenly changed, then the instantaneous new value of the ionic current density is due only to the change in velocity of the ions, their concentration remaining constant. Thus, if the subscript tran refers to this process, $(\Delta E/\Delta \log J)_{tran} = kT/qa$. Vermilyea (70) found that a determined in this way increased with temperature in such a way that $(\Delta E/\Delta \log J)_{tran}$ decreased with temperature rather than increasing as predicted or staying constant as previously found for steady state $(\partial E/\partial \log J)_T$. Vermilyea explained this in terms of some kind of structural change in the amorphous or glassy oxide with the passage of current, which he considered to be in keeping with the variability of the properties of glasses in general.

Van Winkel, Pistorius, and Van Geel (71) used a method in which an ac voltage was superposed on the dc voltage to obtain $\partial E/\partial \log J$, as a function of frequency. They found values which changed from the steady state value to the above transient value as the frequency was increased. They considered this to be explained in terms of a range of site parameters in an amorphous oxide with the basic theory otherwise unchanged.

It was later shown (34) that, in the production of Frenkel defects, processes with different activation distances act in parallel, whereas an ion traversing the oxide has to take a number of jumps in series. The effect of a range of site parameters on a' and a is therefore in the opposite direction, which is not what is seen. Expressions were derived for normal distributions of a and a'.

8. Nonlinear Dependence of log J on E

In further work on the steady state kinetics (34) a spectrophotometric method was used to determine the wavelengths of minimum reflectivity due to the interference and hence to obtain the thickness (23). The method is probably the most precise available. It was found that the results (Fig. 8) could be described by

$$J = J_0 \exp - \left[(W - \alpha E + \beta E^2) / kT \right]$$

where the quantities J_0 , W, α , and β are constants. The idea of trying this type of formula was that if an activation energy (or free energy) is dependent of E, then perhaps one must consider a quadratic term as well as a linear term in an expansion in powers of E, despite the received doctrine in electrochemical kinetics (at the time) that Tafel lines (log J versus overpotential)



FIG. 8. (a) Log_{10} (ionic current density) versus *E* for, left to right, 94, 75, 50, 25 and 0°C. Data are for films showing fourth-order interference at 3500 Å, i.e., thickness 2490 Å. Bottom scale shows overpotential. (b) Slope of above plots multiplied by absolute temperature, \bigcirc , 0°C; \bigoplus , 25°C; +, 50°C; \square , 75°C; \triangle , 94°C. [After Young (34).]

must be straight. The necessity for an expression of this or related type is shown by the $(T\Delta \log J/\Delta E)$ data shown in Fig. 8. The curvature was greater in more concentrated solutions (Fig. 9). A similar method was found to



FIG. 9. Overpotential for films of same optimal thickness (second-order interference at 3500 Å) in concentrations of H_2SO_4 . Top, 50°C; Bottom, 94°C. [From Young (34).]

describe the anomalies in "Tafel slope" for transient conditions (37). The reason the Tafel slopes for steady state data had been found to be independent of T was that a fixed range of J had been used because of experimental convenience and a straight line fitted to the resulting data: at constant E there is no anomaly in the temperature dependence. The same effect in taking a constant initial J in determining $(\Delta E/\Delta \log J)_{tran}$ gives the opposite temperature dependence to that expected. The anomaly disappears for constant initial E.

This form of expression was found to apply for aluminum by Dignam, Goad, and Sole (72), Dignam and Goad (73), and by Young and Zobel (42a) for niobium. Dreiner (74) has recently used pressure vessels to extend the range of temperature available with aqueous solutions and has confirmed the expression for tantalum, withdrawing his previous rejection (44).

9. Explanations of Nonlinear Dependence of $\log J$ on E

The first explanation proposed was that of electrostriction (75). With an amorphous and hence isotropic material, the compression on applying a field is proportional to E^2 . Hence, the compression leads to a change in W with E which is of the correct form to explain the nonlinearity of plots of log J versus E. Dignam (76) dismissed this theory on the grounds that the effect calculated for data with halide crystals is much too small. This is hardly a conclusive objection since the present materials are less dense than the crystalline material and have larger infrared polarizability than alkali halides. The recently observed electro-optic effect experiments offer some hope of a meaningful calculation particularly if the secondary electro-optic effect, involving strain, could be separated out.

Thus, Holden and Ullman (77), and Frova and Migliorato (78) have observed a quadratic electro-optic effect in Ta_2O_5 and Nb_2O_5 films. The interference spectrum is shifted to shorter wavelengths. The effect is large enough to be of interest for light modulation devices. An advantage for this application is that a large electric field can be obtained in the oxide for a small voltage applied. The effect may also be of use for thickness determination (77).

In previous work it had been suggested from time to time (34, 42) that, on the basis of the classical model, small changes in activation distances should be observed with changes of field, that is, a periodic potential energy plot with superposed ramp due to the applied field. This explanation has been taken up by Dignam and various forms for the potential energy curve were used; it was found that a Morse function gave the right relation between α and β for various materials (76). Dignam's view seems to be that this function is to be expected to apply and that the correctness of the derived β value confirms the mechanism.

Christov and Ikonopisov (79) do not accept the inevitability of the Morse function. They have proposed an explanation of the curvature of $\log J$ versus E plots which is indeed basically similar in that the activation distance is supposed to change due to the superposition of a ramp qEx on the periodic potential energy function. However, instead of assuming a function to represent the whole barrier, a parabolic approximation to the barrier at its maximum is employed. The ion at the maximum potential energy may be considered to be in the "transition state" of the transition state method of calculating reaction rates.

A somewhat different explanation was proposed by Young and Zobel (4, 42a). The basic idea is that in an open-structure amorphous glassy oxide, the metal ions perhaps should be regarded as traveling rather freely down meandering channels in the oxide but becoming trapped at occasional excesses of negative charge. This is different from a crystal in which the successive

sites are sharply fixed by the nearby ions and the activation distance would therefore not be expected to change much with field and in which the ion is very likely to suffer a deactivating collision after each jump rather than cause collision multiplications. If the mobile traps are far enough apart not to interact and if the traps may be treated as coulombic, then we have an exact analogy to the so-called Poole–Frenkel law for electronic currents. The maximum potential energy is where the force on the ion is zero:

$$0 = q_1 E - q_1 q_2 / 4\pi \varepsilon_0 \varepsilon_r 2x^2$$

where x is measured from the trap, q_1 is the charge on the ion, and q_2 that on the trap. The work done on the ion by the field in moving to this point is $\gamma E^{1/2}$ where $\gamma = q_1 q_2^{1/2} / (4\pi \varepsilon_0 \varepsilon_r)^{1/2}$ and the current density is

$$J = J_0 \exp{-(W - \gamma E^{1/2})/kT}$$
(7)

This expression curiously enough gives a quite adequate fit to the steady state data for tantalum over the available (E, T) range, a fit which is only slightly less accurate than that given by the expression with powers of E. The mathematical origin of the E^2 term is essentially the same as in the theories of Dignam and Christov *et al.* but the physical basis is different.

Ibl (80) has treated the curvature of $\log J$ versus E plots in the language of transition state theory by introducing the question of the energy stored in the dielectric and has shown that curvature would arise due to a term $(\partial \varepsilon / \partial c - \partial \varepsilon / \partial c^*)$ where ε is the relative permittivity of the medium (oxide), c the concentration of reacting species (defects), and c^* the concentration of the activated complex. It was shown that a similar curvature should appear in any electrode process. Numerically, the theory was expected to fit Dignam's mosaic model better since the basic unit is a crystallite bearing a carrier and hence is more polarizable. Ord (81, 82) has used a computer-controlled ellipsometer to follow a variation in real time of the refractive index of films on tantalum following changes in current density. For example, at 6328 Å wavelength and 75° angle of incidence with a few hundred angstroms of oxide the index changed from 2.194 at 140 μ A cm⁻² to 2.199 at 2 μ A cm⁻². This was attributed to a change in the film structure, not a nonlinear electrooptic effect since the fields were too low. The effect is in the same direction as that found by Masing, Orme, and Young (83) by the Abelès method after removal of the films from the solution. A change in relative permittivity in the same direction was also observed using phase sensitive detection, e.g., by 3% when the current density was changed from 400 to $2 \mu A \text{ cm}^{-2}$. It will be observed that, if an effective field is assumed to operate in ionic conduction, then this effect is in the correct direction to correspond to curvature of the Tafel line in the observed way. Neglect of this effect gives a small

error in optical thickness measurements. This suggestion of Ord's represents a further mechanism for "Tafel line" curvature: it is not the same as Dignam's theory though an effective field is common ground.

10. EVIDENCE THAT BOTH IONS ARE MOBILE

a. Introduction. With tantalum and aluminum, it is now generally accepted that not only are both metal and oxygen ions mobile, but they are mobile to about equal extents. By contrast, with zirconium nearly all the growth is due to oxygen ion transport.

All known methods which have been used to determine the transport number of metal and oxygen ions involved the use of a marker layer. (By transport number of a given ion at a given place in the oxide, we mean the proportion of the current density at that place which is carried by the ion in question.) A marker layer is a layer of oxide which can by some means be distinguished from the rest of the oxide and its use seems to depend on the idea that ionic motion occurs through a meaningfully stable lattice or network with respect to which the marker is immobile. If further anodization results in the growth of a thickness S of oxide on the solution side of the marker layer and a thickness M on the metal side, the metal ion transport number is taken to be S/(M + S) provided that the oxide is basically the same on either side of the marker layer.

b. Implanted Inert Gas Atoms, Oxygen Isotopes. Work by Davies, Pringle, and their colleagues at Chalk River has relied mostly on the use of rare gas isotopes which were implanted either in the metal or into an existing anodic oxide film. The position of the marker has been followed during subsequent anodization either by observing the loss of energy of electrons or alpha particles emerging from the oxide or by removing the oxide a few atomic layers at a time and determining the amount of marker left in the film, the thickness of oxide being determined by the spectrophotometric method.

Davies et al. (84) used β -ray spectroscopy with ¹²⁵Xe initially implanted in the metal to show that both ions were comparably mobile in Ta₂O₅. Davies and Domeij (85) confirmed this with α -spectroscopy using ²²²Rn. In addition, the lack of spreading-out of the marker layer which was shown by this method indicated that new oxide was not being produced within the existing oxide but at the interfaces. Subsequent work with ¹²⁵Xe by Davies et al. (86) gave further results for Ta, Nb, W, Hf, and Zr, the metal ion transport number being very low for the latter two metals. It was also shown that little tantalum went into solution.

The sectioning technique was used by Whitton (87). The oxide was removed by vibratory polishing and the earlier result (84) was confirmed. When ⁸⁶Rb, ⁸⁵Kr, and ⁸²Br were all implanted into a film on tantalum, and further

anodization done, the alkali and halide atoms were found on either side of the inert gas atom. This was consistent with the direction of motion of the implanted atoms being determined by their charge. However, with zirconium, although implanted ⁸²Br did not move inward with respect to the inert gas atoms, if the film was initially grown in solution containing ⁸²Br, later anodization produced a film which contained ⁸²Br throughout.

Pringle (88) has implanted ¹²⁵Xe and several other rare gas marker layers into an anodic film grown on tantalum in dilute H_2SO_4 . The profile of the distribution of implanted atoms was determined initially and after periods of further anodization by stepwise dissolution of the oxide in an $HF + NH_{A}F$ solution, the marker atoms remaining in the undissolved film being determined at each stage. The precision and reproducibility of the results on a scale of angstroms was very high. It was found that the distribution of the marker atoms was broadened slightly during subsequent anodization. The broadening was greater the smaller the mass of the inert gas marker atoms. Nevertheless, the center of the normal distributions was found at the same point in the films regardless of the mass of the marker atoms. This was taken to mean that, although the rare gas atoms are not stationary, the center of the distribution may be used as a marker plane, enabling transport numbers to be determined. The results, however, are inconsistent with conventional ideas of ionic transport, and it was proposed that the "simultaneous movement of a group of atoms, both tantalum and oxygen, occurs in such a way that charge and material is transported from one side of the group to the other." The marker atoms are subjected to what was called a form of Brownian motion which spreads them out without changing their mean position. The conclusion that a grouping of tantalum and oxygen atoms is involved is necessary to explain the results because buffeting of the marker by separate currents of tantalum and oxygen ions would surely lead to a net displacement of the marker atoms which would depend on their mass.

Experiments were also done with ¹⁸O and ¹⁶O which indicated that the oxygen atoms built into the oxide first are later found nearer to the metal than those incorporated later, in agreement with earlier work by Amsel and Samuel (89). A given oxygen atom does not move right through the oxide: either the oxygen atoms take turns at being mobile as would occur in oxygen vacancy transport, or metal ion motion occurs. Details, beyond a presentation at a recent meeting and an extended abstract, have not been released but Table II of transport numbers is believed to be correct. It applies for 0.2 $N H_2SO_4$.

Evidence that the implantation does not affect the transport process e.g., due to damage to the oxide—is available in that the interference colors of the films are the same after subsequent anodization on implanted and undisturbed areas (89a). Amsel and Samuel (89), in addition to the oxygen

(mA/cm ²)	0°C	25°C	50°C	75°C	95°C
10	0.712	0.726	0.741	0.756	0.770
1	0.729	0.744	0.763	0.784	0.803
0.1	0.750	0.767	0.793	0.817	0.841

TABLE II
Oxygen Ion Transport Number

isotope work above, used a marker layer of aluminum on tantalum which was located by the ${}^{27}Al(p, \alpha)$ ${}^{18}Si$ reaction. During subsequent anodization, this remained near the tantalum.

c. Electrolyte-Labeled Marker Layers and Other Methods. Work by Vermilyea, Franklin, and others prior to 1961 was reviewed in that year (3). Marker layers were made by formation in concentrated H_2SO_4 , etc., in which electrolyte inclusion modified the rate of dissolution in HF, but the result as regards transport numbers was inconclusive. Work by Randall, Bernard, and Wilkinson (27) in 1964 using labeled phosphoric and sulfuric acids showed that even in very dilute solutions appreciable quantities of phosphate and to lesser extent sulfate were built into the films on tantalum. Capacitance and tracer measurements were made on the films after stepwise dissolution. These showed that the electrolyte was incorporated in an outer layer only. The concentration in terms of atoms of P to atoms of Ta ranged from 4% in 0.001 M to 18% in 14.7 M H₃PO₄ for formation at 1 mA cm⁻² at 25°C. It was shown that the permittivity of the affected layer was decreased and its ionic conductivity increased in such a way that the CV product was almost constant. The amount of incorporated material increased linearly with inverse capacitance (which may be taken as measuring approximately total thickness) during formation at constant current. The amount of incorporation increased with increasing current density and decreasing temperature.

If the incorporated material is immobile, then these results can be explained only in terms of both metal and oxygen ion transport. The metal ion transport number in 0.2 N H₂SO₄ at 1 mA cm⁻² and 25°C was 0.48, which is distinctly larger than the value of 0.256 \pm 0.002 found by Pringle using implanted inert gas atoms. Similar data was obtained by Cheseldine for oxides formed in formic acid and other organic electrolytes (90).

Pawel found that oxides formed on tantalum in phosphoric acid were more effective in protection against reaction with oxygen gas at $500-650^{\circ}$ C than oxides formed in other electrolytes (91). This fits in with Randall *et al.*'s results.

Klein (92) studied the behavior of films formed in phosphoric acid, depleted of oxygen by annealing at elevated temperatures *in vacuo*, and then anodized

at constant current. Changes in dV/dt were observed corresponding to the replenishment of oxygen in the two layers. Evidence was obtained which appears to confirm the immobility of the incorporated phosphate. Transport numbers were obtained from the ratio of the voltages corresponding to the repair of the two parts of the film.

Finally, a technique of nuclear microanalysis has been applied to anodic oxide films by Amsel *et al.* (93). The oxide is bombarded to induce nuclear reactions such as ${}^{16}O(d, p) {}^{17}O$ or ${}^{18}O(d, p) {}^{15}N$, the particles emitted by the target are detected, and counted. Comparison with emissions from a standard specimen allows, for example, the concentration of ${}^{16}O$ and ${}^{18}O$ to be measured. The amount of oxygen in the films was found to be larger than that expected from the charge passed during anodization in concentrated solutions. This confirmed the incorporation of polyatomic anions containing oxygen from the electrolyte.

11. Ellipsometric Evidence of Two Layers

Optical methods are particularly useful for determining the thickness of anodic films. Details of methods developed up to that time were reviewed (3) in 1961 and therefore will not be discussed here. The principal method involved the use of a spectrophotometer to locate the wavelengths of minimum reflectivity due to interference (72). Intensity reflectivity in p light polarized in the plane of incidence had been investigated and it was shown that a modification (83) of a method due to Abelès was useful to determine refractive indices and was sensitive enough to detect the small changes which occur with current density of formation. Most of the earlier work was done with dilute solutions of electrolyte such as sulfuric acid, which are not taken up as strongly as phosphoric acid. The results indicated (for tantalum and niobium) uniform, nonabsorbing films with indices independent of thickness. Exceptions were an anomaly at the Brewster angle (83) which suggested a very thin outer absorbing layer, and also that films formed in more concentrated sulfuric acid were absorbing and nonhomogeneous. Nonuniform films reported by Heavens and Kelly (94) with tantalum were probably due to the peculiarities of their substrates, which were thin electron bombardment evaporated films, and their results are not supported by any other investigations.

Ellipsometry was apparently first applied to the films on tantalum by Kumagai and Young (95) and later by Young and Zobel (42a). The results were in agreement with earlier work by other methods. It has since been found by Dell'Oca and Young (96) that the two layers may be detected by ellipsometry if the films are made in dilute phosphoric acid. Presumably, given sufficient accuracy, they could also be detected with dilute sulfuric

acid, but this has not been achieved. The method is as follows. In ellipsometry ψ and Δ are determined. These quantities are defined by

$$\tan\psi \exp i\Delta = R_p/R_s \tag{8}$$

where R_p and R_s are the complex reflectivities in light with electric vector in the plane of incidence and perpendicular to this plane respectively. For a single layer, each R is of the form

$$R = (r_1 + r_2 e^{-2i\delta})/(1 + r_1 r_2 e^{-2i\delta})$$
(9)

where r_1 and r_2 are the Fresnel coefficients for the outer and inner interfaces of the oxide in p or s light as the case may be, $\delta = 2\pi nD \cos \phi/\lambda$, n is the refractive index, D the thickness, ϕ the angle of refraction, and λ is wavelength. For two uniform layers of oxide,

$$R = \frac{r_1 + r_2 e^{-2i\delta_1} + r_3 e^{-2i(\delta_1 - \delta_2)} + r_1 r_2 r_3 e^{-2i\delta_2}}{1 + r_1 r_2 e^{-2i\delta_1} + r_2 r_3 e^{-2i(\delta_1 + \delta_2)} + r_1 r_3 e^{-2i\delta_2}}$$
(10)

where r_1 , r_2 , r_3 refer to the interfaces starting at the outer surface, and δ_1 and δ_2 refer to the phase change for a single passage through the individual oxide layers. For two layers which are nonabsorbing and which do not differ much in index, the terms in δ_1 and δ_2 return nearly to their original values only after $2(\delta_1 + \delta_2)$ has gone through two cycles of 2π increase. Figure 10 shows a typical experimental curve as well as a calculated curve. The film shown was grown on mechanically polished tantalum at 1 mA/cm² in 0.07 M H₃PO₄ at 25°C. Electropolished substrates give similar results. Ellipsometry measurements were made in air, first on the unanodized metal and then at intervals during oxide growth (angle of incidence 67.5° and wavelength 5461 Å). The experimental points cover more than three cycles in Δ . Beginning at the bare surface on unanodized metal, as anodization proceeds, thickness increases and the cycles denoted by crosses, circles and ×s are obtained in succession ending part way into the fourth cycle at 285 V.

Curve fitting of these results indicates that there are two layers which grow simultaneously during anodization with the ratio of outer layer thickness to total oxide thickness equal to 0.51. The index of the inner layer was found to be 2.21, that of the outer layer 2.14. The metal index was found to be 3.3 - i2.24.

It is thought that ellipsometry may provide a useful method of investigating the structure of the two-layered films and hence of determining transport numbers. This, of course, depends on the accuracy with which the parameters may be assigned. This is rather a complicated matter and will not be discussed here.

In the case of oxide growth at about 1 mA/cm^2 in concentrated H_3PO_4 at 25°C about three quarters of a cycle of the ellipsometry curve was obtained



FIG. 10. Ellipsometry data for formation in 0.07 $M H_3PO_4$ at 25°C. Curve is computed for two layer model as in text.

before breakdown. However, if the metal index and that of the inner layer are taken as fixed from previous work, then the index of the outer layer was found to be 1.98 and the outer film is 0.65 of the total thickness. The fit obtained (standard deviation between computer and experimental points) is almost tenfold better using two layers, then a single absorbing layer. Ellipsometry results for successive anodization in concentrated H_3PO_4 followed by dilute H_2SO_4 or H_3PO_4 confirmed the presence of three layers.

12. THEORIES OF THE MOBILITY OF BOTH IONS

The mobility of both ions was unexpected because it seemed unlikely (as was pointed by Dewald and others) that the various parameters and in particular the activation energy should accidentally produce independent metal and oxygen ion current densities of comparable magnitudes. Some connection between metal and oxygen ion motion must be sought. For example, Vermilyea (96a) has considered the idea that when a bond is broken, both participants in the bond are freed. Dignam considered that the mobility of both ions was explained by his mosaic model as being due to the momentum transferred to a molecular group when a mobile ion entered it. (In later work, which is not yet textually available, he has discussed the nature of the molecular groups and the effects of the interfaces and has claimed to have an explanation.) Pringle has proposed a similar idea, as already mentioned.

Except in vague terms of some form of local disintegration of the structure, we consider that the comparable mobility of both ions remains unexplained. It is, of course, possible to formulate equations of conventional form for both ions independently mobile, their concentrations being linked through Poisson's equation. Such a condition could lead to transient behavior similar to that observed in that the concentration of the more mobile ion will increase sluggishly after changing the field as the concentrations of the other ion builds up (63). Some form of momentum transfer process must, in our view, still be postulated to explain the constant field transients.

13. Reinterpretation of Ionic Conduction Data on the Two-Layer Model

a. Correlation between Permittivity and Ionic Conduction. A reappraisal is needed of the experimental data on ionic conduction to take cognizance of the now generally accepted view that the films on tantalum always consist of two layers which grow due to oxygen ion and metal ion transport, respectively, and that, in some electrolytes, even when dilute, the outer layer will have its properties modified by the inclusion of electrolyte species. The effect is to reduce the permittivity (and the refractive index) and to reduce the ionic current for a given average field. In what amounts to an extension of the work of Randall et al., Dell'Oca and Young have recently analyzed formation data for films formed in dilute phosphoric acid in terms of this two-layer model. Figure 11 shows $\log J$ versus E (mean field) for such films obtained at constant voltage by the method of Young and Zobel (42a); i.e., ellipsometry data were fitted by a two-layer model and the ionic current density was calculated from the rate of increase in thickness. If we assume that the electrolyte-free inner part of the film is essentially the same material as that of the whole film for films formed in dilute sulfuric acid in which electrolyte effects are smaller (and, in fact, undetected), then we may use previous $\log J$ versus E data for the latter to calculate the $\log J$ versus E relation for the outer, modified part of the film. The $\log J$ versus E relations for the inner and outer parts of the film fall, of course, on either side of the log J versus mean E data, as shown in Fig. 11.



FIG. 11. Log₁₀ (ionic current density) versus field for 0.07 M H₃PO₄ at 25°C. Left: inner part of film. *Middle*: mean values (experimental data). Right: outer part of film.

The interesting point is that (Fig. 12) if we plot $\log J$ versus $D/\varepsilon_0 = \varepsilon_r E$ (where D is displacement), the two plots nearly superpose. Here we estimated ε_r for the outer part of the film by assuming that ε_r for the inner part is the same as for films formed in dilute sulfuric acid.

Three explanations, at least, are possible on present models of ionic conduction for this correlation between ionic conductance and permittivity which has been noted for oxides of different metals and for films formed in different electrolytes on the one metal. First, we have the notion of some kind of effective field which will tend to be proportional to D rather than E. Second, one might try to argue that the same structural factors determine permittivity and ionic conductivity. Here it may be noted that the change in permittivity is due to infrared polarization (associated with the normal modes of the lattice) not to defect processes associated with mobile ions and which have relaxation times in the audio region, since in this region of frequency there is apparently little difference between the values of frequency dependence of ε' (or value of ε''). Finally, Dignam (58) seems to postulate that no explanation is necessary in that D is continuous through the film as a result of the electrostatic boundary conditions. However, there seems no reason to exclude a dense space charge (effectively a sheet charge) between the two layers, just as there must be a charge layer near the interfaces to



FIG. 12. Data of *left* and *right* curves of Fig. 11 plotted against electric displacement $(D/\varepsilon_0$ is plotted).

adjust the rate of injection to that of bulk transport, even though the bulk of the oxide is neutral.

b. Possible Explanation of Nonlinear log J versus E Relation in Terms of Two-Layer Model. The metal ion transport number is believed to increase with increasing field. If so, the relative thickness of the outer layer will be greater for films made at high fields and currents. If electrolyte incorporation occurs, the field required for a given current density in this outer layer is larger than that in the inner layer. Hence, the mean field will increase more than linearly with E, as observed. A quantitative treatment of this effect has not been made and we do not know whether the log J versus E relation for the oxide in the absence of all electrolyte inclusion would be completely linear or not. One would not now expect a linear relation. We note that the ratio of the thicknesses of the two parts and the profile of electrolyte content in the outer part depend on the sequence of currents at which the film is grown. We do not know if the transport number is a function of current density only and not partly of film structure. This adds to the difficulty in analyzing the results. (In Fig. 11 the ratio of thicknesses was estimated partly

ANODIC OXIDE FILMS

from ellipsometry, which gave the initial ratio, and partly by assuming that the transport number was a function of J only so that the data of Randall *et al.* (27) could be used to determine the change during subsequent formation. The change in amount of electrolyte incorporated with changes in Jwas not allowed for.) However, the excellent agreement between constant J and constant V formation data in dilute sulfuric acid, by Young (34) and Young and Zobel (42*a*); the agreement (after allowing for the different basis of thickness determination) with Vermilyea's data for dilute nitric acid (42*a*), and with Dreiner's recent work (74), suggest that any electrolyte incorporated in these experiments had little influence so that the curvature *may* not have been due to this effect.

c. Bulk or Interface Control. If the local field at a given depth in the film is determined by the local material rather than by the solution interface, then on changing from one electrolyte to another, the mean field should slowly approach the mean field typical of formation entirely in the second electrolyte. Theory and experiment are shown in Fig. 13. It was assumed that the transport number was a function of J and the electrolyte only (and was thus known from ellipsometric data for formation in the dilute phosphoric acid), and that the fields in the new inner and outer layers were the same as



FIG. 13. Mean field versus time during formation at 1 mA cm⁻² and 25°C after changing from 14.7 M H₃PO₄ to 0.07 M H₃PO₄. Initial thickness 550 Å (shown by circle with dot).

for formation entirely in the second electrolyte (and were thus known from previous work). The differential field $\partial V/\partial D$ changed quickly to the value typical of the new electrolyte. The product CV where C is the capacitance was unchanged to within 1%.

14. SUMMARY OF SOME PRINCIPAL FACTS AS REGARDS IONIC CONDUCTION

The present position is, therefore, that a theory or model is required which will explain the following:

1. The comparable mobility of both ions in several systems (and the fine points of the tracer experiments).

2. The steady state dependence of J on E and T. This may or may not for pure Ta₂O₅ films turn out to require the βE^2 term in the equation $J = J_0 \exp[-(W - \alpha E + \beta E^2)/kT]$ when the two-layered nature of the films is properly allowed for. We imply no dependence of E on thickness of oxide or on the crystal face of the substrate metal.

3. The relation between permittivity and the α and β parameters in (2) both for different metals and for varied oxide on the same metal.

4. The transient behavior, in particular the accelerating, autocatalytic build-up of J at constant E.

5. Why ultraviolet radiation increases J for given mean E in the oxide.

15. Limitations of Classical Model and Need for Normal Mode Treatment

In an ionic crystal, the ions are held in place by other ions and cannot be regarded as independent oscillators. This is, of course, well recognized in the theory of lattice dynamics and dielectric properties (97-99). The basis of the classical treatment of ionic conduction, which is that the potential energy of the mobile ion depends only on its own coordinates, is therefore very unsatisfactory. The true independent oscillators (for small amplitudes) are the normal modes of the crystal. These are perturbed by the presence of the interstitial ions or vacancies which are the supposed mobile species. The difficulties which are met with in trying to introduce concepts of effective field or effective charge seem to us to be largely due to the basic inadequacy of the model. Any effective field will probably not be constant either through the volume of an individual ion, as Szigeti (98) noted, or over the path from minimum to maximum potential energy. Thus it is clear that the work done in moving from one stable site to the next is determined by the internal or Maxwell field. Thus, any additional acceleration up to the barrier due to polarization effects has to be balanced out on the way from the top of the barrier to the next stable site. This idea has recently been developed by Dignam ANODIC OXIDE FILMS

(12). With the present systems, it may indeed be the case that there is a much closer approach to the classical model than for ionic conduction in crystals. since the structures are appreciably less dense than the corresponding crystals and the ions may be fairly loosely confined to channels through the glass network, as we have already noted in Section III,9. Since there is good evidence for an autocatalytic effect in which momentum transfer from mobile ions sets other ions into motion, the notion of focused collisions may also be relevant to the process, as suggested previously (37). It is interesting, however, to consider what can be done by using the theory of normal modes. The problem is to formulate the transition state in terms of normal modes and their interactions, which would seem to require many-body theory. A very naïve treatment, representing the simplest possible assumption, could be based on assuming that an ionic jump occurs when a critical amplitude exists in some particular mode. To interact with the constant applied field, this mode may be assumed to be of infinite wavelength. For a slab of dielectric with an external field E_{ext} normal to its face, then as shown by Szigeti, a mean displacement is caused of

$$\bar{q} = E_{\text{extl}} (\partial \mu / \partial q)_{\perp} / \omega_{\perp}^{2}$$
(11)

where q is the normal mode coordinate per primitive unit cell, μ is the dipole of the mode per unit cell, ω its angular frequency and the symbol \perp is Szigeti's symbol for this configuration. An ionic jump may be supposed to occur when $q = q_c = q_c' + \bar{q}$, where q_c' is the thermal amplitude. The current density at high fields would then be

$$J = 2aNv_{\perp}e\exp(-W(E)/kT)$$

where 2a is the jump distance, N the concentration of mobile ions, e the electronic charge, and

$$W(E) = \frac{1}{2}\omega_{\perp}^{2}(q_{c} - \bar{q})^{2} = W_{0} - AE + BE^{2}$$

and

$$A = \varepsilon q_c (\partial \mu / \partial q)_\perp$$

The formula $\exp(-W(E)/kT)$ has been applied for the chances of an independent oscillator having energy W(E). Actually, the W(E) used is per unit cell. Using the relations between the frequencies and $\partial \mu / \partial q$ of the above and of the transverse and longitudinal modes and by taking the internal field as $E_{\text{extl}}/\epsilon_r$, we obtain

$$A \propto (\varepsilon_{\rm r} - n^2)^{1/2} \varepsilon_{\rm r} / n^2 \tag{12}$$

where ε_r is relative permittivity. If this is of any significance, it indicates a clue to the relation between permittivity and ionic conduction; or, if one

prefers, an indication that an effective field should be used in the classical expressions. Ibl's treatment in terms of transition state theory indicates the same thing by a different route.

16. Electronic Effect on Ionic Conduction

Fritzsche (100) has recently proposed that in the anodic oxidation of silicon the mobile ions are produced by collision ionization involving electrons. With silicon the ionic current is only of the order of 1% of the electronic current. He noted that when an electron-hole pair is produced a valence bond may be considered to have been broken, and he postulated that this process is a necessary preliminary to ion motion. This is analogous to the need for positive holes for anodic dissolution. He did not consider an electron wind effect although the momentum would be in the right direction to assist oxygen ion transport. He derived an explanation of the increase of ionic/electronic current ratio with increasing current and of a constant *Jt* product at constant voltage. The idea of an electronic excitation prior to ion transport may be relevant also to the UV-induced growth where a similar high electronic current occurs.

IV. Gaseous Anodization

1. INTRODUCTION

The ordinary process of anodization, described above, has some disadvantages in the fabrication of devices, particularly integrated devices. It is preferable that all the steps in the manufacture be compatible with automated production in a multistation vacuum system, the sample being moved from station to station for each stage of development, e.g., deposition of semiconductor films, evaporation or sputtering of metal films, the anodizing of metal or semiconductor, deposition of counterelectrodes. One way in which thin dielectric films can be grown while still satisfying the above conditions is by the technique of plasma anodization, in which the usual aqueous electrolyte is replaced by gaseous plasma, and the material to be anodized is suspended in the plasma and biased positively with respect to it from an external source. Devices that have already been made by this technique include thin film capacitors (101), Josephsen junctions (102, 103), MOS transistors employing gate, insulation made by plasma anodization of deposited Al films (25, 103a, 103b), and thin films for electrical noise studies (104) and tunneling experiments involving the investigation of barrier heights (105, 106), electronic conduction (106), and molecular spectroscopy (107).

There is thus considerable interest in the technique and since the pioneer work of Miles and Smith (108) a wide range of metals and semiconductors including Al (101, 105, 108–113), Ta (108, 110, 114–122), Mg (108), Cr
(108), Sb (108), Bi (108), Be (108), Ge (109, 123, 124), Si (108, 123, 125, 126), Ti (127), Nb (128), Zr (129), La-Ti (130), and GaAs (131, 142b) have been anodized by this method. Although the bulk of the literature refers to work in oxygen plasmas, the process is not limited to oxide production and, for example, nitride films on Al (132) and Si (133, 133a) have been produced using a nitrogen plasma.

An immediately striking difference between anodic growth in solutions and plasmas is the extremely low current efficiencies of the latter process. However, for many technical applications which require other than very thin films, the actual growth rate is more relevant, and it appears that high growth rates may be obtained by using high density plasmas. Academically, the technique is of importance as an extension of aqueous solution studies, chiefly in view of the radically changed nature of the oxide-electrolyte interface. The possibility of modifications to the kinetics of the oxide growth process is of interest and, despite the low current efficiency, it is possible to obtain data on the dependence of the ionic current on field.

2. METHODS OF PRODUCING THE PLASMA

a. The Low Pressure Glow Discharge.

(1) Cold cathode. This type of plasma has been the most commonly used for plasma anodization presumably because it is the most easily produced and there is relatively extensive information available on it [see, e.g., Cobine (134)]. The main regions of the cold cathode discharge are shown in Fig. 14,



FIG. 14. The dc cold cathode discharge: (a) Appearance; (b) potential distribution.

and are the Crookes dark space (CDS), the negative glow (NG), Faraday dark space (FDS), and positive column (PC). The small glowing region near the cathode is called the cathode glow and is separated from the cathode by the cathode drop region. There is a net negative space charge in this region

due to the many electrons being emitted. Positive ions are attracted to the cathode and the cathode dark space is a region of high positive ion density. There is thus a high potential difference across the cathode drop and electrons accelerated through this region begin to ionize gas molecules in the negative glow region, where the electron concentration increases such that the net charge density is nearly zero and the potential reaches a maximum value with a very low field. The electrons are thus accelerated very little between collisions in this region and hence the ratio of ions to electrons per unit volume decreases causing the potential to fall slightly through the negative glow. The minimum of potential is somewhere in the Faraday dark space after which it rises, causing acceleration of the electrons and leading to the positive column, where there are almost equal concentrations of positive ions and electrons. The electron concentration existing in glow discharges is high $(10^{10} \text{ cm}^{-3})$, and it is possible that some effect like that proposed by Fritsche (100) (Section III,16) causes the growth rate to be influenced by the large electronic contribution to the anodizing current. This is in contrast to growth in aqueous solutions where few electrons with sufficient energy to enter the oxide are present. A typical current efficiency of 0.4%for growth of Ta_2O_5 at an anodizing current density of 1.5 mA/cm², a pressure of 1 Torr and in the positive column of a glow discharge with a sample temperature of 31° C has been reported (122). Slightly higher values were obtained at higher substrate temperatures.

The fact that high growth rates can be achieved in some dense plasmas suggests that the controlling factor is the concentration of some charged oxygen species. However, the actual concentration of the various species of ionized oxygen in a dc discharge tends to depend markedly on the presence of various trace impurities; e.g., Thompson (135) has reported 90% of the ionized gas to consist of approximately equal amounts of O^- and O_2^+ , whereas Knewstubb et al. (136) postulate that the O_2^+ ion is significantly predominant in the glow discharge, particularly in the negative glow region. These data do not suggest which part of the discharge is likely to be most suitable for plasma anodization, and this information has not so far been given by actual anodizing experiments, although they have been carried out in the three principal regions of the discharge, i.e., the negative glow (108, 114, 116), Faraday dark space (114), and positive column (101, 108). This is because sample preparation and position in the system (which could be important as regards film contamination) (136a) as well as gas pressure and discharge current density have varied from experimenter to experimenter. However, Miles and Smith (108), using an experimental arrangement similar to that shown in Fig. 15, observed growth rate maxima at oxygen pressures of 50×10^{-3} and 1 Torr, and it has been suggested (105) that the reason for this was that at these two pressures the anodizing sample was engulfed



FIG. 15. Typical plasma anodizing apparatus. [After O'Hanlon (136a).]

in the densest regions of the plasma, i.e., the negative glow and positive column, respectively. The optimum pressure for anodization will depend on the geometry of the system, and the relevant factor may well be that the plasma electron density is pressure dependent (136b).

Obviously spectroscopic or other diagnostic studies of oxygen plasma need to be carried out simultaneously with anodization experiments in the same system for the relative importance of the various oxygen species to be determined. Another diagnostic technique that may be employed is that in which the sample to be anodized is considered as a Langmuir probe. When the substrate is allowed to float electrically in the plasma, it will be bombarded by many more electrons than other particles and hence assume a negative potential with respect to the plasma potential. Thus, any ionic current carried by the substrate will be due to the bombardment of positive ions as the negative ions in the plasma are produced with only small thermal energy. Only when the substrate is biased positively to an extent that the drift current becomes comparable to the random electron and ion currents will significant contributions to the anodizing current result from negative ions. Films about 30 Å thick on Al have been reported (*108*) to grow in dc discharges with no voltage applied to the sample, but the thickness versus time relationships closely resembled those obtained for thermal oxidation. No growth has been reported with samples biased negatively in a glow discharge and, in fact, a cathodic reduction action has been observed by Nazarova (123) for oxide films on Ge. It is likely that this reduction in thickness results from the sputtering away of the oxide film by the bombarding action of positive ions. When the sample is biased positively with respect to the plasma, growth does occur which would suggest that some form of negatively charged oxygen ion is important in the growth process.

Since cold cathode plasmas are usually generated at kilovolt potentials, the ions present can be expected to have a wide range of energies and it is also not impossible that different ion species may be formed during the energetic bombardment of the substrate. The presence of high energy ions in the plasma may lead to sputtering away of the anodic film. Locker and Skolnick (112) reasoned that this phenomenon may impose a limit to the thickness of Al₂O₃ that can be grown on Al. The limit would depend on the particular geometrical arrangement of the electrodes and the electric field gradient in the different systems. They found that a film could be grown at constant current to a certain thickness, after which the film ceased to grow although the constant current continued to flow, suggesting that at this stage a steady state condition between sputtering and growth was reached. The value of the anodizing voltage at this growth limit was about 20 V with respect to the anode which probably implies a potential of from 50 to 100 V positive with respect to the neighboring plasma. At these voltage levels sputtering has also been observed to occur by Jennings and McNeill (137) who deposited different thicknesses of gold onto tantalum substrates and noted the time taken for the gold to be sputtered off at various positive potentials of the substrate with respect to the plasma. They found that the rate of sputtering increased with positive increase in the substrate voltage up to about 80 V with respect to the plasma, and then remained nearly constant as the voltage was further raised. It was also noted that in this latter region the current drawn by the positively biased substrate increased rapidly as the voltage was increased, probably due to an increase in the fraction of the anode current which is carried by electrons. Possible collision processes that might account for the above relative increase in electron current are oxygen negative ion dissociation by impact with gas molecules, or ionization of oxygen by electron impact.

Besides sputtering away of the sample being anodized, the actual removal of material from the discharge electrodes is also an important factor to consider in dc discharge anodization because it may lead to contamination of the growing film. To prevent sputtered material from the electrodes from reaching the sample, the spacing between the sample and discharge electrodes should be adequate. For instance, at a pressure of 0.1 Torr, a spacing of 20 cm corresponds to a distance of about 200 mean free paths and hence any material sputtered off the electrodes should be scattered to the walls before reaching the sample. It follows that the electrodes, particularly the cathode which is continually bombarded by heavy positive ions, should be of material with a low sputtering rate. W, Ta, Ni, Al, Si, Au, Pt, duraluminum, and stainless steel have all been used, but Al has been employed most commonly since it has a very low sputtering yield because of the protective coating of oxide which normally forms over its exposed surfaces. Si has been recommended since it can be thoroughly degassed, has a low sputtering yield, and its oxide has no tendency to flake or powder. Another potentially useful property of Si is that single crystal silicon to Pyrex seals can be made and are vacuum tight at temperatures from -195 to $450^{\circ}C$ (125).

A further problem at the cathode in cold cathode discharges is the difficulty in obtaining stable and uniform electron emission and it is desirable to use either brush cathodes (138) or so-called inverse brush cathodes (139) to improve this situation. The brush cathode consists of a closely spaced uniform array of sharp pointed needles fastened end-on to a flat cathode baseplate. Increased current densities are obtainable with this device owing to the enhanced cathode field at the needle tips. The increased stability of the discharge probably results from the elimination of ill-defined "hot spots" which move around on a flat cathode surface. Similar stability can be achieved by use of an inverse brush cathode in which a closely spaced uniform array of holes are drilled into the cathode surface. Musal (139) reasoned that inverse brush cathodes produce a higher current density than flat cathodes operating under the same conditions due to their large surface area being nearly parallel to the incoming ions and photons that cause electron emission from the cathode surface. On this argument the cathode configuration would be optimized by maximizing the surface area at a grazing angle to the bombarding ions. Musal (139a) has found that an electrode with concentric circular V-grooves cut into the flat end surface of a round cathode gave a further increase in current density with no loss of plasma stability.

It would appear, to summarize, that in cold cathode dc discharges high discharge current densities and plasma stability can be achieved, but the plasma is only weakly ionized in that the charged species necessary for oxide growth are not abundantly available. This fact, probably coupled with the removal of the film by bombarding high energy ions, leads to very slow rates of growth.

(2) Hot cathode. The essential differences between a gaseous discharge with a hot cathode and one with a cold cathode lie in the region of gas at the cathode-gas interface, i.e., the cathode fall region. Near the hot cathode there is a space charge of electrons whose density determines the current leaving the

cathode. As these electrons cross the cathode dark space, they are accelerated by the field and their space charge becomes less and less dense. When they have been accelerated through the ionization potential of the gas, they start to ionize its molecules and, at this plane, the plasma begins. The electrons at this position have much smaller kinetic energies than those entering the negative glow of a cold cathode discharge, because the cathode fall is less. But, as there are far more electrons in the hot-cathode discharge, they are able to maintain a more intense ionization in the plasma. An arrangement for plasma anodization using such a cathode should presumably, then, enable faster growth rates to be achieved. Furthermore, the potential drop across the plasma to maintain the discharge is small, and thus there is a diminution of high-energy particles that may lead to sputtering of the oxide film. Despite these advantages there has been no published work on plasma anodization using thermionic cathodes, although Ligenza (139b) has achieved rapid oxidation rates for silicon with this method. The difficulty is to find a hot cathode which does not deteriorate in the oxygen atmosphere. Ligenza has used heated oxide-coated metals for this purpose and Schuermeyer (personal communication) and the present authors have used thoria-coated iridium cathodes* with some success.

b. High-Frequency Plasmas. The theory of high-frequency discharges has been considered in some detail by Francis (140) and apparently greater electron densities ($\sim 10^{13}$ cm⁻³) than those existing in dc discharges can be obtained. This would be expected to lead to increased ionization of the gas and higher gas temperatures resulting in increased rates of anodization. This is apparently the case in practice as silicon oxide films about 2000 Å thick have been reported to grow in 5 min by Kraitchman (126) and thicknesses of 6000 Å have been obtained by Ligenza (125) after 100 min of anodization, although the current efficiency of growth does not seem to have increased proportionately, being about 4%. Both these workers used 2.45 kMHz microwave generators to establish the plasma and judged the sample temperature to be in the region of 300-400°C. Undoubtedly little growth due to thermal oxidation occurs at these temperatures. Nevertheless, films of SiO₂ about 4000 Å thick have been grown in 40 min when no voltage was applied to the sample. This may be an indication that the ions have sufficient energy to bury themselves into the oxide. Ligenza (125) has suggested that the acceleration of the growth rate by the presence of an electric field when silicon is made positive with respect to the oxide-gas interface, might explain the inverse dependence of oxidation rate on pressure that he observed. Within limits, as the gas pressure is lowered, electron temperatures in the plasma increase, and consequently wall potentials increase (negatively). It

* Available from Electron Technology Inc., 626 Schuyla Ave., Kearny, New Jersey.

would appear, then, that as a result of this the potential between siliconoxide interface and oxide-plasma interface must increase, leading to an increase in oxidation rate with decrease in pressure.

c. Plasmas Formed by Electromagnetic Ion Guns. Anodization in a plasma formed by this means has been reported by Jennings et al. (118) who used an ion beam system employing an electromagnetic extraction system which was intended to inhibit the flow of electrons to the sample being anodized. The data given in Fig. 7 of their paper indicate that a current efficiency of 4% was obtained for the anodization of Ta although the figure of 17% is also quoted. The relatively high value of current efficiency was to be expected if indeed the electron concentration in the vicinity of the substrate was reduced, although it is not known to what extent negative ions were also diverted away from the sample. It is conceivable that application of magnetic fields to a glow discharge plasma could be used to enhance the current efficiency, e.g., a transverse magnetic field could be employed in the substrate region to divert electrons away from the sample, or a longitudinal magnetic field in the substrate-cathode region should, by increasing the path length of the electrons, increase the rate of ionization per electron. A further experiment would seem to be to use mass spectrometry methods to separate the various oxygen ions and then allow each particular species to strike the substrate (141). Although this would not then be plasma anodization it might throw some light on which ions are responsible for film growth.

3. Comments on Experimental Technique

Although the high-frequency plasmas have the highest electron concentrations of the plasmas discussed above they also give the highest growth rates, presumably due to a higher concentration of some active oxygen species. Another advantage of plasmas induced by high-frequency fields is that problems from contamination by material from discharge-sustaining electrodes do not arise. As to possible drawbacks, it is not yet clear whether film uniformity may be made as good as in dc discharges. Ligenza (125) reported that SiO₂ films made by this method were generally thicker in the center of the specimen than at the edge. Furthermore, if the sample dimensions were comparable to the electrode diameter, the thick central region followed the shape of the specimen, i.e., it was triangular if the specimen was a triangle. However, not all films grown in microwave plasmas exhibit this plateaulike topography, and Kraitchman (126) has reported a valley type of pattern in which the oxide in the region surrounding the thicker uniform central portion was also thinner than the oxide at the sample edges. One method for determining film uniformity is to deposit counterelectrodes on the oxide and perform capacitance measurements, assuming a constant value of dielectric

constant throughout the film. Tibol (127), using a glow discharge in a large bell jar system, has reported formation of films up to $5 \text{ cm} \times 5 \text{ cm}$ over which the capacitance variation from one side of the sample to the other did not exceed 10%. Possibly the film nonuniformities are due to variations in ion concentrations and energies in the plasma, although Vratny (121) suggests that phenomena occurring at the discharge anode are important, e.g., sputtering or the formation of a high-impedance oxide layer, the latter presumably causing a variation in the voltage drop in the plasma between substrate and anode. However, it would seem likely that given a stable plasma and a temperature-controlled substrate, the sample dimensions must be small compared to the cross-sectional dimensions of the plasma tube for uniform growth to occur. This is particularly relevant in glow discharges where probe measurements have indicated that, although the electron temperature does not vary, both the electron concentration and the plasma potential decrease from the tube axis to the walls. In addition it would seem necessary that any inserts into the plasma near the sample, e.g., the specimen holder and temperature-control apparatus, must be small compared to the sample and be introduced along the main axis of the discharge vessel so as not to perturb the plasma across the surface of the sample.

Other problems common to all methods of plasma anodization involve the surface preparation of the sample, the making of electrical contact to the specimen and the purity of the system.

Popiano (109) has claimed that with Al the fine scratches remaining on the surface after mechanical polishing do not influence the anodization process as they would in wet anodization. Preliminary work in this laboratory on the plasma anodization of Ta in a glow discharge has certainly indicated no improvement in the very low current efficiency on changing from mechanically polished to electropolished samples of tantalum. It would appear that the current efficiency of growth in plasmas is not limited by the sample surface preparation but is determined by other factors, e.g., the copious supply of high-energy electrons available in the plasma.

Electrical connection to the sample must be through a well-insulated lead. One method suggested is to use wire of the substrate metal previously anodized to a high voltage, and enclosed in glass tubing the internal diameter of which is smaller than the mean free path at the anodization pressure used. Actual connection of the wire to the sample presents further problems and if spot welding is used to secure the wire to a tab on the sample, the tab must be enclosed in a glass tube to minimize leakage currents from the plasma to the lead at the weld area. The other extreme is the method used by Whitmore and Vossen (130) who made "contact" to the substrate via an array of closely spaced probes (to which a common voltage was impressed) and used the plasma between the probes and the sample as a resistive connector.

There has been little published work on the effect of the gas purity or, for that matter, of the general cleanliness of the system on the anodization, and it would seem that modern high vacuum techniques and some form of residual gas analysis are required to test these factors. Miles and Smith (108) remarked that when the oxygen is contaminated with water vapor, the system pressure is raised during anodization by the evolution of hydrogen. It was thought that the water vapor, on coming into contact with the substrate, settles on the surface until it reevaporates or is trapped by a reaction with the film. It was suggested that more trapping of the water vapor occurred at the edges of the sample, rendering the oxide thicker in these regions. Other experiments involving anodization in water-oxygen gas mixtures indicate that only little improvement (136b), or even lowering (128, 145), of the growth rate occurs. Morritz et al. (113) claim that thicker oxides can be grown on Al by using "wet" hydrogen peroxide as the plasma oxidant although this suggests that the films may be porous. In some work on plasma anodization a closed system has been used in which the chamber is originally pumped down to only medium vacuum $(10^{-5}$ to 10^{-6} Torr) and then filled to the desired pressure with gas. With such an arrangement the impurities driven from the walls of the discharge tube due to bombardment of the walls by energetic species in the discharge will build up to further contaminate the system as the anodization proceeds. To minimize contamination from this source, the apparatus may be operated as a dynamic flow system. The isolation of the discharge vessel from pump oil, mercury vapors and vacuum grease sealants is obviously a necessity, and it is hence desirable to use either sorption or ion pumps and employ metal seals.

4. RESULTS

Information on the "anodization constant" has been presented by most authors. For Ta₂O₅, values range from 17 Å/V (114) to 28 Å/V (110) and for Al₂O₃, from 13 Å/V (110) to 22 Å/V (101). The spread in results is partly attributable to the different methods used in estimating thickness and voltage drop across the oxide as well as to uncontrolled substrate temperature, although it is pertinent to mention that the present authors have obtained for Ta₂O₅ inverse electric fields of 18 Å/V and 29 Å/V for the same value of total current density, depending on whether the substrate was facing the anode or the cathode, respectively (122). In the latter case, the film was heavily contaminated with sputtered cathode material. O'Hanlon (136a) has suggested that the films of many workers may have been similarly affected. The thickness of the oxide can conveniently be determined by *in situ* ellipsometry (122, 128, 142) (Fig. 16). However, estimation and, even, control of the voltage drop across the growing film presents some difficulty. Some authors have anodized with a substrate voltage maintained constant with respect



FIG. 16. Apparatus for in situ ellipsometry. [After Locker and Skolnick (142).]

to the anode, but in this case the contribution from the voltage drop in the plasma is unknown, and also variable. This is because the plasma potential tends to fluctuate due to events at the cathode and pressure variations and it is difficult to maintain the voltage drop in the plasma between substrate and anode constant over the lengths of time necessary to grow a reasonable oxide thickness. One solution to the problem is to use probes at their floating potentials to map out the voltage variations and distributions in the plasma around the substrate. Anodization at constant voltage with respect to a nearby probe could then be carried out and the voltage drop between substrate and probe allowed for. However, difficulties remain with regard to estimating the interface p.d.'s and to what extent account need be taken of the free energy of formation of the oxide (142a).

Besides allowing estimation of film thickness, *in situ* ellipsometry also enables information on the refractive index of the films to be obtained. A typical ellipsometer curve for the plasma anodization of Nb is shown in Fig. 17 (128). The experimental data are best fitted to a model which consists of two layers of oxide, the outer having a refractive index of 2.15 and the inner 2.37, i.e., the inner layer has a refractive index similar to that of solution-grown films, while the outer layer has a lower value. Similar results have been obtained for the anodization of Ta (122, 128), the inner film having a refractive index of 2.22, and the outer 1.89. For both Ta and Nb, the outer film comprised about 40% of the total oxide thickness.

The further utility of *in situ* ellipsometry is illustrated by Fig. 18, which shows anodization of a thin layer of Al on GaAs, in both plasma and solu-



FIG. 17. Ellipsometer curve for the plasma anodization of Nb (incident light at 65° and of wavelength 5461 Å). [After Lee *et al.* (128).]

tion methods (142b). The curves are similar although unusual in shape and the apparent difference between them is largely due to the difference in angles of incidence used in the ellipsometry measurements. Computer models have best described the oxide films initially as Al_2O_3 forming on the electrolyte-side surface of the Al until, at points *B*, all the aluminum is used up. After points *B*, oxidation of the GaAs occurs. Weinreich (131) has studied this latter growth in plasma and obtained a value of 1.78 ± 0.02 for the refractive index using the method of observing the disappearing contrast between film and substrate when viewed through a liquid of appropriate index. The film was smooth, uniform, amorphous, and was attacked by hot water. This would seem to suggest that the plasma-anodized films differ in composition from those obtained by solution oxidation which are insoluble in hot water (143). The oxide composition in the latter case is believed to be Ga₂O₃ + As₂O₅, with a Ga/As ratio of 1/3.

A difference in structure of the dielectrics formed by plasma and solution methods is likely and evidence of this is indicated by the relatively low values of dielectric constant measured for plasma-grown films, e.g., Tibol (127) gives dielectric constants of 7 to 8 for Al_2O_3 , 18 for Ta_2O_5 , and 25 for titanium oxide. The present authors have recorded values of relative



FIG. 18. Ellipsometer curves for the anodization of GaAs; O using dc cold cathode discharge in oxygen (incident light at 65° and of wavelength 5461 Å), \times using dilute animonium pentaborate (1.67 mg per cc) electrolyte (incident light at 67.5° and of wavelength 5461 Å). [After Lee *et al.* (122).]

permittivity of 17 and 34 for plasma-grown Ta_2O_5 and Nb_2O_5 , respectively, at 1 kHz, using gold counterelectrodes and determining the oxide thickness by ellipsometry (128). The dielectric constants of Ta_2O_5 and Nb_2O_5 films grown in solution depend on the conditions but tend to be about 27–28 and 41–43, respectively. A lower value is to be expected in the plasma-grown case from the lower values of refractive index, reported above.

Presently available data for the dissipation factor for plasma-grown films do not show any order of magnitude differences from those for solutiongrown films, e.g., about 1% for Al-Al₂O₃-Al capacitors in the frequency range 1 kHz-1 MHz (144) and about 0.9% for Ta-Ta₂O₅-Au sandwiches at 1 kHz (122). However, there may be an effect at lower frequencies, since in SiO₂ films produced by plasma anodization a higher incidence of defects has been found in comparison with films grown in solution (145). There is some difference in the magnitude of the leakage currents for Al-Al₂O₃-Al sandwiches as reported by Tibol and Hull (101) and Worledge and White (110) for growth in dc and rf plasmas, respectively. At about one tenth of the forming voltage, the latter workers reported leakage currents of 4 μ A/cm², while Tibol and Hull (101) obtained currents about three orders of magnitude lower than this. This may be an indication that the increased temperature, and possible electron and ion bombardment, of the high frequency plasma have a deleterious effect on the oxide structure.

5. Possible Mechanisms of Oxide Growth

It would appear from such data as presently exist that the growth mechanisms of oxide films in plasmas depend on the type of plasma being used. For microwave-discharge anodization of Si it has been suggested (125, 126)that a diffusion-controlled process involving the migration of some oxygen species is operative, while for the dc discharge anodization of some valve metals it seems probable that the process is basically the same as in wet anodization.

In plasma anodization and particularly with high frequency plasmas the ions, electrons, and neutral species that may be involved in oxide-forming reactions are likely to possess thermal energies that are not ordinarily encountered in conventional electro-chemical systems. It is probable then that growth of films in these plasmas involves implantation and subsequent migration of some oxygen species in the film. The oxidation of Si in a microwave plasma proceeds when no electric field is applied, but much faster growth rates and layer thicknesses can be obtained with anodic operation. This electric field effect indicates that oxygen ions, as opposed to oxygen atoms and oxygen molecules, are the predominant species diffusing into the oxide. Ligenza (125) suggested that the species was O⁻ which was implanted into the oxide and that there was an exceedingly large concentration gradient of this species which resulted in growth being due to a diffusion limited mechanism (i.e., following the simple parabolic expression dx/dt = k/x where x is the oxide thickness and k is a constant). It is likely that occurring simultaneously with the film growth there will be a removal of the film due to the sputtering action of the bombarding high energy ions. For a constant oxide plasma interface potential the rate of removal of the film by sputtering will be constant and thus the simple parabolic growth expression modifies to the linear-parabolic law dx/dt = k/x - s. Results for the microwave discharge anodization of silicon have been found by Kraitchman (126) to agree well with a law of this form.

For the case of dc discharge anodization the data suggest a growth mechanism that is more analogous to that of wet solution anodization. In this latter case both metal and oxygen ions are mobile in the formation of the oxide and this would appear to be the case in dc discharge anodization since the ellipsometric results discussed earlier are fitted by a two-layer film (122, 128). This further suggests that there is some difference in the oxides produced at the substrate-oxide interface and the oxide-plasma interface. Electrolyte incorporation evidently cannot be used to explain the differences. A possibility is that growth at the oxide-plasma interface is affected by UV irradiation from the plasma, or that the structure of the outer part of the film is modified by the continual bombardment of high-energy particles. Further indications (122) that both metal and oxygen ions are mobile have resulted from plasma anodization of a sample which had been previously solution-anodized to a known thickness. This initial film acted as a sort of marker layer and, according to ellipsometric data, the subsequent plasma growth occurred on both sides of it.

The ionic current J flowing during oxide formation appears to be determined by the field E in the oxide (128) although the Tafel plots for plasmaand solution-anodization are not identical, i.e., for the plasma anodization of Ta and Nb the value of $d \log J/dE$ is less and $J_0 \exp - W/kT$ in the usual high field ionic current relation $J = J_0 \exp - (W/kT - \beta E)$, is greater than for the wet case (see, for example, Fig. 19).



FIG. 19. Tafel plot for anodization of Ta at 31° C and 77° C; O, \bigcirc using d.c. cold cathode discharge in oxygen, solid line using dilute sulfuric acid [from data of Young and Zobel (42*a*)]. [After Lee *et al.* (122).]

These two changes would seem to correlate with the observed lower refractive index and permittivity of the plasma oxide, or at least of the outer layer. The lower refractive index suggests a less dense film so that the zero field activation energy should be less, thus giving the higher intercept on the log J axis at zero field. If the ionic conduction is controlled by an effective field the lower plasma oxide permittivity would predict the observed change in slope.

The question of which is the relevant oxygen specie, or how it is formed, still remains to be answered. The data discussed above have suggested that the pertinent negative oxygen ions are formed in the plasma but, as has been mentioned by O'Hanlon (136a) the unsuccessful attempts (135, 145a) to extract a measurable negative ion current density from the negative glow of an oxygen discharge may indicate that surface anion formation, by, for example, electron attachment or dissociation of positive molecular ions upon impact, is the more likely mechanism. Certainly, because of the large electron-negative ion ratio in the plasma, one might expect the electrons to play an important part in the anodization and if, for example, the ionic current in the oxide is controlled by the electronic current, which is itself a function of field in the oxide, then log J would even be expected to show some dependence on E.

V. Dielectric Properties

1. INTRODUCTION

Dielectric polarization is sometimes divided into the following: electronic polarization, which arises from the deformation of the electron shells; ionic polarization, which comes from the displacement of ions with respect to each other; and polarizability involving potential wells in which an ion or electron either moves from an equilibrium position, where it has no electric moment, to a normally empty site after overcoming some barrier of potential energy or hops between equivalent sites with a reversal of direction of the net moment. The further mechanism of orientation of molecules with permanent dipoles is unlikely to arise in these films, since it is improbable that molecular groups having permanent dipole moments could be incorporated in the film in such a way as to rotate with the field, though the motion of molecular chains may occur, as postulated for glasses (146).

The division of polarization into atomic and electronic contributions is not ideal because they are not in fact independent quantities, i.e., the displacement of ions causes a shift in the electron cloud (short-range effect) and the field set up by the ions polarizes the electrons and vice versa (long-range effect). It is thus better (98, 99) to characterize polarization as either ultraviolet (solely electronic displacements) or infrared (to which the displacements of nuclei and electrons contribute). Szigeti has allowed for the short-range interaction between atomic and electronic displacements by introduction of a factor s in the following equation for the dielectric constant of an ionic crystal with one anion and one cation of valency z per primitive unit cell

$$\varepsilon_{\rm r} = n^2 + \left(\frac{n^2 + 2}{3}\right)^2 S^2 \frac{(Ze)^2 N}{\pi v_{\rm t}^2} \left(\frac{1}{m_1} + \frac{1}{m_2}\right) \tag{13}$$

where *n* is the refractive index, *N* is the number of unit cells/unit volume, v_t the frequency of the transverse vibrations, m_1 and m_2 the masses of the positive and negative ions comprising the solid. Values of *s* for a variety of cubic materials have been calculated by Szigeti and found to vary between 0.48 and 1.10. The calculation cannot be performed for crystalline Ta₂O₅ and Nb₂O₅ (and still less for anodically grown films) because the structures and v_t are not presently known. Thus little can be said about the actual magnitudes of ε_r .

Much of the published work has been concerned with the dielectric loss mechanisms in the audio and subaudio range of frequencies. The polarization mechanism of particular interest in this range involves the movement of ions or electrons between potential energy wells. A distribution of potential energy barriers, which must be invoked if the experimental data are to be explained in this model, may well exist in practice by virtue of the amorphous nature of the anodic oxides. Step response and ac bridge measurements can be used to gain information of the dielectric behavior over a wide frequency range and the former technique also yields information on the so-called steady state conduction currents (see Section V,3).

Any effects on polarization and conduction currents due to electronic space charge are likely to arise when the magnitude of the step voltage becomes large enough to cause sufficient carrier injection. This principle may be the key to determining the parts played by dielectric polarization and electronic space charge in the step response, a question about which some discrepancies of interpretation have existed in the literature.

Of obvious practical importance is the study of dielectric breakdown in insulating amorphous films, and a discussion on this topic relevant to anodic materials appears in Section V,4.

2. POLARIZATION PROCESSES

a. Effects of the Previous History of the Film. As will be outlined later, step response and ac bridge measurements give information about ε' and ε'' , the real and imaginary parts, respectively, of the permittivity. However care must be taken in the interpretation of these measurements since they depend on the way in which the films are made and their subsequent history. To illustrate this, Fig. 20 shows some typical variations of ε' and ε''



FIG. 20. Temperature dependence of permittivity before annealing $Ta-Ta_2O_5-Au$ sample. [After Pulfrey *et al.* (147).]

in Ta₂O₅ films with temperature (147). As the temperature was raised above that at which the film was formed, the capacitance and losses increased very rapidly. Then, on keeping the temperature constant at 380°K for 3 hours, ε' and ε'' fell irreversibly by 0.4% and 1.5%, respectively. On subsequent cooling, there was the expected fall, but the interesting effect is that noticed at constant temperature. Similar effects occur when the sample is held at its formation temperature and could be due to the annealing out of lattice defects. These phenomena are very likely related to the fall with time which is apparent on measuring the ionic conductivity and which has been discussed in Section III,4 in terms of the recombination of interstitial ions and lattice vacancies due to local electrostatic fields. However, other effects may also occur, e.g., those involving loss of water from the film (148) as well as the process involving oxygen loss which has been studied by Smyth *et al.* (149). It is possible in work involving dielectric loss measurements on anodic films to minimize such changes by a short treatment of the specimen at a higher temperature than that at which measurements are to be carried out.

The dielectric losses in the low-frequency range tend to vary between supposedly identical specimens and this could be due to the difference in flaw content of the samples such as might result from variations in surface finish or inclusion content. With $Ta-Ta_2O_5$ -solution systems, the losses at low frequencies sometimes depend on the conductivity of the solution, and this would be expected if the electrolyte penetrated cracks or flaws in the oxide (150). It is also possible that the material of a solid counterelectrode could penetrate into the films if the flaws are of the correct atomic dimensions. Silcox and Maissel (151) attributed such a mechanism of Al penetration into films with Al counterelectrodes as being responsible for the observed low values of film breakdown strength, whereas samples with gold counterelectrodes gave higher values of electric strength, supposedly because this more massive material bridged the fine cracks in the oxide.

b. AC Bridge and Step Response Measurements. The techniques involved in bridge measurements, from which ε' and ε'' can be obtained after eliminating series resistance, are straightforward (3). Measurements are most satisfactorily made using transformer ratio arm bridges in the three terminal mode to eliminate stray capacitance effects, and by use of several bridges and small values of capacitance the frequency range 5 Hz to 500 kHz can be easily covered. In the measurement of practical capacitors such as foil, sintered anode, and thin film devices, the results at high frequencies are affected by the distributed nature of the system (152–154). With thin film devices these effects occur at lower frequencies the higher the resistance of the substrate or evaporated counterelectrode. Such effects may even be made use of (155). Extension of the lowest frequency range to about 0.01 Hz has been reported by Williams (156) who used a bridge devised by Schieber (157), and by Masing *et al.* (35) using a method due to Heroux.

For the case of a wide range of anodic oxide films (including Al_2O_3 , HfO_2 , Ta_2O_5 , Nb_2O_5 , ZrO_2) $\varepsilon''(\omega)$ is generally found to be relatively independent of frequency in the audio range (35, 150, 158–60) (see Fig. 21). However, there is a tendency for $\varepsilon''(\omega)$ to increase at lower frequencies (35, 147, 160). MacFarlane and Weaver (161) have noticed this effect in other dielectrics (polycrystalline alkali halides) and attributed it to interfacial polarization mechanisms involving the blocking of cation vacancies at both intercrystalline boundaries and the electrodes. The amorphous nature of the oxide and the possibility of flaws being present could provide similar trapping



FIG. 21. Variation of permittivity with frequency at 295, 77, and 4°K for Ta-Ta₂O₅-Au sample $(c_0 K' = c_0 \varepsilon' / \varepsilon_0$ and $c_0 K'' = c_0 \varepsilon'' / \varepsilon_0$). [After Cherki *et al.* (158).]

centers in anodic films that would lead to a dispersion process giving a peak of relaxation times in the correct frequency range. However, incorporation of metal impurities into the network may lead to impurity ion-cation vacancy dipoles, which again would contribute to the low frequency dielectric losses.

The implications of the relatively slight variation of $\tan \delta$ in the audiofrequency range, and also the effect of temperature at a given frequency on the losses, are discussed with reference to possible polarization processes in Section V,2,d.

Step response measurements consist of either applying or removing a step voltage and measuring the corresponding charging or discharging current transients. The usual precautions necessary for measurement of currents in the picoampere range must be employed, and enclosing the sample in a low vacuum chamber will minimize any spurious effects due to absorption by the film of moisture in the air. The times either of shortcircuiting or charging the sample, between applications or removals of step voltages, respectively, is of importance and these "steady state times" must be long compared with the duration of the subsequent transients which are to be recorded. The charging currents are complicated by the presence of the dc conduction currents, which are highly nonlinear, and hence the discharge currents are more amenable for polarization studies. The dc conduction current adds to the charging current which is otherwise symmetrical to the discharging current (see Fig. 22).



FIG. 22. Polarization and depolarization currents at various temperatures (S = sample area, e =thickness). [After Cherki and Coehlo (164).]

Now, if linear response theory (99) applies, then the current i(t) as a function of time on applying or removing a unit step voltage V and the real and imaginary parts of the permittivity are linked as

$$\varepsilon'(\omega) = C_0^{-1} \left[\int_0^\infty \frac{i(t)}{V} \cos \omega t \, dt + C_a \right]$$
(14)

$$\varepsilon''(\omega) = C_0^{-1} \left[\int_0^\infty \frac{i(t)}{V} \sin \omega t \, dt + \frac{G}{\omega} \right] \tag{15}$$

where C_a is the capacitance of the sample at very high frequencies, C_0 is the equivalent capacitance of the system if the dielectric between the electrodes is replaced with air or vacuum, G is the steady state dc conductance and ω the angular frequency.

The methods are readily available for obtaining the low frequency behavior of $\varepsilon''(\omega)$ from the step response data. Both methods involve fitting the step response data by an empirical expression of the form $\phi(t) = \beta t^{-n}$, where $\phi(t) = i(t)/V$ and β and *n* are constants; then integration of (15) gives (162, 163)

$$\varepsilon''(\omega) = \omega^{n-1} \frac{\beta}{C_0} \Gamma(1-n) \cos \frac{n\pi}{2} + \frac{G}{\omega C_0}$$
(16)

where Γ is the gamma function. As mentioned above, only discharge currents are considered, and in the following G is neglected. The dc conductance is highly nonlinear, and so, in the charging case, the ohmic conductance at zero bias would be excessive if the observed values of current were taken without extrapolating to step voltages of the order of the small ac voltages used in bridge measurements.

Recent work on Ta-Ta₂O₅-metal systems (147, 158, 164, 165) has shown n to vary between 0.9 and 1.0. The cause of this slight variability in behavior between samples is not clear, but possibilities are the effect of flaws or differences in annealing and formation procedure. For the case of n = 0.9, the frequency dependence of ε'' follows from (16) and is $\varepsilon'' = (\lambda \beta / C_0) \omega^{-0.1}$, where λ is a particular constant relating to *n*. Equation (16) cannot be used for the case of n = 1 as the function $\Gamma(0)$ arises, and for this case, Eq. (15) has to be employed, giving $\varepsilon'' = \text{constant} = \pi\beta/2C_0$. C_0 can be calculated if the thickness of the film and the area of the counterelectrode is known. The value of $\beta (= \phi(t)t^n)$ must be chosen for a particular voltage if the step response is not linear in V, and it would seem that this voltage should be low so that the discharge currents will most nearly approximate to polarization currents, i.e., space charge effects due to carrier injection will be a minimum. A plot of $\phi(t)t^n/V$ versus voltage for both polarities of applied voltage will enable β at V = 0 to be interpolated, and hence allow calculation of ε'' at low frequencies (see e.g., the continuous line of Fig. 23) from the data of Pulfrey et al. (147).

The second method again follows from (16) and it can be shown (162, 163) that provided $\phi(t)$ approximates the above power law with *n* within the limits 0.3 to 1.2, the value of i(t) at a particular time *t* can be used to immediately calculate ε'' at a particular frequency $\omega = 0.63/t$ using

$$\varepsilon''(\omega) = i(t) / V \omega C_0 \tag{17}$$

Again, a low value of step voltage V must be taken and the filled circles



FIG. 23. Variation of dielectric losses with frequency: comparison of bridge and step response data for Ta-Ta₂O₅-Au sample. [After Pulfrey *et al.* (147).]

of Fig. 23 represent data obtained from the discharge currents for a $Ta-Ta_2O_5$ -Au system after removal of the charging voltage of 1.0 V. The results shown in Fig. 23 demonstrate reasonable agreement between step and extrapolated bridge response, indicating that nonlinear effects were in this case negligible at bias voltages up to at least 1 V (equivalent to a field in the oxide of 1.5×10^5 V cm⁻¹). Cherki *et al.* (158, 164, 165) found a linear response in a similar system to extend up to 5×10^5 V cm⁻¹ and reported good agreement with ac bridge measurements, while Dreiner (44), using a solution "counter electrode" on Ta_2O_5 films, found the response to be linear to the much higher fields of 4×10^6 V cm⁻¹. This might be expected because the oxide-solution interface is highly blocking with the tantalum positive.

c. Space Charge Contribution to the Step Response. In the previous section approximately 1/t laws for the step response currents were discussed in terms of the decay of polarization currents. Alternatively, however, Dreiner (44) and Lindmayer (166) have observed similar time dependencies of the step

response currents, in $Ta-Ta_2O_5$ -solution and $Si-SiO_2$ -metal systems, respectively, but have interpreted their measurements solely in terms of space charge effects. Space charge regions may exist in the film due to contact potentials, and under an applied voltage additional charge may be injected into the insulator and trapped. Traps may be present due to impurities, structural defects, or simply the amorphous nature of the insulator. On short circuiting a sample containing trapped space charge, this space charge will decay and may result in an externally observed discharge current which would add to the polarization discharge currents considered above.



FIG. 24. Band diagrams for metal-insulator-metal systems during discharge.

In Fig. 24a and c are shown band diagrams for an oxide with shorted electrodes of similar metal and for the two cases of a no space charge and c negative space charge. Figure 24b, d, and e show the corresponding situation when counterelectrodes of dissimilar metals are used, i.e., b represents the case of no space charge in the oxide and d and e depict the conditions where there is space charge present of magnitude above and below a certain critical density respectively. The critical density is that at which the space charge so bends the bands that there is a region of zero gradient.

Lindmayer (166) considered the case of Fig. 24c. He showed that with some assumptions a uniform distribution of traps in binding energy could lead to the rate of release of electrons from traps following a 1/t law. This does not immediately prove that the external current will follow the same law. The external current in this case is

$$I_{\text{ext}} = Aqn_t(x^*, t) \, dx^*/dt$$

where A is the area, q the electronic charge, and n_t the trapped charge density. However, the traps were assumed to be originally filled to higher energies in the region where injection occurs, i.e., near the cathode. Hence, since electrons will be released more rapidly from the shallower traps, these regions will dominate during the first part of the discharge, and if electron release in these regions follows a 1/t law while the rest of the oxide is effectively not releasing electrons I_{ext} will also do so. It was noted recently (147) that after the electrons in traps below a certain depth have been released, and dn_t/dt everywhere follows a 1/t law, the space charge density in the oxide becomes uniform, x^* is at the mid-point (l/2) of the oxide and so the external current is zero.

However, in the case of an insulator sandwiched between counterelectrodes with different work functions and of space charge sufficiently small for no x^* to exist (Fig. 24e), the discharge current can follow a 1/t law as given by (147)

$$I_{ext} = qN_t kTAl/2t$$

where N_t is a constant.

Both polarization and space charge decay currents can therefore, under certain circumstances, obey a 1/t law. To differentiate between these two possible contributors to the external current the linearity of the I_{ext} versus applied step voltage V relation must be considered. Departures from linearity can be expected when V is sufficiently high for injection of electrons into the oxide to occur. The injection of electrons increases more than linearly with V, so I_{ext} should increase similarly with V, unless the injection occurs so easily that saturation results.

d. Models of the Polarization Process. The near frequency independence of tan δ discussed in Section V,2,b is found in many practical dielectrics. It

has been shown that a Maxwell layer type model in which there was an exponential dependence of the conductivity on distance into the oxide gives a constant ε'' (159). However, it is difficult to account for the required dependence of parameters on total thickness. Also, as Smyth (167) has pointed out in his recent review, this treatment leads to excessively steep gradients in thinner films (such as having the conductivity change by an order of magnitude for each nearest-neighbor atomic spacing), although it must be pointed out that a constant tan δ for extremely thin films has not actually been reported. Furthermore, the experiments of Wood and Brock (168) on a wide range of anodic oxides suggest that the independence of the losses on frequency is unlikely to be due to the above mechanism because the thinning of the oxides causes the conductivity to vary very little (and never exponentially) with thickness.

However, for films of anodized tantalum and niobium which have been heated to a few hundred degrees in air or oxygen and then quenched. Smyth and Shirn (169) considered that the above model is applicable. The observed exponential conductivity gradient across the oxide was attributed to a gradient of stoichiometry, which supposedly resulted from the equilibration of the oxide film between the reducing action of the underlying metal and the oxidizing properties of the ambient atmosphere. We must agree with Smyth (167) that it is a remarkable coincidence that while the dielectric properties of heat-treated anodic oxide films on tantalum and niobium do seem to be based on an exponential conductivity gradient, those of unheated films cannot be so explained but must find their origin in some other mechanism which, however, obeys precisely the same mathematics. Lehovec (170) has suggested that this mechanism may in fact be one involving (in the case of $Ta-Ta_2O_5$) tunneling of electrons from the tantalum metal into the adjoining oxide. The recipient sites are believed to be oxygen vacancies and the rate of transition of such an electron to the receptor state is in proportion to the electron density at the position of the receptor state, and has the required exponential dependence on the distance d from the metal-oxide interface, i.e., as e^{-2Kd} where K is the wave number. Thus the time constant for the exchange process is $\tau' = \tau_0' e^{2Kd}$ where τ_0' is a suitable average over all energies of tunneling electrons and their respective capture cross sections by the recipient state. τ_0' and K are required by the model to be independent of bias but, in fact, will vary with the applied potential due to the modification in shape of the barrier through which the electrons tunnel. Furthermore, Lehovec estimates a recipient-center concentration of 10^{21} to 10^{22} cm⁻³, and, as he remarks, at such high concentrations the model's use of a single well-defined energy level is unlikely to represent the physical system satisfactorily.

It thus seems more likely that the near frequency independence of ε'' and tan δ can be explained (as are similar effects with many practical bulk

dielectrics) (171, 172) by a superposition of Debye-type processes involving ion hopping.

This process supposes that an ion, although the mechanism could easily refer to electrons also, is normally bound to an equilibrium position (A) in which it has no electric moment, but it can move to a normally empty site (B) at distance, say a, from the original one after overcoming some activation energy W. Let this position of the particle give rise to a dipole moment Wa. In thermal equilibrium with a field E applied, the potentials V_A and V_B will differ by an amount eaE and thus the probabilities of occupation of sites A and B will be different, i.e., the distribution over the equilibrium and nonequilibrium sites will change and as a consequence a dipole moment will be induced, and the dipole orientation time τ depends on the activation energy W in a manner $\tau = \tau_0 e^{W/kT}$, where τ_0 is a constant equal to the reciprocal of the jump frequency. A single value of activation energy W gives the Debye relations

$$\varepsilon' = \varepsilon_{\infty} + (\varepsilon_{s} - \varepsilon_{\infty})/(1 + \omega^{2}\tau^{2})$$
$$\varepsilon'' = (\varepsilon_{s} - \varepsilon_{\infty})\omega\tau/(1 + \omega^{2}\tau^{2})$$

where ε_s and ε_{∞} are the values of permittivity at zero and infinite frequencies respectively. In practice the above situation of one site with a single activation energy will not be valid, and we have to consider many sites with some distribution of relaxation times, say $f(\tau)$, or activation energies, say G(W). A range of site energies or occupancies such that the distribution is $f(\tau) d\tau =$ $(1/\tau) d\tau$ gives the required condition of ε'' constant with frequency. A model with such a distribution was proposed by Garton (172) in which ions make transitions between "lattice sites" of fixed depth and sites of varying depth W with frequency of occurrence proportional to exp(-W/kT). Gevers and du Pré (171) arrived at the same result merely by assuming that in an amorphous material the distribution of susceptibilities and activation energies was very flat. Evidently, the temperature dependence of the losses will vary according to whether the ions continue to occupy the same set of pairs of sites or whether they move to occupy a different selection of sites with changes of temperature. Gevers and du Pré considered the former case and the following equation was derived to obtain the actual spectrum of activation energies G(W)

$$\varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty)(\pi/2)kTG(W)$$

from which a constant value of ε''/T is predicted. This situation prevails over the range from 80 to 250°K for Ta-Ta₂O₅-Au samples, but ε''/T apparently increases at higher temperatures (147). This may suggest a redistribution of ions among available sites, i.e., to shallower traps from which there may be an added contribution to the dielectric losses from increased conduction through the oxide. Alternatively, the phenomena could be linked with the increasing losses toward lower frequencies which have already been suggested as associated with flaws in the material.

At liquid nitrogen temperatures, for the system Ta-Ta₂O₅-Au, Cherki et al. (158) reported losses independent of frequency, while Pulfrey, Wilcox, and Young (147) found losses which increased slightly with frequency for apparently similar films. At even lower temperatures (4.2° K) Cherki et al. still find losses which are essentially flat with frequency (see Fig 21). As they pointed out, the very low activation energies which need to be invoked to explain losses at these temperatures seem improbable for an ionic process. It might be argued, though, that any ions so loosely bound would be essentially free at room temperatures and would therefore tend to move around until they fell into deeper traps. If these ions were not trapped at room temperature, then ionic conduction would be expected to occur at low fields. However, another possibility is that two contiguous sites might be deep with respect to neighboring sites but be themselves separated by only a low barrier. Yet a further likelihood is that the losses are in fact a superposition of ionic and electronic processes. Cherki's results (Fig. 21) show that $C_0 \varepsilon'$ becomes much less temperature dependent as the temperature decreases, and this may perhaps indicate that an electronic tunneling process between localized sites may be involved. However, it is also possible that some form of electron hopping takes place and a tentative model for such a process would require an exponential trap distribution in the bandgap of the form $N_t \propto \exp[(E_c - E_f)/kT]$, where E_{c} and E_{f} refer, respectively, to the energy levels of the conduction bands and Fermi level. Above the Fermi level, the trap occupation would be given by a Boltzmann distribution, $\exp[-(E_c - E_f)/kT]$. Thus, the number of electrons at a particular trap level will be independent of that trap level, which is essentially the same situation as was assumed in calculating the ionic relaxation losses. The possibility of substantial electronic contribution to the dielectric losses is currently receiving much attention: Maserjian (173) has considered electron trap to conduction band transitions in connection with Nb₂O₅ anodic films and electron hopping mechanisms have been discussed by Jonscher (174) and Harrop et al. (160).

At present, these questions as to the nature of the dielectric losses cannot be answered with any degree of certainty. However, it does seem probable that losses could be associated with lattice defects, and that both electronic and ionic phenomena do contribute to the dissipative processes.

3. DC Electronic Conduction

Various aspects of electronic conduction in thin insulating films have been discussed at a recent symposium (9) and by Lamb (175), Jonscher (176), Goruk *et al.* (4), and Chopra (177). Many intriguing special phenomena have

been investigated which may have technical significance. We shall merely note that tunneling (178), switching effects (176), memory effects (179), hysteresis (4), and negative resistance (180, 181) have been observed. Some aspects of the behavior are doubtless attributable to the amorphous nature of the oxide films. This leads to some doubt about the applicability of the normal concepts of band theory (182-184). Jonscher (176), for example, considered that electron conduction would involve a hopping process, with or without thermal activation. On the other hand, some authors (185-187) postulate p-n or p-i-n junctions in certain amorphous oxide films. The effect of dopants should become apparent only at higher concentrations because of the effect of defects in providing localized states which may act as traps. Again, however, some authors have observed traps with well-defined energies (e.g., in reactively sputtered Ta₂O₅ films) (188).

A perennial problem is the question of whether the dc conduction is controlled by Schottky or Poole-Frenkel effects. In general, the rate of injection of electrons into the oxide (Schottky effect) and the bulk conduction (usually attributed to the Poole-Frenkel effect) will not be expected to be balanced at equal fields. In this event, space charge should develop to alter the interface and bulk field strengths until a steady state is reached (189). Evidence of the occurrence of this adjustment period should be obtainable by rapidly sweeping through a log J versus $E^{1/2}$ plot and observing the change in slope which, from the observed high-field J-E relation $[J \propto \exp(\beta E^{1/2}/kT)]$ is proportional to β . If the Schottky effect is operative, the conductivity is given by

$$\sigma_{\rm S} = \sigma_0 \exp(\beta_{\rm S} E^{1/2} / kT)$$

where $\beta_{\rm S} = (q^3/\pi \epsilon)^{1/2}$ and ϵ is the high-frequency dielectric permittivity. The derivation of an expression for the rate of release of electrons from coulombic traps within the insulator leads to a result similar to the Schottky equation, but the charge on the trap is fixed in position and thus the attractive force is proportional to $1/x^2$ instead of $1/(2x)^2$. This gives an apparent difference of 2 in the slope $d \log J/dE^{1/2}$ depending on whether the Poole–Frenkel (PF) or Schottky (S) mechanisms are operative, i.e., $\beta_{\rm PF} = 2\beta_{\rm S}$.

In practice, steady state currents are difficult to obtain. The currents are typically time dependent; this may be due to space charge effects as suggested above, after allowance for the step-response associated with slow dielectric polarization corresponding to other mechanisms.

The use of the slope of log J versus $E^{1/2}$ plots to distinguish between Poole-Frenkel and Schottky mechanisms may encounter further difficulties which were pointed out in a recent controversy (190, 191). It was proposed that $d \log J/dE^{1/2}$, for the Poole-Frenkel effect in an insulator containing compensated donors is twice that obtaining when a Schottky mechanism dominates, but $d \log J/dE^{1/2}$ is the same for both mechanisms when uncompensated donors are present. In fact, it seems likely that measured $\log J - E^{1/2}$ plots will, depending on film thickness and space charge, exhibit a spectrum of behavior in which Schottky and Poole-Frenkel mechanisms will be the limiting characteristics. Recent computations (191a) have illustrated this. An unambiguous method of studying Schottky emission is that demonstrated by Goodman (192), which relies on the fact that at an abrupt interface between a metal and insulator the photoemission threshold energy is a function of the voltage applied across the insulator. If the Schottky mechanism is operative, there will be a lowering of the work function ϕ according to $\Delta \phi = \frac{1}{2}(qE/\pi\epsilon)^{1/2}$ and thus plots of the decrease in photoelectric threshold energy (relative to zero bias) versus $E^{1/2}$ will be linear. This method has been used with success by Mead *et al.* (193) for Al₂O₃ films.

In recent work on the system Ta-Ta₂O₅-metal (147), the slope of log J versus $E^{1/2}$ plots indicated the Schottky mechanism with the counterelectrodes (Au or In) negative, while a Poole-Frenkel slope was observed when the Ta electrode was negative (see Fig. 25). This would perhaps be expected for a sufficiently low barrier $\phi - \chi$ (where ϕ is the Ta work function and χ is the electron affinity of the oxide) at the Ta-Ta₂O₅ interface, but it is then somewhat surprising that a similar situation did not arise when a low work function metal counterelectrode (indium) was negative. One source of disagreement about such matters may be the fact that prior application of high



FIG. 25. DC conduction currents as a function of $E^{1/2}$ for Ta-Ta₂O₅-Au sample. [After Pulfrey *et al.* (147).]

fields to samples can affect the log $J - E^{1/2}$ relation (147), and, for example, can cause semipermanent "deformation" leading to conditions of high conductivity (194). Localized conduction of flaws is a source of irreproducibility and may occur in "formed" specimens, as recently suggested by Hickmott (180). Krüger's experiments (195) give further recent evidence of localized electronic conduction. Various redox reactions were studied at the oxide-solution interface of a Ta-Ta₂O₅-solution system subjected to UV illumination. From the precipitates at the oxide-solution interface, it was concluded that the photoelectric current through the oxide film was not homogeneous over the whole of the illuminated area, but was concentrated in localized regions of a micron diameter. Such effects might a priori be due to areas of different photosensitivity arising from fluctuations in the impurities in the metal. However, a further experiment in which Krüger used the formation and coloring of an iodine-starch complex for revealing the electronic conduction currents showed an inhomogeneous pattern to result in the absence of UV.

4. DIELECTRIC BREAKDOWN

a. Types of Breakdown. The dielectric breakdown of thin films has been reviewed recently by Klein (196) and by Forlani and Minnaja (197). The study of the phenomena of dielectric breakdown in solids is complicated by the fact that insulation failure can occur by a number of processes, e.g., electromechanical deterioration, dendrite formation, breakdown in gaseous occlusions, electromechanical collapse, and mechanisms involving purely thermal or electric effects. The first three mechanisms can be prevented by proper sample preparation and measuring techniques, while electromechanical breakdown, in which the specimen collapses due to the electrostatic attractive forces, presently appears to be applicable only in the case of some soft polymers. Thus dielectric breakdown in anodic films strictly should be concerned only with thermal or electrical phenomena which result in destruction of the dielectric by melting and evaporation.

Thermal breakdown may be initiated by an increase in the electrical conductance by joule heating or, with ac currents flowing, by dielectric heating. If a thin homogeneous film could be prepared (i.e., without any weak spots) the breakdown should occur at a definite voltage and occur simultaneously over most of the insulator. It is, in principle, possible to determine the thermal breakdown voltage $V_{\rm T}$ without destroying the sample, i.e., by observing the *I-V* characteristic (Fig. 26) before the onset of thermal runaway at point *D*. This technique is presumably applicable to anodic films although it has so far only been reported for evaporated SiO films (198). Thermal breakdowns in anodic oxides can be arranged to be "self-healing" [see Kennedy (199) for work on Al₂O₃ and Young (3, 35) and Klein



FIG. 26. I-V characteristic showing thermal breakdown voltage. [After Klein (196).]

(196) on Ta_2O_5] by making one electrode thinner than 1000–2000 Å, such that it evaporates at the breakdown site before sample destruction occurs. In this way defects can be "self-healed" enabling, eventually, breakdown characteristics of the homogeneous film, as opposed to weak regions, to be studied. No detailed investigation of purely thermal breakdown of anodic films has been carried out but, as in the case of thermal breakdown in other materials [e.g., alkali halides (200), Si_3N_4 (201) and SiO_x (196)], any theoretical estimate of the thermal breakdown voltage will involve solution of the equation of conduction of heat for the specimen and the adjacent solids.

The term electric breakdown relates to events which are known in the literature from bulk dielectric studies as, variously, intrinsic, avalanche, and field emission breakdown [see O'Dwyer (202) and Klein (203) for detailed discussion].

b. Electric Breakdown. Electric breakdown is initiated by a sudden increase in the electric conductance by, for example, an electronic avalanche. The incidence of breakdown is of a statistical nature and hence breakdown occurs over a range of voltages. The breakdown destroys a very small part of the insulator and this cannot be avoided owing to the rapid nature of the process, although subsequent damage to the sample from the heavypostbreakdown currents can be avoided by employing current-limiting or -diverting circuit components.

Dielectric breakdown studies in anodic films have so far usually involved the observation of the voltage at which either sparking occurred during the growth of the film in aqueous electrolytes or physical rupture took place in metal-anodic oxide-counterelectrode systems. The number of samples tested by each experimenter to arrive at a figure for the breakdown strength has been very low; if the scatter in breakdown voltages turns out to be as large as experienced in other, thicker dielectrics (204), the actual values so far calculated must only be used with caution. Nevertheless, a start has been made to the study of the problem of dielectric breakdown in anodic films and the problems of irreproducible data due in part to impurities and the otherwise inhomogeneous nature of the film, have already been encountered.

c. Experimental. Wood and Pearson (205), who observed the sparking of anodic films on Ta and Nb grown in aqueous electrolytes, found the breakdown voltage to vary inversely as the logarithm of the electrolyte conductivity. In addition the breakdown voltage depended on the type of electrolyte used and also on the metal being anodized, although the purity of the latter does not seem to have influenced the breakdown voltage. Presumably thermal effects due to temperature rise in the film can be ruled out as being responsible for breakdown because the breakdown voltage was found to be independent of the rate at which the electrolyte was circulated. Assuming that the degree of purity of the substrate metal was related to the defects in the subsequent oxide, and also noting that the breakdown voltage was related to the melting point of the oxides grown (on Hf, Ta, Nb, Zr, Al), Wood and Pearson suggested that breakdown is a function of the bulk properties of the oxide and the nature of the electrolyte rather than being due to flaws in the film. The actual breakdown mechanism was postulated as being due to some form of electron avalanche with electrons entering the oxide from the electrolyte. The effect of electrolyte on breakdown voltage was tentatively accounted for by the suggestion that different electrolytes can supply different quantities of electrons. Further evidence that there is an electrolyte effect is demonstrated by measurements of the electric strength of Ta₂O₅ films as a function of anodizing acid concentrations (206). The breakdown voltage decreased as the percentage weight of H₃PO₄ in solution increased, although no data on how many samples were tested are given so that the results may not be statistically significant. This particular electrolyte effect may not be due to the ability of electrons to move from the electrolyte to the oxide but may be related to the modification of the oxide structure by electrolyte incorporation in the film which is known to occur with this acid.

Alwitt and Vijh (207) found reasonable agreement with the above results of Wood and Pearson (205), except for the case of Al_2O_3 which they reported to have a higher breakdown voltage than ZrO_2 . The ranking of the various oxides tested as regards breakdown voltage was thus Al_2O_3 , ZrO_2 , Ta_2O_5 , Nb_2O_5 which no longer related directly to the oxide melting point as Wood and Pearson had found. Instead, a direct correlation of sparking voltage ANODIC OXIDE FILMS

with the heat of formation of the oxide and the reciprocal of the oxide dielectric constant was suggested. However, the sparking voltage is a rather poorly defined property of the complex phenomena of dielectric breakdown and it is difficult to assign any meaningful physical significance to the above relations.

Alternatively, other workers (148, 151, 196) have assumed that the inhomogeneity of the anodic film is likely to strongly influence the breakdown properties. Axelrod and Schwartz (148) used differential interference microscopy to directly observe the behavior of flaws in the oxide during application of voltage to sputtered Ta-Ta₂O₅-systems with either metal or electrolyte counterelectrodes. The behavior of the flaws was asymmetrical with voltage, as indeed were the conduction currents and breakdown voltages (Fig. 27). Furthermore, the breakdown voltage depended on whether evaporated metal or electrolytes were used as electrodes. The presence of water may explain this, and in experiments with metal-counterelectrode samples in atmospheres



FIG. 27. Comparison of I-V characteristics for Ta-Ta₂O₅ with gold and aqueous counterelectrodes (positive voltage is for T_a). [After Axelrod and Schwartz (148).]

of reduced humidity, Axelrod and Schwartz noticed a decrease of cathodic (Ta-) breakdown voltage, but no change in the anodic (Ta+) case, leading to, in desiccated samples, almost symmetrical behavior. The cathodic breakdown voltage varied inversely as the area of the evaporated contact (Fig. 28), which suggests that the breakdown is through flaws in the oxide



FIG. 28. Cathodic breakdown voltage (Ta) as a function of capacitance for two printed tantalum oxide capacitors. All oxide formations at 100 V and 110°C. [After Axelrod and Schwartz (148).]

and the results are compatible with a model of the oxide with one flaw per 0.05 mm^2 . The extent of the breakdown voltage change varies from specimen to specimen, which could be explained by differences in flaw content caused by small changes in process parameters, and if the flaw density is high enough the cathodic breakdown voltage becomes independent of area. Silcox and Maissel (151) have noticed large increases in anodic breakdown voltage with decrease in electrode area, indicating that flaws are important in anodic conduction also. Klein (196) has observed electric breakdown due to weak spots in Al₂O₃, HfO₂, and Ta₂O₅ by employing sequential tests, in which the applied voltage rises typically within seconds to breakdown value, collapses, rises again to breakdown, etc. These tests showed that initially the breakdown voltage was low but gradually increased to a constant (within

a scatter of a few percent) value V_s . The initial breakdowns were attributed to weak spot failure and the latter to bulk breakdown. The magnitude of applied dc voltage V_D also influenced the rate at which breakdowns repeated, and while several hours might elapse between breakdowns at $V_D = .60V_s$, many breakdowns per second occurred at $V_D = 1.20V_s$. It would seem, though, that at the lower values of V_D the breakdown may not have been completely electric and thermal effects may have been important.

It would appear from the above that flaws in the material play a major role in the breakdown of anodic films. The presence of water is also of importance and, since conduction currents are so time dependent at low moisture contents, it is possible that an electronic mechanism is operative which depends markedly on the absence or presence of water, perhaps affecting some trap levels in the conducting oxide (208).

It was mentioned in Section V.3 that in an amorphous solid the effect of impurities on the low-field electrical properties is not likely to be so pronounced as in insulators having a more regular structure. However, in considering dielectric breakdown, when high fields are present, there does seem to be an impurity effect, e.g., Wilson et al. (209) observed a decrease in the breakdown voltage of anodic films on Co, Cr, and V when contaminated by foreign ions (especially halides) from the electrolyte. Impurities arising from the metal substrate apparently behave similarly and a lowering of the breakdown voltage of oxide films grown on niobium when the metal was contaminated with differing amounts of Zr, Ti, W, Mo, and V has been reported (205). These phenomena could be qualitatively explained if it was possible to describe the amorphous solid in terms of the familiar band structure ideas, e.g., the impurity atoms could be thought of as providing additional electronic traps, which were shallower than those generally existing in the solid. On application of a high field, electrons residing in these traps would be relatively easily released so providing "free electrons" for the breakdown process. This effect would then lead to a decrease in the electric strength below that of the "true" oxide, as reported above. A more detailed study of the effect of substrate impurities in sputtered Ta films has been carried out (148). Apparently, for impurity concentrations up to 1 at.%, the cathodic breakdown voltage (Ta -) is not affected but the anodic breakdown voltage (Ta +) increases. At greater impurity concentrations the breakdown voltage falls in both cases.

The implication so far has been that electric breakdown in anodic oxides proceeds by some electronic process. A suggestion that this process may in fact be an avalanche mechanism is given by Platonov (210-212) whose work on Ta_2O_5 and ZrO_2 , with oxide thickness ranging from 100 to 5000 Å, showed that the electric strength decreased with thickness. However, not all anodic oxides exhibit this behavior, e.g., InSb anodized in KOH appears to

have a breakdown strength which is independent of thickness and equal to about 10^6 V/cm (213). A further observation by Platonov (211) that the time lag to breakdown (presumably measured from the instant of application of a voltage of breakdown proportions) increased linearly with thickness does not directly support an avalanche mechanism in Ta₂O₅ and Al₂O₃. Platonov explained this apparent discrepancy by suggesting that traps in the oxide capture electrons and the subsequent formation of a negative space charge distorts the electric field in the cathode region. Electrons (cold-emitted from the cathode) are thus consumed by traps and hence "the destructive power" of the avalanche is inhibited. As a result, several weak avalanches may precede breakdown and serve just to fill up traps, hence preparing the way for breakdown. Thus, the time lag (t_{T}) to breakdown can be thought of as having two components, i.e., a time (t_1) for the filling of the traps and a time (t_2) for the formation of the destructive avalanche. t_2 is likely to be much less than t_1 and thus the filling of traps is the rate-determining factor and the observed increase of $t_{\rm T}$ with thickness is to be expected. If, in fact, prebreakdown avalanches do occur, then the prebreakdown currents should be "noisy," as von Hippel et al. (214) have observed in the case of bulk alkali halides. Platonov has also recorded that the breakdown of Ta₂O₅ and Al_2O_3 with fast pulse voltages (rate of rise 5 × 10⁷ V/sec) exceeded that with slow pulses (15 V/sec) by 20–30 %. This phenomenon may be tentatively fitted into the above hypothesis by suggesting that while the traps are being filled up, the applied voltage in the fast pulse case actually overshoots the minimum required voltage for breakdown. The role of traps in the breakdown process as envisaged by Platonov suggests a mechanism that increases the oxide breakdown strength, which is contrary to the data previously discussed.

d. Discussion. Although no experiments on the rate of collapse of voltage during breakdown of anodic films have been reported, it is probable that the phenomenon will be similar to that already observed in bulk dielectrics (215) and other thin films (196), i.e., the voltage collapse can be interpreted as a discharge of the electrostatic energy stored in the sample through a spot in the specimen, the resistance of which rapidly decreases as the ionized channel between the electrodes develops into a highly conducting plasma. It would appear then that electric breakdown consists of two stages: (1) the formation of a conducting channel in the insulator; and (2) the discharge of the specimen's stored energy through this channel, leading to destruction of the material. The second process can be explained in terms of the heating and evaporation of the dielectric, but the main problem is in identifying and interpreting the conducting channel formative processes. The evidence so far presented indicates that some form of electronic avalanche process is responsible for this stage in the breakdown of anodic films, and that the mechanism is greatly affected by the presence of flaws and impurities in the
oxides. No doubt these inhomogeneities are in part responsible for the scatter that is observed in the breakdown voltage results, but nevertheless this absence of a sharply defined destruction voltage renders inapplicable most of the theories that have been developed to explain breakdown phenomena in other dielectrics (196, 216). The single electron avalanche theory (217) has received much attention in breakdown studies with many types and thicknesses of dielectric since it predicts a dependence of electric strength on thickness and also the existence of time lags to breakdown, both of which have been experimentally observed. However, the theory is now only tenable when the development of the avalanche is not determined solely by impact ionization in the insulator, but also by field emission at the cathode (216, 218). The developing avalanche has been postulated as leaving behind a positive space charge at the cathode, either due to the ionized lattice points (218) or to the mobility of holes (216) which leads to enhancement of field emission from the cathode and, by ensuring current continuity, enables development of a destructive avalanche.

In anodic oxides, it is easily seen that electrons could be emitted into the solid by some Schottky-type process, but it is usually assumed that holes are not mobile, and thus any enhancement of the cathode field would appear to have to arise through impact ionization of centers by collision with highenergy electrons or by cation migration (219). If, in fact, the occurrence of electrons at the cathode is a necessary criterion for breakdown, then, as Klein (196) has suggested, specimens in which free carriers are produced in the insulator by internal photoemission from the electrodes should exhibit lower breakdown voltages. The techniques involving internal photoemission as outlined by Goodman (192) could also prove of assistance in establishing whether in fact holes in anodic oxides do have finite mobility at the breakdown fields.

ACKNOWLEDGMENTS

We thank Drs. Amsel, Diggle, Dreiner, Ord, and others who have made available to us prepublication drafts of their work, the National Research Council of Canada and Dept. of Communications, the Sprague Electric Company and the U.S. Air Force for financial support for our work in this field and Diane Mackenzie for her patience in deciphering our manuscript.

REFERENCES

- 1. P. S. Jorgensen, J. Chem. Phys., 37, 874 (1962).
- 2. J. L. Miles, New York Meet., Electrochem. Soc., 1969 Abstr. No. 26 (1969).
- 3. L. Young, "Anodic Oxide Films." Academic Press, New York, 1961.
- W. S. Goruk, L. Young, and F. G. R. Zobel, in "Modern Aspects of Electrochemistry" (J. O'M. Bockris, ed.), Vol. 4, p. 176. Plenum Press, New York, 1966.
- 5. N. G. Bardina, Usp. Khim. 33, 602 (1964).

- D. A. Vermilyea, *in* "Advances in Electrochemistry" (P. Delahay, ed.), Vol. 3, p. 211. Wiley (Interscience), New York, 1963; also *in* "Non-Crystalline Solids" (V. D. Freschette, ed.), p. 328. Wiley, New York, 1960.
- 7. J. W. Diggle, T. C. Downie, and C. W. Goulding, Chem. Rev. (1970) (in press).
- 8. New York Meet., Electrochem. Soc., 1969 Extended abstr. bookl. (1969).
- Dallas Meet., Electrochem. Soc., Extended abstr. bookl. Vol. 6, No. 1 (1967); also in "Electrolytic Rectification" (P. F. Schmidt and D. M. Smyth, eds.). Electrochem. Soc., New York, 1967.
- 10. L. Young, Trans. Faraday Soc., 53, 841 (1957).
- A. T. Fromhold and E. L. Cook, J. Appl. Phys. 38, 1546 (1967); Phys. Rev. 175, 877 (1968).
- 12. M. J. Dignam, J. Phys. Chem. Solids 29, 249 (1968).
- 12a. L. Young, Acta Met. 5, 711 (1957).
- 13. C. G. Dunn, J. Electrochem. Soc. 115, 219 (1968).
- 14. S. F. Bubar and D. A. Vermilyea, J. Electrochem. Soc. 114, 882 (1967); 113, 892 (1966).
- A. Aladjem and D. G. Brandon, Proc. Int. Symp. Thin Films, 1969, J. Vac. Sci. Tech. 6, 635 (1969).
- 16. A. C. Harkness and L. Young, Can. J. Chem. 44, 641 (1966).
- 17. R. W. Berry, P. M. Hall, and M. T. Harris, "Thin Film Technology." Van Nostrand, Princeton, New Jersey, 1968.
- 18. W. E. Patterson and C. L. White, "Thin Films Formed by Electrochem. Reactions." Tex. Inst. Co., Rep. 03-63-27 (1963); see *Chem. Abstr.* 66, 120004 (1967).
- 19. D. Mills, L. Young, and F. G. R. Zobel, J. Appl. Phys. 37, 1821 (1966).
- 20. J. Klerer, J. Electrochem. Soc. 112, 869 (1965).
- 21. J. Sitarik, New York Meet., Electrochem. Soc., 1969 Extended abstr. No. 27 (1969).
- 21a. D. G. Muth, J. Vac. Sci. Tech. 6, 749 (1969).
- 22. D. A. Vermilyea, Acta Met. 1, 282 (1953).
- 23. L. Young, Proc. Roy. Soc., London, Ser. A 244, 41 (1958).
- 24. A. J. Schrijner and A. Middelhoek, J. Electrochem. Soc. 111, 1167 (1964).
- 25. A. Waxman and K. H. Zaininger, Appl. Phys. Lett. 12, 109 (1968).
- 26. D. A. Vermilyea, Acta Met. 2, 482 (1954).
- 27. J. J. Randall, W. J. Bernard, and R. R. Wilkinson, Electrochim. Acta 10, 183 (1965).
- 28. P. H. Draper, Electrochim. Acta 8, 847 (1963); Acta Met. 11, 1061 (1963).
- 29. G. Amsel, C. Cherki, G. Feillade, and J. P. Nadai, J. Phys. Chem. Solids (1970) (in press).
- 30. L. Young, Trans. Faraday Soc. 50, 153 (1954).
- 31. D. A. Vermilyea, J. Phys. Chem. Solids 26, 133 (1965).
- 32. P. F. Schmidt, "Symposium on Electrolytic Specification and Conduction Mechanisms in Anodic Oxide Films," p. 1. Electrochem. Soc., New York, 1967.
- 33. P. D. Lukovtsev, Elektrokhimiya 4, 379 (1968).
- 34. L. Young, Proc. Roy. Soc., London. Ser. A 258, 496 (1960).
- 35. L. Masing, J. Vitins, and L. Young, Dielectrics 1, 45 (1963).
- 35a. D. A. Vermilyea, J. Electrochem. Soc. 104, 140 (1957).
- 36. D. A. Vermilyea, J. Electrochem. Soc. 104, 427 (1957).
- 37. L. Young, Proc. Roy. Soc., London, Ser. A 263, 395 (1961).
- 38. J. F. Dewald, unpublished data.
- 39. L. Young, J. Electrochem. Soc. 111, 1289 (1964).
- 40. L. Young, Acta Met. 4, 101 (1956).
- 41. V. V. Egorov and P. D. Lukovtsev, Elektrokhimiya 3, 1071 (1967).
- 42. J. F. Dewald, J. Phys. Chem. Solids 2, 55 (1957).
- 42a. L. Young and F. G. R. Zobel, J. Electrochem. Soc. 113, 277 (1966).
- 43. A. Güntherschulze and G. Betz, "Electrolytkondensatoren," Krayn, Berlin, 1937.

- 44. R. Dreiner, J. Electrochem. Soc. 111, 1350 (1964).
- 45. M. J. Dignam and D. Goad, J. Electrochem. Soc. 113, 381 (1966).
- 46. D. A. Vermilyea, J. Electrochem. Soc. 102, 207 (1955); 104, 542 (1957).
- 47. D. A. Vermilyea, J. Electrochem. Soc., 104, 485 (1957).
- 48. J. Harvey and H. Wilman, Acta Cryst. 14, 1278 (1961).
- 49. L. D. Calvert and P. H. Draper, Can. J. Chem. 40, 1943 (1962); cf. K. Lehovec, J. Less-Common Metals 7, 397 (1964).
- 50. R. E. Pawel and J. J. Campbell, J. Electrochem. Soc. 111, 1230 (1964).
- 51. J. Spyridelis, P. Delavignette, and S. Amelinckx, Phys. Status Solidi, 19, 683 (1967).
- 52. J. Spyridelis, P. Delavignette, and S. Amelinckx, *Mater. Res. Bull.* 3, 31 (1968); 2, (1967).
- 52a. C. J. Dell'Oca and L. Young, unpublished data (1968).
- 53. For recent papers, see M. Hartl. Z. Angew. Phys. 23, 337 (1967).
- 54. J. D. Venables and R. M. Broudy, J. Appl. Phys. 30, 1110 (1959).
- 55. J. D. Venables and R. M. Broudy, J. Electrochem. Soc. 107, 296 (1960).
- 56. A. R. Brag, P. M. W. Jacobs, and L. Young, J. Nucl. Mater. 4, 356 (1959).
- 57. A. Güntherschulze and H. Betz, Z. Phys. 92, 367 (1934).
- 58. M. J. Dignam, New York Meet., Electrochem. Soc., 1969 Extended abstr. No. 10 (1969).
- 59. E. J. W. Verwey, Physica (Utrecht) 2, 1059 (1935).
- 60. N. F. Mott, Trans. Faraday Soc. 43, 429 (1947).
- 61. N. Cabrera and N. F. Mott, Rep. Prog. Phys. 12, 163 (1948-1949).
- 62. J. F. Dewald, J. Electrochem. Soc. 102, 1 (1955).
- 63. L. Young, Can. J. Chem. 37, 276 (1959).
- 64. L. Young, Trans. Faraday Soc. 52, 502 and 515 (1956).
- 65. C. P. Bean, J. C. Fisher, and D. A. Vermilyea, Phys. Rev. 101, 551 (1956).
- 66. M. J. Dignam, J. Electrochem. Soc. 112, 722 (1965).
- 67. C. J. Dell'Oca and L. Young, Appl. Phys. Lett. 13, 228 (1968).
- 68. M. J. Dignam and P. J. Ryan, Can. J. Chem. 46, 549 (1968).
- 69. D. A. Vermilyea, J. Electrochem. Soc. 102, 655 (1955).
- 70. D. A. Vermilyea, J. Electrochem. Soc. 104, 427 (1957).
- 71. P. Van Winkel, C. A. Pistorius, and W. C. Van Geel, Philips Res. Rep. 13, 277 (1958).
- 72. M. J. Dignam, D. Goad, and M. Sole, Can. J. Chem. 43, 800 (1965)
- 73. M. J. Dignam and D. Goad, J. Electrochem. Soc. 113, 381 (1966).
- 74. R. Dreiner and T. B. Tripp, New York Meet., Electrochem. Soc., 1969, Extended abstr. No. 21 (1969).
- 75. L. Young, J. Electrochem. Soc., 110, 589 (1963).
- 76. M. J. Dignam, Can. J. Chem. 42, 1155 (1964).
- 77. B. J. Holden and F. G. Ullman, J. Electrochem. Soc. 116, 280 (1969).
- 78. A. Frova and P. Migliorato, Appl. Phys. Lett. 13, 328 (1968).
- 79. S. G. Christov and S. Ikonopisov, J. Electrochem. Soc. 116, 56 (1969).
- 80. N. Ibl, Electrochim. Acta 12, 1043 (1967).
- 81. J. Ord, Dallas Meet., Electrochem. Soc., 1967, Extended abstr. No. 42 (1967).
- 82. J. Ord, personal communication (1969).
- 83. L. Masing, J. E. Orme, and L. Young, J. Electrochem. Soc., 108, 428 (1961).
- 84. J. A. Davies, J. P. S. Pringle, R. L. Graham, and F. Brown, J. Electrochem. Soc. 109, 999 (1962).
- 85. J. A. Davies and B. Domeij, J. Electrochem. Soc. 110, 849 (1963).
- J. A. Davies, B. Domeij, J. P. S. Pringle, and F. Brown, J. Electrochem. Soc. 112, 675 (1965).
- 87. J. L. Whitton, J. Electrochem. Soc. 115, 58 (1968).

- 88. J. P. S. Pringle, Dallas Meet. Electrochem. Soc., 1967 Extended abstr. No. 35 (1967); New York Meet., Electrochem. Soc., 1969 Extended abstr. No. 11 (1969).
- 89. G. Amsel and D. Samuel, J. Phys. Chem. Solids 23, 1707 (1963).
- 89a. J. P. S. Pringle, personal communication (1968).
- 90. D. M. Cheseldine, J. Electrochem. Soc. 111, 1128 (1964).
- 91. R. E. Pawel, J. Electrochem. Soc. 114, 1222 (1967).
- 92. G. P. Klein, Dallas Meet., Electrochem. Soc., 1967 Extended abstr. No. 38 (1967).
- 93. G. Amsel, C. Cherki, J. P. Nadai, and J. Siejka, New York Meet., Electrochem. Soc., 1969 Extended abstr. No. 12 (1969).
- 94. O. S. Heavens and J. C. Kelly, Proc. Phys. Soc., London 72, 906 (1958); cf. H. E. and J. M. Bennett, Phys. Thin Films 4, 78 (1967).
- 95. S. Kumagai and L. Young, J. Electrochem. Soc. 111, 1411 (1964).
- 96. C. J. Dell'Oca and L. Young, Proc. Conf. Ellipsometry 1968; Surface Sci. 16, 331 (1969).
- 96a. D. A. Vermilyea, personal communication (1961).
- 97. M. Born and K. Huang, "Dynamical Theory of Crystal Lattices." Oxford Univ. Press, London and New York, 1954.
- 98. B. Szigeti, Trans. Faraday Soc. 45, 155 (1949).
- 99. H. Fröhlich, "Theory of Dielectrics." Oxford Univ. Press, London and New York, 1958.
- 100. C. R. Fritzsche, Solid State Commun. 6, 341 (1968).
- 101. G. J. Tibol and R. W. Hull, J. Electrochem. Soc. 111, 1368 (1964).
- 102. W. Schroen, J. Appl. Phys. 39, 2671 (1968).
- 103. S. Shapiro, Phys. Rev. Lett. 11, 80 (1963).
- 103a. K. H. Zaininger and A. Waxman, IEEE Trans. Elec. Dev. 16, 333 (1969).
- 103b. A. Waxman and G. Mark, Solid State Electr. 12, 751 (1969).
- 104. G. Lecoy and L. Gonsov, Phys. Status Solidi, 30, 9 (1968).
- 105. S. R. Pollack and C. E. Morris, Trans. AIME 233, 497 (1965).
- 106. C. A. Mead, New York Meet., Electrochem. Soc., 1969 Extended abstr. No. 45 (1969).
- 107. J. Lambe and R. C. Jaklevic, Phys. Rev. 165, 821 (1968).
- 108. J. L. Miles and P. H. Smith, J. Electrochem. Soc. 110, 1240 (1963).
- 109. P. L. Popiano, IEEE Trans. Parts, Mater. Packag. 1, 217 (1965).
- 110. P. L. Worledge and D. White, Brit. J. Appl. Phys. 18, 1337 (1967).
- 111. L. E. Terry and E. E. Komarek, U.S. At. Energy Commun., SC-TM-307-63-(14) (1963).
- 112. L. D. Locker and L. P. Skolnick, Appl. Phys. Lett. 12, 396 (1968).
- 113. F. L. Morritz, R. Shima, D. E. Rees, and A. Miller, 8th Symp. Aerosp. Mater. Proc. Eng., 1960 (1965).
- 114. M. Scharfe, U.S. Armed Forces Tech. Rep. AFAL TR-67-72 (1967).
- 115. E. Hartel, Thesis Diploma, Inst. Tech. Elec., Tech. Hochschule, Munich, 1967.
- 116. K. Asano, M.Sc. Thesis, University of Minnesota, 1964.
- 117. M. C. Johnson, IEEE Trans. Component Parts 11, 1 (1964).
- 118. T. A. Jennings, W. McNeill, and R. E. Salomon, J. Electrochem. Soc. 114, 1134 (1967).
- 119. D. A. Lavrinets, U.S. Armed Forces Tech. Rep. AFAL TR-67-73 (1967).
- 120. N. F. Jackson, J. Mater. Sci. 2, 12 (1967).
- 121. F. Vratny, J. Amer. Ceram. Soc. 50, 283 (1967).
- 122. W. L. Lee, D. L. Pulfrey, and L. Young, New York Meet., Electrochem. Soc., 1969 Extended abstr. No. 22 (1969).
- 123. R. I. Nazarova, Russ. J. Phys. Chem. 36, 522 (1962).
- 124. J. F. O'Hanlon, Appl. Phys. Lett. 14, 127 (1969).
- 125. J. R. Ligenza, J. Appl. Phys. 36, 2703 (1965).
- 126. J. Kraitchman, J. Appl. Phys. 38, 4323 (1967).

- 127. G. J. Tibol, Insulation (Libertyville, Ill.) 11, 25 (1965).
- 128. W. L. Lee, G. Olive, D. L. Pulfrey, and L. Young, J. Electrochem. Soc. 117, 1172 (1970).
- 129. N. Ramasubramanian, New York Meet., Electrochem. Soc., 1969 Extended abstr. No. 24 (1969).
- 130. R. E. Whitmore and J. L. Vossen, IEEE Trans. Parts, Mater. Pakag. (1), S10 (1965).
- 131. O. A. Weinreich, J. Appl. Phys. 37, 2924 (1966).
- 132. G. Lewicki and C. A. Mead, J. Phys. Chem. Solids 29, 1255 (1968).
- 133. J. H. Alexander, R. J. Joyce, and H. F. Sterling, Montreal Meet., Electrochem. Soc., 1968 Extended abstr. No. 462 (1968).
- 133a. R. Frieser, J. Electrochem. Soc. 115, 1092 (1968).
- 134. J. D. Cobine "Gaseous Conductors." Dover, New York, 1968.
- 135. J. B. Thompson, Proc. Roy. Soc., London, Ser. A 262, 503 (1961).
- 136. P. F. Knewstubb, P. M. Dawson, and A. W. Tickner, J. Chem. Phys, 38, 1031 (1963).
- 136a. J. F. O'Hanlon, J. Vac. Sci. Technol. 7, 330 (1970).
- 136b. J. F. O'Hanlon, Los Angeles Meet., Electrochem. Soc., 1970 Extended abstr. No. 13 (1970).
- 137. T. A. Jennings and W. McNeill, Appl. Phys. Lett. 12, 25 (1968).
- 138. K. Persson, J. Appl. Phys. 36, 3086 (1965).
- 139. H. Musal, J. Appl. Phys. 37, 1935 (1966).
- 139a. H. Musal, personal communication (1969).
- 139b. J. R. Ligenza, personal communication (1969).
- 140. G. Francis, "Ionization Phenomena in Gases." Butterworth, London and Washington, D.C., 1960.
- 141. K. W. Ehlers, U.S. Pat. 3,341,352 (1967); see Chem. Abstr. 67, 111071 (1967).
- 142. L. D. Locker and L. P. Skolnick, Montreal Meet., Electrochem. Soc., 1968 Extended abstr. No. 483 (1968).
- 142a. G. Olive, D. L. Pulfrey, and L. Young, J. Electrochem. Soc. 117, 945 (1970).
- 142b. W. L. Lee, G. Yan, and L. Young, unpublished data (1968).
- 143. A. G. Revesz and J. Jaininger, J. Amer. Ceram. Soc. 16, 606 (1963).
- 144. G. J. Tibol and W. M. Kauffman, Proc. IEEE 52, 1465 (1964).
- 145. E. R. Skelt and G. M. Howells, Surface Sci. 7, 490 (1967).
- 145a. W. S. Whitlock and J. E. Bounden, Proc, Phys. Soc. 77, 845 (1961).
- 146. J. M. Stevels, J. Soc. Glass Technol. 34, 80 (1950).
- 147. D. L. Pulfrey, P. S. Wilcox, and L. Young, J. Appl. Phys. 40, 3891 (1969).
- 148. N. N. Axelrod and N. Schwartz, J. Electrochem. Soc. 116, 460 (1969).
- 149. D. M. Smyth, G. A. Shirn, and T. B. Tripp, J. Electrochem. Soc. 110, 1271 (1963); 111, 1331 (1964); 113, 100 (1966).
- 150. L. Young, Trans. Faraday Soc. 55, 842 (1959).
- 151. N. W. Silcox and L. Maissel, J. Electrochem. Soc. 109, 1151 (1962).
- 152. R. H. Broadbent, Electrochem. Technol. 6, 163 (1968).
- 153. R. M. Peekema and J. P. Beesley, Electrochem. Technol. 6, 166 (1968).
- 154. B. Goudswaard, Electrochem. Technol. 6, 178 (1968).
- 155. R. W. Wyndrum, IEEE Int. Conv. Rec. 13, 90 (1965).
- 156. G. Williams, in "Molecular Relaxation Processes" (R. C. Cross, ed.). Academic Press, New York, 1966.
- 157. D. J. Schieber, J. Res. Nat. Bur. Stand., Sect. C 65, 23 (1961).
- 158. C. Cherki, R. Coehlo, and J. L. Mariani, Solid State Commun. 4, 411 (1966).
- 159. L. Young, Trans. Faraday Soc. 51, 1250 (1955).
- 160. P. J. Harrop, G. C. Wood, and C. Pearson, Thin Solid Films 2, 457 (1968).
- 161. J. C. McFarlane and C. Weaver, Phil. Mag. [8] 13, 671 (1966).

- 162. B. V. Hamon, Proc. IEE 99, 151 (1952).
- 163. M. E. Baird, Rev. Mod. Phys. 40, 219 (1968).
- 164. C. Cherki and R. Coehlo, Phys. Status Solidi 19, K91 (1961).
- 165. C. Cherki and J. L. Mariani, Rev. Gen. Elec. 75, 769 (1966).
- 166. J. Lindmayer, J. Appl. Phys. 36, 196 (1965).
- 167. D. M. Smyth, New York Meet., Electrochem. Soc., 1969 (1969).
- 168. G. C. Wood and A. J. Brock, Nature (London) 209, 773 (1966).
- 169. D. M. Smyth and G. A. Shirn, J. Electrochem. Soc. 115, 186 (1968).
- 170. K. Lehovec, J. Electrochem. Soc. 115, 520 (1968).
- 171. M. Gevers and F. K. du Prè, Trans. Faraday Soc. 42A, 47 (1946); M. Gevers, Philips Res. Rep. 1, 159, 197, 279, 361, and 447 (1945).
- 172. G. Garton, Trans. Faraday Soc. 42A, 47 (1946).
- 173. J. Masserjian, Proc. Int. Symp. Thin Films, 1969, J. Vac. Sci. Tech. 6, 843 (1969).
- 174. A. K. Jonscher and P. A. Walley, Proc. Int. Symp. Thin Films, 1969, J. Vac. Sci. Tech. 6, 662 (1969).
- 175. D. R. Lamb, GEC (Gen. Elec. Co. Ltd.) J. 32, 107 (1965).
- 176. A. K. Jonscher, J. Electrochem. Soc. 116, 217C (1969).
- 177. K. L. Chopra, "Thin Film Phenomena." Macmillan, New York, 1969.
- 178. R. M. Hill, Thin Solid Films 1, 39 (1967).
- 179. J. G. Simmons and R. R. Verderber, Proc. Roy. Soc., London, Ser. A 301, 77 (1967).
- 180. T. W. Hickmott, Proc. Int. Symp. Thin Films, 1969, J. Vac. Sci. Tech. 6, 828 (1969).
- 181. R. Pinto and B. M. Shaha, Jap. J. Appl. Phys. 7, 1542 (1968).
- 182. N. F. Mott and W. D. Twose, Advan. Phys. 10, 107 (1961).
- 183. A. I. Gubanov, "Quantum Electron Theory of Amorphous Conductors." Consultants Bureau, New York, 1965.
- 184. A. F. Ioffe and A. R. Regel, Progr. Semicond. 4, 239 (1960).
- 185. F. Huber, Dallas Meet., Electrochem. Soc., 1967 Extended abstr. No. 30 (1967).
- 186. E. K. Oshe and I. L. Rozenfel'd, Sov. Electrochem. 4, 1081 (1968).
- 187. E. G. Kuznetsova, T. I. Borisova, and V. I. Veselovskii, Sov. Electrochem. 4, 142 (1968).
- 188. F. G. Ullman, J. Phys. Chem. Solids, 28, 279 (1967).
- 189. J. G. Simmons, Phys. Rev. 166, 912 (1968).
- 190. J. G. Simmons, Phys. Rev. 155, 657 (1967).
- 191. P. Mark and T. E. Hartman, J. Appl. Phys. 39, 2163 (1968).
- 191a. D. L. Pulfrey, A. H. M. Shousha, and L. Young, J. Appl. Phys. 41, 2838 (1970).
- 192. A. M. Goodman, J. Electrochem. Soc. 115, 276C (1968).
- 193. C. A. Mead, E. H. Snow, and B. E. Deal, Appl. Phys. Lett. 9, 53 (1966).
- 194. T. W. Hickmott, J. Appl. Phys. 35, 2679 (1964).
- 195. G. Krüger, Electrochim. Acta 13, 1389 (1968).
- 196. N. Klein, J. Electrochem. Soc. 116, 963 (1970).
- 197. F. Forlani and N. Minnaja, Int. Symp. Proc. Thin Films, 1969, J. Vac. Sci. Tech. 6, 518 (1969).
- 198. N. Klein and H. Gafni, IEEE Trans. Electron Devices 13, 281 (1966).
- 199. D. R. Kennedy, E.R.A. Rep. L/T 374. Leatherhead, England, 1958.
- 200. J. J. O'Dwyer, J. Electrochem. Soc. 116, 239 (1969).
- 201. S. Sze, J. Appl. Phys. 38, 2915 (1967).
- 202. J. J. O'Dwyer, "The Theory of Dielectric Breakdown in Solids." Oxford Univ. Press, London and New York, 1964.
- 203. N. Klein, Advan. Electron. Electron Phys. 26, 309 (1969).
- 204. R. Cooper, Brit. J. Appl. Phys. 17, 149 (1966).
- 205. G. C. Wood and C. Pearson, Corros. Sci. 7, 119 (1967).

- 206. Belg. Pat. 649,202 (to Philips Res. Labs.) (1964); see Chem. Abstr. 66, 43311 (1967).
- 207. R. S. Alwitt and A. K. Vijh, J. Electrochem. Soc. 116, 388 (1969).
- 208. N. Schwartz and M. Gresh, J. Electrochem. Soc. 112, 296 (1965).
- 209. J. R. Wilson, I. A. MacDonald, and J. T. N. Atkinson, Dallas Meet., Electrochem. Soc., 1967 Extended abstr. No. 48 (1967).
- 210. F. S. Platonov, Gumanitarn. Fiz. Nauk 1, 87 (1965).
- 211. F. S. Platonov, Izv. Vyssh. Ucheb. Zaved., Fiz. 10, 7 (1967).
- 212. L. L. Odynets, F. S. Platonov, and G. M. Savina, *Izv. Vyssh. Ucheb. Zaved.*, Fiz. 10, 121 (1967).
- 213. T. Sakurai, T. Suzuki, and Y. Noguchi, Jap. J. Appl. Phys. 7, 1491 (1968).
- 214. A. von Hippel, E. P. Gross, J. G. Jelatis, and M. Geller, Phys. Rev. 91, 568 (1953).
- 215. A. Bradwell and D. L. Pulfrey, Brit. J. Appl. Phys. [2] 1, 1581 (1968).
- 216. J. J. O'Dwyer, J. Phys. Chem. Solids 28, 1137 (1967).
- 217. F. Seitz, Phys. Rev. 76, 1378 (1949).
- 218. R. Cooper and C. T. Elliott, Brit. J. Appl. Phys. 17, 481 (1966).
- 219. K. H. Gundlach and P. Schnupp, Z. Angew. Phys., 21, 468 (1966).