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Annealing effects and oxide structure in alumina tunnelling barriers

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Abstract. In this work we have studied changes in aluminium-oxide-aluminium tunnel barrier parameters that result from annealing at different temperatures with and without an applied potential difference. We identify two processes: irreversible increase in mean barrier height which takes place under all conditions and reversible changes in the internal field produced by applied bias. We explain the observations in terms of a detailed microscopic model involving excess Al^{3+} in the barrier region and field-induced movement of ions. The model implies that the oxide grows by the classic Cabrera–Mott mechanism with aluminium as the mobile species, and it sheds light on the nature of the oxide and of the interfacial regions in this technologically important system.

1. Introduction

Grown aluminium oxide is the classic tunnelling barrier because of its ease of preparation and good insulating properties, these being required for good tunnelling characteristics at low layer thicknesses. In early work (Fisher and Giaever 1961) it was observed that the current–voltage characteristics of aluminium-oxide-aluminium junctions are asymmetric despite the apparent symmetry of the structure. Electrical asymmetry must result from structural asymmetry in the barrier and its interfaces with the metal electrodes, so the study of tunnelling characteristics and the ways in which they may be changed has the potential for yielding information about the microscopic nature of the barrier region and, by implication, about the mechanism of oxide growth. Surprisingly, little work has been done to use tunnelling information in this way.

In this paper, we give an account of experiments on aluminium-grown oxide–aluminium tunnel junctions in which we have studied the form of the electrical characteristics and how they change on annealing. Annealing was carried out both with and without an externally applied field in order to distinguish processes involving movement of charge. Similar techniques were used by Konkin and Adler (1980) in studies with aluminium-grown oxide–lead junctions.

2. Sample preparation and method of analysis

The junctions were prepared at a base pressure below 10^{-6} mbar; glass microscope slides served as substrates. Aluminium base electrodes, 1 mm wide, were evaporated to a

thickness of about 60 nm. The tunnel barrier was then formed by plasma oxidation using an oxygen pressure of 0.15 mbar and 60 mA discharge current for typically 50 min. The preparation was completed by deposition at right angles of 1 mm wide Al top electrodes 60 nm thick. The completed samples, usually five junctions on one substrate, were wired up using indium contacts and connected to the measuring electronics as soon as possible, the whole taking not much more than five minutes from the time they had been taken out freshly prepared from the vacuum chamber. The derivative dV/dI of the tunnel junction characteristics was measured using a modulation technique in a bridge circuit (see descriptions elsewhere, e.g. Adler and Strauss 1975). Results were taken automatically by micro-computer with standard software controlling the current source and the recording of data.

In order to represent the changes taking place, data were fitted to the theoretical expression for tunnelling through a simple trapezoidal barrier. Best fits yielded values for the barrier parameters: Φ_1 and Φ_2 , the barrier heights at the bottom electrode (that next to the substrate) and top electrode respectively, and d , the effective tunnelling thickness. This choice of model does not imply that we think it accurately represents the barrier shape. It is used because it is the simplest form that can represent the aspects of the characteristics that we wish to study.

We used the analysis of Brinkman *et al* (1970) who expanded the WKB expression for the current density in powers of the voltage up to terms quadratic in V for $T = 0$ and obtained an expression for the conductance $\sigma(V)$ which is estimated to be accurate to roughly 10% for $d > 1$ nm and $(\Phi_2 - \Phi_1)/[(\Phi_1 + \Phi_2)/2] < 1$. A computer routine was used in the present work to fit a parabola to the measured conductance and from the three coefficients the barrier parameters were extracted via the expansion mentioned above. The least-square parabolic approximation was obtained by fitting over the regions -300 mV to -125 mV and $+125$ mV to $+300$ mV. The region between must be ignored because of phonon structure, and beyond 300 mV the second-order approximation is too much in error. The calculated barrier parameters for a given tunnelling spectrum were then printed out. Since systematic errors associated with the model and with the use of the parabolic approximation are possible, we base our discussion on *changes* in fitted barrier heights before and after a particular treatment of a sample rather than on the absolute values.

3. Experimental results

In the experiments, junctions have been subjected to either thermal conditions alone at 18 °C or 28 °C, or to a standardized electric field corresponding to 1.0 V across the barrier thickness of about 2 nm (i.e. an externally applied field of about 5×10^8 V m⁻¹) at those temperatures. Spectra were taken at successive times in order to monitor the barrier parameters as a function of time under the various conditions. The parameter fit method yielded typical values for a virgin junction $\Phi_1 \approx 0.7$ eV, $\Phi_2 \approx 1.9$ eV and $d \approx 1.3$ nm. There was little variation in the fitted thickness between samples but the barrier heights varied by up to ± 0.2 eV for Φ_1 and ± 0.3 eV for Φ_2 . It should be noted that barrier thicknesses obtained by fitting to a trapezoidal barrier are always smaller than those obtained from measurement of capacitance. For our samples, the capacitance thickness was typically 2 nm (assuming a relative permittivity of 7). Qualitatively, the difference can be accounted for by assuming some degree of interfacial roughness since tunnelling is heavily weighted towards regions of minimum electrode separation.

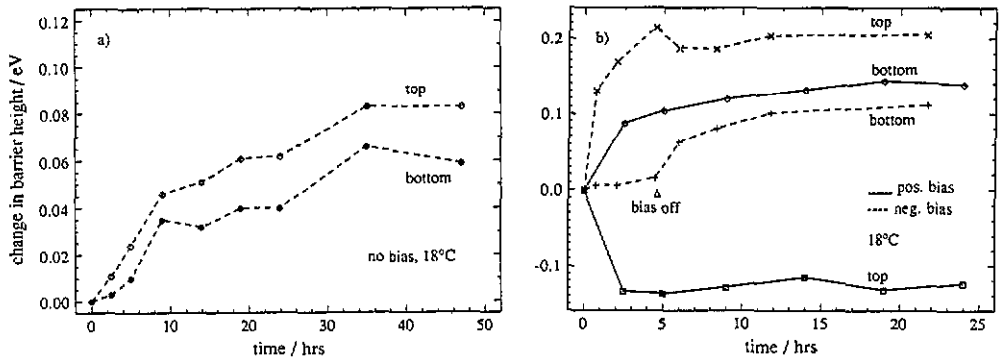


Figure 1. Drift experiments at 18°C = 291 K. (a) Junction with no applied bias, i.e. simple thermal annealing. (b) Full lines: Junction kept under positive bias of +1.0 V (i.e. top electrode positive); broken lines: negative bias of -1.0 V which was switched off after 4.5 h. After removal of bias, the field-induced effects relax and both barrier heights approach a long-time limiting behaviour similar to that for simple thermal annealing.

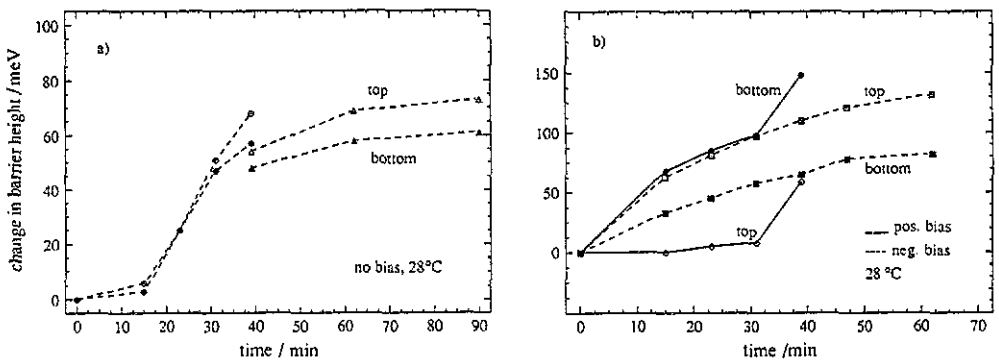


Figure 2. Drift experiments at 28°C = 301 K. (a) Junction with no applied bias. A second set of measurements is added to cover times up to 90 min. (b) Solid lines: positive bias of +1.0 V; broken lines: negative bias of -1.0 V.

During annealing, variations of the fitted thickness were very small. There was evidence of an initial 1–2% (20 pm) increase in thickness (occurring in the first five hours for room-temperature anneals), but after that there was no measurable change. In contrast, there were pronounced changes over much longer times in barrier heights under thermal conditions alone and with positive or negative applied fields. Changes were of order ± 0.1 to ± 0.2 eV. While Φ_1 and Φ_2 depend sensitively on preparation conditions and tend to vary in particular between different substrate slides, it was found that changes in these quantities are reproducible within $\pm 30\%$ for junctions on different substrates and within $\pm 7\%$ for neighbouring junctions on the same substrate.

Typical results are displayed in figures 1 and 2 for annealing under thermal conditions alone and with positive and negative drift fields. (The convention is 'positive' if the top electrode is positive.) In all cases, results at 18°C (figure 1) are similar to those at 28°C (figure 2) except that changes occur much more rapidly at the higher temperature. Thermal conditions alone (figures 1(a) and 2(a)) produce an increase in the mean barrier

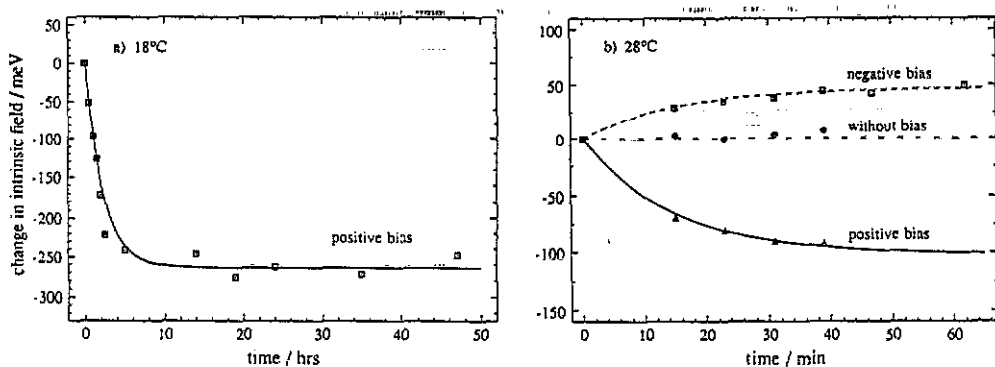


Figure 3. Decay of intrinsic field under permanent influence of an applied external field. The lines are fitted exponentials that give characteristic time constants (a) 130 min at 18 °C and (b) 15 min at 28 °C.

height by increases in both Φ_1 and Φ_2 , but do not significantly alter the intrinsic internal field $E_{\text{int}} = (\Phi_2 - \Phi_1)/d$. Annealing with an applied field, in contrast, does cause changes in the intrinsic field, the induced changes showing a relaxation-type behaviour. Figure 3 shows fits to the simple exponential form:

$$\Delta\Phi(t) = A + B \exp(-t/\tau).$$

The characteristic times τ are 130 min ($\pm 20\%$) and 15 min ($\pm 20\%$) at the two temperatures. The increase in mean barrier height also occurs in the presence of applied bias, but the rate of increase is affected by the bias, being increased by negative bias (top electrode negative) and decreased by positive.

We find that the built-in field E_{int} cannot be changed permanently by an externally applied field. After removal of the external field, changes that had previously been brought about by the presence of the field decay on a similar time scale, and one is left with the slow irreversible changes of barrier heights produced by thermal conditions alone. Thus, we distinguish two distinct processes:

(i) *Irreversible increase in mean barrier height with no significant change in intrinsic field.* This takes place under all conditions but the rate is affected by applied bias being increased by negative bias and decreased by positive.

(ii) *Reversible changes in intrinsic field caused by application or removal of an applied field.* These reversible changes have a relaxation-type time dependence. Their sign should be noted: application of a positive bias increases Φ_1 and decreases Φ_2 .

4. Discussion

We have distinguished two aspects of barrier behaviour in our experimental results: annealing, giving an increase of mean barrier height but no significant change in the intrinsic field E_{int} , and reversible effects of applied bias, positive bias decreasing the internal field, the induced changes showing relaxation-type behaviour with characteristic rates increasing with increase of temperature. We propose a model of the barrier that is able to explain these observations.

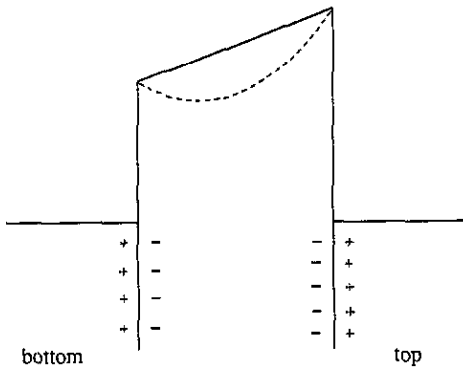


Figure 4. Energy structure of tunnelling barriers with zero applied potential difference. The horizontal lines in the electrodes are the Fermi levels. The broken line indicates how the potential is modified by presence of a uniform density of ionised donors (Al^{3+}) in the oxide. Compensating negative charge resides in the electrodes.

The energetics of a simple trapezoidal barrier are illustrated in figure 4. In the absence of applied bias, the Fermi levels in the electrodes are equal and the barrier results from dipole layers at the interfaces with the electrodes. (We are not implying that gross charge transfer is necessarily present: the work function of a metal results from a surface dipole layer where the electron orbitals extend beyond the outermost positive ion cores. The dipole layers at the interfaces in our tunnelling structures may therefore be of atomic dimension.) The polarities of the dipole layers are indicated in the figure.

It is instructive to look at magnitudes in relation to this representation. The existence of the built-in field implies an asymmetry of the electrode-barrier-electrode structure which could result from the mechanism of oxide growth or from the different ways in which the two interfaces are formed. Considering first the former possibility, we could envisage a structural asymmetry of the oxide left by the growth process. If the built-in field were the result of a relative displacement of the mean positions of aluminium and oxygen ions in the oxide, the displacement required would be about 1 pm, namely less than 0.5% of an interatomic spacing. Only a very small structural asymmetry would therefore be required. Similarly, the work functions themselves correspond to charge densities in the dipole layers which are small in comparison with the available charge: if the interfacial dipole layers correspond to charge layers separated by a distance of 0.1 nm, then their surface charge density to produce a barrier height of 1.3 eV (a typical mean value from our work) would be about 0.1 C m^{-2} . In a close-packed plane of oxygen ions in alumina, the charge density is 10 C m^{-2} so, related to the available charge density, the charge in the dipole layer is small, about 1%. The effects we are studying therefore correspond to small features of the microscopic structure of the experimental system.

We first discuss the reversible changes of intrinsic field produced by application of a large bias. The fact that changes of intrinsic field show relaxation behaviour both on application and on removal of a bias show that we are moving between different equilibrium configurations of the electronic structure. We must first point out, however, that the changes cannot be the result of conventional electron trapping (such as gives rise to the long-time-constant processes believed to produce $1/f$ -noise in semiconductor devices). The essential point is that we have a tunnelling structure in which any potential electron trap is so strongly coupled to extended states in the metallic electrodes that long lifetimes cannot occur. For the occupancy of a trap to be changed by applied potential differences of the magnitude used in these experiments, the trap would have to lie within 1 eV of the Fermi level. The coupling to electrode states would therefore be similar to that responsible for tunnelling across the barrier, so the trap lifetime could not be

substantially longer than the tunnelling time between electrodes which is believed to be much less than 1 ps. Therefore the lifetimes we observe cannot be the result of electron trapping. This is a point not often understood in relation to metal-insulator-metal tunnelling structures. The observed relaxation phenomena must therefore result from ionic motion.

We propose that the system contains ions that have neighbouring energy minima between which they can hop (with low probabilities). When a field is applied, mean occupation probabilities change and the system relaxes towards a displaced average configuration. This is reminiscent of the two-site model used to explain linear heat capacities at low temperatures in disordered insulators (Phillips 1987), but here, the changes are electrically driven and result in electrical polarization. That such sites should exist in our tunnelling system is entirely reasonable in view of the disorder in the oxide and at the interfaces.

If ionic motion of this sort is responsible for the effects we observe, the relaxation rates should be consistent with known barrier heights for ionic mobility. We can check this by reference to the temperature dependence of the relaxation times. For ionic motion, τ^{-1} has the meaning of a transition rate. This will be of the form

$$\tau^{-1} = \nu \exp(-\varepsilon/k_B T)$$

where ν is the attempt frequency and ε the barrier height. The Boltzmann factor is the low-temperature limit of a Bose factor, valid for $\varepsilon \gg k_B T$. (We assume the ion is excited over the barrier and not that it tunnels through it.) When a field is applied, the system relaxes towards the new equilibrium configuration with time constant τ . Using measurements at two different temperatures to eliminate ν , one obtains

$$\tau_1/\tau_2 = \exp\left[\frac{\varepsilon}{k_B}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right].$$

Substituting with the values measured at 18 °C and 28 °C one obtains an estimate for the activation energy: $\varepsilon \approx 1.7$ eV. This may be compared with results for *crystalline* materials: 1.5 eV for Al in aluminium (Lundy and Murdock 1962); and, in alumina, 5.0 eV for Al and 4.4 eV for O (Fehlner 1986). It is well known that in regions of high disorder (e.g. grain boundaries) ionic movement takes place much more easily than in material that has crystalline or vitreous order. (This difference plays a significant role in later stages of oxidation; see Fehlner (1986).) The temperature dependence of the relaxation times is therefore consistent with an origin in ionic movement in a disordered region.

We can, however, carry the argument further in trying to identify the processes responsible for the observed changes by noting the polarity of the effects. A positive field (top electrode positive) causes a decrease in intrinsic field. That is, $\Phi_2 - \Phi_1$ decreases. Now positive bias must cause negative charge to move towards the top (positive) electrode. If 'bulk' charge moved to accumulate at the interface, it would cause the barrier at the top electrode to *increase* and that at the lower to decrease (see figure 4). This is opposite to what is observed. If, on the other hand, the adjustments appear in the position of *interfacial* charge, the motion *reduces* the top potential barrier and increases the lower one. This is what is seen, so we argue that the relaxation effects observed on application or removal of a bias field result from motion of ions at the interfaces between oxide and electrodes. One would expect much greater disorder here, so this conclusion is entirely reasonable and consistent with the observed activation energies. Konkin and Adler (1980) also deduced that changes at the interfaces in their

structures were responsible for the annealing effects that they observed. In alumina, we might expect the aluminium ions to respond more readily to applied fields because of their higher charge and smaller size, and because of the availability of vacant sites between the close-packed oxygen ions (Sleigh *et al* 1989). They are, in fact, generally believed to be the mobile species during the field-driven process of oxidation (see below). However, we see no reason to rule out motion of oxygen ions in the disordered interfacial regions between the oxide and the electrodes.

We now return to the slow irreversible increase of mean barrier height that takes place under all conditions. We can rule out the possibility that this results simply from infusion into the junction of reactive species such as water. Infusion of larger molecules can certainly occur with top electrodes that do not bond intimately to the alumina tunnelling barrier but, to our knowledge, it has never been demonstrated with aluminium top electrodes. Experiments on ageing of junctions in conditions of high humidity suggest that water can penetrate with aluminium top electrodes, but only slowly and always with a corresponding increase in barrier thickness (Bellingham *et al* 1991). In the present experiments, we have noted that there is no evidence for barrier thickening after the early stages of annealing. Thus, although we cannot rule out infusion of water as contributing to initial changes in junction parameters, it does not seem possible that it could be significantly involved thereafter. This conclusion is supported by the observation that the steady ageing is unaffected by storage of a completed junction in vacuum or in a desiccator. Konkin and Adler (1980) also found strong resistance increase for junctions stored in vacuum. However, their experimental system was more complicated than ours in that they used aluminium-grown oxide-lead structures with incorporated $-OH$. Their use of lead top electrodes allowed them to use the technique of inelastic electron tunnelling to monitor the incorporated $-OH$ and some of the annealing effects they observed were shown to be the result of changes in orientation of those groups. Our system was simpler in that by using aluminium, incorporated species, if present at all, were inactivated as regards interaction with the tunnelling electrons (Sleigh *et al* 1989). We can therefore conclude that the irreversible increase in mean barrier height that we observe results from a mechanism that is intrinsic to the aluminium-grown oxide-aluminium structure.

We suggest that the process of oxide growth leaves an excess of Al^{3+} in the barrier. The corresponding space charge results in a lowering of the potential between the electrodes. The broken curve in figure 4 illustrates the form of the modified potential for a uniform distribution of the excess Al^{3+} . These ions act as donors with the compensating negative charge falling to the Fermi level in the metallic electrodes. (The depletion length would be very much greater than the thickness of the oxide.) Excess aluminium during early stages of oxide growth has also been indicated in ellipsometry studies (Grimblot and Eldridge 1981, 1982) and is a possible explanation for structure seen in x-ray photoemission work (Eberhardt and Kunz 1978). The sign of the Seebeck coefficient, which implies that the oxide is n-type (Hunt and Ritchie 1970), is also consistent with the presence of Al^{3+} .

The magnitude of the changes in mean barrier height observed during annealing enable us, on the basis of this explanation, to estimate the corresponding loss of Al^{3+} from the barrier. For a change of 60 meV, a value typical for annealing with no applied field, the charge loss from the barrier assuming a uniform distribution is about 2×10^7 C m $^{-3}$. This is 0.1% of the charge present in Al^{3+} stoichiometrically incorporated in the oxide, so the explanation is quantitatively acceptable.

This picture provides a ready explanation for the annealing behaviour by which the mean barrier height increases with time, and more rapidly with increasing temperature.

The dopant aluminium gradually diffuses to the electrodes to reduce the doping level of the oxide and increasing the height of the tunnelling barrier. This explains how the resistance of tunnel junctions with grown aluminium oxide barriers can increase in time without barrier thickening. Barrier thickening is the explanation often put forward. Although this can occur, our results show that most of the resistance change is associated with increase of barrier height, and this we explain by loss to the electrodes of Al^{3+} dopant.

The model also explains the effect of applied bias on the change of mean barrier height. When the standardized negative bias of -1 V is applied, it roughly doubles the total internal field and the rate of increase of mean barrier height is also roughly doubled. Conversely, positive bias produces a large reduction in the rate. We conclude that the loss of Al^{3+} from the barrier is primarily driven by the internal field. In this case, most of the Al^{3+} diffuses to the top electrode.

Finally, we point out that the presence of excess Al^{3+} in the barrier oxide enables us to infer that the oxide in these alumina layers grows by the classic Cabrera–Mott mechanism (Cabrera and Mott 1948) with cations as the mobile species. In this mechanism, oxide grows by diffusion through the oxide of cations, here Al^{3+} , driven by the electric field that results from charge transfer across the oxide by tunnelling of electrons from the underlying metal (here aluminium) to the more electronegative oxygen incident at the outer surface. On reaching the outer surface, the ions combine with the oxygen ions to form more oxide. The excess Al^{3+} in our newly prepared junctions is therefore present as a remnant of the growth process. It is, in fact, the generally held view that the early stage of oxide growth on aluminium is by this mechanism (Fehlner 1986).

We thus have a complete and consistent explanation for all the phenomena we observe.

5. Summary

We have described experiments in which we have measured changes in aluminium-oxide-aluminium tunnel junction parameters resulting from annealing at different temperatures with and without an applied potential difference across the barrier. We have identified two distinct processes. Firstly, there is an irreversible ageing that takes place in all conditions. It is characterized by an increasing mean barrier height, but the internal field corresponding to the difference in work functions at the top and bottom electrodes does not change significantly. The rate of increase of mean barrier height is changed by application of a bias field across the oxide. The second process is a reversible change in the internal field produced by an applied bias. All processes take place more rapidly at raised temperatures.

We have proposed a microscopic model that is able consistently to explain all our observations and from which we are able to infer the mechanism of oxide growth. We associate irreversible ageing with gradual loss from the barrier of excess Al^{3+} ions. Since the barrier is very thin, compensating charge resides in the electrodes and there is no significant conductivity in the insulator from the dopant aluminium. As the ions are lost from the barrier, the Fermi level gradually drops and the mean barrier height increases. The dependence of the rate of change of mean barrier height on the total internal electric field shows that motion of the ions is primarily determined by the field. It follows that they are predominantly deposited at the top electrode. The excess Al^{3+} ions in the

barrier are present as remnants of the mechanism by which the oxide grew, namely the classic Cabrera–Mott mechanism.

The reversible changes produced by application of large potential gradients we explain by polarization changes at the metal–oxide interfaces. These changes are produced by field-driven movement of ions between neighbouring configurations, such movement being possible at the interfaces because of the large disorder in the regions of changing composition.

These experiments (which have been made on an archetypical metal–oxide system of considerable technological importance) have shed light on the mechanism of oxide growth on aluminium, on the electronic properties of the resulting oxide and on the nature of the interfacial regions between metal and oxide. Our conclusions suggest further experimental work to explore in more detail oxide growth and we are pursuing a programme to this end.

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