Substrate Purity Effect on the Defect Formation and Properties of Amorphous Anodic Barrier Al_2O_3

Miriam González-Castaño,^{1,2} Max Döbeli,² Vicente Araullo-Peters,¹ Lars P. H. Jeurgens,¹ Patrik Schmutz,^{1,*} and Claudia Cancellieri¹

¹EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Joining Technologies and Corrosion, Dübendorf, Zürich 8600, Switzerland

²Ion Beam Physics, ETH Zürich, CH-8093 Zürich, Switzerland

A comprehensive study concerning the effect of different Al metal substrate purities (i.e. 99.5 versus 99.99%) on the properties of amorphous anodic barrier Al_2O_3 is presented. The experimental findings demonstrate that only tiny variations in the purity of the employed Al materials lead to different oxide growth rate, surface charge, structural defect and impurities content. Below the ionic recombination potential characterized by Scanning Kelvin Probe Force Microscopy, an increase of the anodizing voltage leads to an improvement of the oxide barrier properties. The larger growth rate exhibited by the higher purity Al substrate however indicates the formation of highly disordered and inhomogeneous barrier oxides. A combination of photoelectrochemical and photoluminescence spectroscopies was used to characterize structural defect concentration and confirmed the presence of significantly higher concentrations in the oxide grown on the purer Al substrates. FT-IR and RBS/ERDA results indicate that H and C species are incorporated from the electrolyte solution in the barrier oxides with higher H amounts detected in the oxide grown on the purer Al substrate.

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The outstanding chemical and physical properties of Al_2O_3 make it a very attractive material for numerous technological applications.^{1,2} For instance, porous Al_2O_3 is widely applied as a catalyst support because of its thermal stability and heat conductivity.^{3–7} Dense and compact Al_2O_3 layers (i.e. without porosity and thus, with a much lower specific surface area) are also of great industrial importance, particularly, for protective and decorative coatings.⁸ Additionally, the high electrical insulation displayed by barrier Al_2O_3 layers has raised interest in the microelectronics community to apply them as dielectric capacitors.^{8–10} The functionality and performance of such barrier-type oxide layers generally depend on multiple factors, such as layer thickness, composition, morphology, density, impurities and/or residual stresses.¹¹

Industrially, barrier Al_2O_3 oxides of well-defined thicknesses are commonly produced by anodizing a parent metal or alloy substrate in an electrolyte solution under the influence of an externally applied electric field.¹² Oxide-layer growth then proceeds by in- and outward migration of ionic species and their vacancies, as well as electrons and holes, across the developing oxide layer under the influence of the applied anodizing voltage, V_{anod} . Importantly, in parallel, impurity species from the electrolyte and/or the metal (or alloy) substrate may be incorporated into the growing oxide layer.^{13,14} The resulting performance of these anodically grown barrier oxide layers (e.g. corrosion resistance, electrical insulation, surface protection) strongly depends on the type, concentration and spatial distribution of such incorporated impurity species within the barrier oxide layer.^{3,15–18} Notably, such impurities can either improve or deteriorate the oxide barrier properties. Accordingly, intentional incorporation of impurities in anodic Al_2O_3 layers is widely employed for tailoring the oxide properties:^{6,8,19} e.g. the presence of small amounts of Cr(VI) enhances the corrosion resistance of Al_2O_3 ;^{20,21} the addition of Zr or Y to Al_2O_3 enhances the thermal resistance against sintering.

Anodizing of metals and alloys in organic electrolytes of controlled pH (5–7), such as oxalic and citric acids, generally results in the formation of dense and low-defective barrier oxide layers with relatively low electrolyte impurity concentrations.^{11,22,23} Nevertheless, the incorporation of minor impurity concentrations from the electrolyte solution into the grown Al_2O_3 barrier layer seems unavoidable. For organic/aqueous electrolyte solutions, H- and C- containing species

are the main impurities in the anodically grown oxide layer. The incorporation of OH and/or H into Al_2O_3 barrier layers is known to affect the electrical insulation characteristics,²⁴ while incorporation of H species at the metal/oxide interface may increase the susceptibility of Al_2O_3 barrier layers to pitting corrosion.²⁵ The integration of C species increases the concentration of defective centers in Al_2O_3 and affects its optical and electrical properties.²⁶

The aim of this work is to evaluate the impact of Al substrate purity on the structural properties (density, defect level) of anodic Al_2O_3 barrier layers. Relationships between the generated defects during anodic growth, density related ionic migration properties measured by AFM-SKPFM and impurity concentration level found within the barrier oxides is established. Characterization of the oxide electronic and optical properties by combined photoelectrochemistry and photoluminescence is shown as a very sensitive methodology to track the structural defect concentration. Indeed, tuning of the properties of anodically grown Al_2O_3 barrier layers requires fundamental knowledge and engineering know-how. For this purpose, two typical Al sheet purities of 99.5% and 99.99%, as widely employed in various fields from light weight applications to microelectronics, are anodized in 0.1 M citric acid (pH = 5.8) for different anodizing potentials in the range of 50 to 200V. This resulted in the formation of overall stoichiometric Al_2O_3 barrier layers with various thicknesses in the range of 50 to 300 nm. Atomic Force Microscopy based Scanning Kelvin probe force microscopy (AFM-SKPFM) is employed to obtain information on the surface roughness and surface potential of the grown oxide layers. Rutherford Backscattering (RBS) and Fourier Transformed Infrared (FT-IR) spectroscopy techniques are applied to investigate the type and concentration of impurities in the grown oxide layers. The relationships between the substrate purity, the electronic and structural defects, as well as the incorporated H- and C-based impurity concentrations are disclosed. Contrary to intuition, anodizing of the purer Al substrates results in less dense and more defective barrier oxides, which also contain a higher content of impurity species from the electrolyte solution.

Experimental: Materials and Methods

Anodizing surface treatments were performed for two commonly-used Al substrate purities of 99.5% and 99.99%, further referred to as A199.5 and A199.99, respectively. The main impurities of the A199.99 substrate are 0.00041% Cu, 0.00035% Fe and 0.00041% Si. The A199.5 has higher impurity concentrations of 0.2% Fe and

*Electrochemical Society Member.

²E-mail: mirian.gonzalez-castano@empa.ch

Figure 1. Current transient profiles obtained during the anodizing experiments at different voltages (30s ramp, 60s holding time) for both type of polished samples: A) Al99.5; B) Al99.99.

0.2% Si. Both metallic substrates were mirror-like polished by subsequent grinding (until P4000 grit with SiC paper) and final polishing with diamond paste down to 1 μm . On some selected samples, electropolishing surface finish was performed in acidic solutions composed by HClO_4 in EtOH (1:3 v/v) at 20 V during 2 minutes. Prior to the anodizing, the substrates were ultrasonically cleaned in ethanol, rinsed with milli-Q water and then dried with pure Ar gas. Potentiostatic anodizing was performed using a two-electrode electrochemical cell with a Pt rod as the cathode and a Keithley power source Model 2400. The anodic oxidations were performed in an 0.1 M citric acid ($\text{pH} = 5.8$) electrolyte at room temperature for a defined area of 1 cm^2 and at a fixed anodizing voltage (V_{anod}) of 50, 100, 150 or 200 V, while applying a ramp and dwell time of 30 s and 600 s, respectively. For the remainder of the paper, the following terminology will be used: e.g. an Al99.9 substrate anodized at $V_{\text{anod}} = 50$ V is labeled Al99.99_50 V.

The average oxide layer thickness was measured by spectroscopic ellipsometry using a M-2000 of J.A. Woollam Co. Inc for three different angles between the incident and detected beam of $\alpha_1 = 50^\circ$, $\alpha_2 = 60^\circ$, and $\alpha_3 = 70^\circ$. For each angle, the UV-Vis spectra were collected in the wavelength range of 370–1720 nm with an integration times of 5 s. The layer thickness was evaluated from the measured series of spectra, according to an established procedure.²²

Atomic-Force-Microscopy-based Scanning Kelvin probe force microscopy (AFM-SKPFM) was employed to gain information on the surface potential and surface roughness of the anodized oxide layers. The surface characterizations were performed with a Bruker Nano Environmental AFM (E-SCOPE) system using a Pt-Ir metallic coated tip with a resonance frequency of $f_{\text{res}} = 100$ kHz and a nominal spring constant $k = 2.8$ Nm^{-1} . After the topography determination in tapping mode, the tip was lifted off from the surface at a distance of 50 nm and an AC voltage of 1 V was applied on the Pt-Ir coated silicon tip (SCM-PIT). An additional DC voltage was superposed on the AC oscillation of the tip and nulling of the signal was performed with the help of a lock-in amplifier. At any point of the surface, the obtained potential was related to the local Volta potential difference (VPD) between the tip and the sample and mapping of the VPD allows the characterization of the local heterogeneities of the oxide. In the case of a “semiconducting” oxide, electronic space charge can be an important contribution to the measured potential, but also ionic defect distribution across the oxide will add a contribution and this aspect is the focus of the AFM-SKPFM analysis. The surface potential is referred to a pure Ni surface previously immersed in distilled water.²⁷

Photoelectrochemical (PEC) characterization was performed using a three electrode cell setup connected to a Jaissle Potentiostat-Galvanostat Model 1002-T-NC. The electrochemical flat cell included a quartz optical window, a Pt wire as counter, a calomel reference electrode and the anodized samples as working electrode in contact to the electrolyte. The light irradiation system was composed of a UV enhanced 150 W Xenon lamp and a LOT-ORIEL monochromator. The

small contribution of dark current photoeffects was accounted for and subtracted with the use of a mechanical chopper (17 Hz) coupled to a lock-in amplifier to obtain the differential electrochemical signal between lamp and ambient illumination. Current spectra data from the photoelectrochemical measurements were recorded at 0.1 V above the OCP and automatically corrected for the lamp spectral sensitivity using a home-made Lab-View software interface.

Photoluminescence (PL) spectroscopy was performed using a Horiba Jobin Yvon Fluorolog spectrometer equipped with a Xe lamp. The system also contains two monochromators and slits that allow controlling the excitation and measuring energy ranges and intensities, respectively. For all the samples, the presented spectra were corrected by the spectral sensitivity of the system. The anodized samples were excited at 260 nm and the recorded emission spectra were confined between 305 and 340 nm^{-1} with an integration time of 4 s. The presented spectra were all background corrected.

Rutherford Backscattering Spectrometry (RBS) measurements²⁸ were performed at the Laboratory of Ion Beam Physics at the ETH Zurich using a 2 MeV 4He beam and a silicon PIN diode detector under 168° . The collected data were evaluated using the RUMP program.²⁹ To measure hydrogen depth profiles, Elastic Recoil Detection (ERD) experiments have been carried out with the same 4He beam with a PIN diode detector under 30° scattering angle using a Mylar absorber foil.²⁸ Absolute concentrations were normalized to a mica standard with 9.5 at% hydrogen. Carbon depth profiles were determined by Heavy Ion Elastic Recoil Detection Analysis (ERDA).³⁰ A 13 MeV 127I projectile beam was used under 18° incidence angle and scattered recoils were identified by the combination of a time-of-flight spectrometer with a gas ionization chamber under a scattering angle of 36° . The data was converted into quantitative concentration depth profiles by means of the Data Furnace code.³¹

Fourier Transmission Infrared (FT-IR) spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer in the range of 4000 to 500 cm^{-1} , 64 accumulations by scan and 4 cm^{-1} of spectra resolution. The presented spectra were all baseline corrected.

The high resolution Scanning Electron Microscopy (SEM) cross sections were collected on an FEI Helios 660 system in secondary electron imaging mode using a 2 keV electron beam at a working distance of 4 mm. The Focused Ion Beam (FIB) cross sections of the anodized oxide were prepared in two steps. A region of interest was protected using electron beam and ion-beam-assisted deposition of a platinum layer. The cross section was then created using focused ion beam cuts.

Results

Anodic oxide growth and morphology.—Figure 1 shows the anodic oxidation current response recorded for both polished substrate purities during the anodizing processes, applying a constant 30 s voltage ramp and 600 s final voltage dwell. For each substrate purity and anodizing voltage, typical current transient profiles for anodic barrier

Figure 2. A) Measured layer thickness and growth rates (GR) from ellipsometry for both purity samples as a function of the anodizing potential (P/P': Mechanically Polished, EP: Electropolished) and B) Cross section SEM images obtained for Al99.5 and Al99.99 anodized at 100V.

layer growth are observed. During voltage ramping, the measured current was related to the formation and growth of a barrier oxide layer induced by the electrical field and the consequent opposite migration of ionic species through the thickening oxide. Both substrate purities exhibited an initial current response proportional to the anodizing voltage. The electric field across the growing oxide decreases approximately linearly with increasing thickness of the formed oxide layer. Once the final voltage was reached, a limiting oxide layer thickness was established. As reflected by the exponential decay of the anodizing current in Figure 1, the electric-field-driven ionic migration of reactants through the oxide layer (i.e. cations, anions and their vacancies) ceased. Then, as long as the maximum applied anodizing voltage is maintained (dwell time), structural relaxations (e.g. local atomic cluster ordering and densification) combined with the recombination of local charges in the grown oxide layer may occur by redistribution of ionic and defect species under the influence of the maintained electrical field, giving rise to the observed residual current. Due to the short dwell times employed (10 min), proper evaluations of the current decay characteristic of high field growth models are hindered. Qualitatively, it can still be observed that very different current decay behaviors occurred. A faster decay was found for the Al99.5 anodized at 50V corresponding to an effective ionic mobility and oxide structure stabilization. Interestingly, when the anodizing voltage was increased for the Al99.5 substrate, the residual current after the initial exponential decay stayed quite high especially for the 150 and 200V most probably due to delayed migration of ionic species. For the Al99.99 substrate, a different behavior was observed with much less dependence of the current decay on the applied anodizing potential above 100V. The similarity of the curves recorded for 100, 150 and 200V could be related to a similar higher migration behavior.

The grown barrier oxides were overall stoichiometric as characterized by RBS (i.e. Al_2O_3) and amorphous, in line with previous findings.²² For the Al99.5 substrate, higher final current densities after 600 s dwell time were observed for increasing V_{anod} (Figure 1A). The increase of the residual current with the V_{anod} is typical for the growth of compact, barrier-type oxide layers, in which ionic migration and related space charge recombination processes are effectively hindered.²² The monotonous increase of measured final current observed for the Al99.5 substrate contrast with the behavior for the Al99.99 substrate, which exhibited an increase of the residual current density up to 150 V; a further increment of the applied V_{anod} to 200 V resulted in a slight drop of the residual final current density (Figure 1B). The detected drop in the final current density at high applied voltage suggests that the Al99.99_200 V oxide layer possessed a less dense, oxide structure than the ones grown at lower anodizing voltages. In general, the final residual currents were smaller for the Al99.5 substrate (except at 200 V).

Figure 2A shows the anodized layer thickness obtained by ellipsometry for several Al99.99 and Al99.5 substrate for which different surface pretreatments e.g. electropolished (EP) and polished (P). No significant changes in the layer thickness are observed for each substrate purity when P and EP pretreatments are compared. In the case of Al99.99 substrate, P and P' indicate different polishing procedures with average roughness (R_a) of about 10–15 and 5–7 nm, respectively. Similar oxide thicknesses as function of anodizing voltages are also obtained for both initial surface roughness (Al99.99-P and Al99.99-P').

For comparable anodizing voltages, thicker oxide layers are systematically formed on the Al99.99 substrate for both polished and electropolished samples. In very good agreement to Figure 1, the higher layer thicknesses observed for all the Al99.99 samples undoubtedly demonstrates that the different growth rates observed between the Al99.99 and Al99.5 substrates are related to the substrate purity and not to other surface differences (nanoscale roughness, pretreatment). For all the investigated conditions the average growth rates (GR) estimated for the Al99.99 and Al99.5 substrates are 14.6 Å/V and 11.8 Å/V, respectively. Comparable anodic growth rates have been previously reported for 99.99% Al foils.³² The small Si and Fe amounts present in the Al99.5 metal substrates should account for the thinner oxides grown on this substrate; hindered growth rates have clearly been observed at higher Si concentrations (above 4% Si) on Al-Si alloys PVD thin film.³³

Even if no differences in oxide growth rate could be evidenced by ellipsometry between P and EP pretreated Al99.5 substrates, AFM-SKPFM measurements (section AFM-SKPFM) showed large scatter between samples in the VPD evolution for oxides grown on electropolished Al99.5 substrates. This scattering could be related to very small Si enrichment on the surface resulting from electropolishing and relevant to the oxide structural defect generation.³³ In order to avoid the uncertainties (e.g. compositional surface enrichment in the % range as a function of the preparation conditions) that EP pretreatment can introduce on Al99.5 samples, the present study is focused on anodic oxidation of mechanically polished Al99.5 and Al99.99 samples. The SEM characterization performed on focused ion beam cross sections of selected polished Al99.99 and Al99.5 samples are shown in the Figure 2B. In concordance with ellipsometry, thicker oxide layers were formed on the Al99.99 substrate. For instance, average oxide layer thicknesses of 155 ± 5 nm and 133 ± 2 nm were determined for the Al99.99_100 V and Al99.5_100 V substrate, respectively. The cross-sectional SEM micrographs also reveal small, but distinct, morphological differences between the oxide layers grown on the two types of substrate. In comparison to Al99.5 substrates, the oxide layers on Al99.99 present more heterogeneity (dark secondary electron emission spots) in the oxide. The softer Al99.99 substrate also

Figure 3. Surface topography A and C and VPD B and D of Al99.99_100 V and Al99.5_100 V, respectively.

shows some more pronounced height steps at the oxide-metal interface (Figure 2B).

AFM-SKPFM.—The AFM-SKPFM analysis of the grown barrier oxides provides information about the surface topography and, more importantly, about the charge distribution at the oxide surface. Selected AFM surface topographies on anodized Al99.99_100 V and Al99.5_100 V substrates are shown in Figure 3. The corresponding Volta Potential Difference (VPD) maps for Al99.99_100 V and Al99.5_100 V are shown in Figures 3B and 3D. The average VPD values for each anodized substrate are derived from representative areas of $10 \times 10 \mu\text{m}^2$. Notably, the lateral variation of the measured VPD over several of such representative analysis areas is a factor of 10 higher for the Al99.99 substrates (i.e. $\pm 100 \text{ mV}$) as compared to the Al99.5_100 V substrate (i.e. $< \pm 10 \text{ mV}$). This indicates the formation of laterally less homogenous oxide layers on the Al99.99 substrate of higher purity, which can be correlated with the larger oxide growth rate possibly indicating the formation of a more defective structure of the barrier oxides formed on the Al99.99 substrate. The overall roughness of the Al99.99 substrate is not significantly higher compared to Al99.5 but deformation and some scratches are more difficult to avoid during polishing of the softer material.

The average VPD values of the anodized sample surfaces extracted from SKPFM mappings is plotted as functions of the anodizing voltage in Figure 4. The VPD values increased with increasing V_{anod} up to 150 V, a trend which was similar for both substrates (with slightly higher values for the Al99.5). For $V_{\text{anod}} > 150 \text{ V}$, the VPD decreases with increasing V_{anod} for the Al99.99 substrate, but continues to increase for the Al99.5 substrate. According to Evangelisti et al.,²² VPD of Al99.5 samples increased up to 8 V for an applied voltage of $V_{\text{anod}} = 250 \text{ V}$ (after which it also starts to drop at higher V_{anod}). Such high VPDs clearly indicated the building-up of an ionic space charge region in the oxide during the anodizing process under the influence of the applied high electrical fields. In general, the detection of such large VPD values cannot be explained by electrochemical double layers or adsorbed dipoles, but typically denote a high density of embedded charges (i.e. ionic space charge regions in the oxide). The observed drop in the VPD at $V_{\text{anod}} > 150 \text{ V}$ for the Al99.99 substrate and at $V_{\text{anod}} > 285 \text{ V}$ for the Al99.5 substrate indicate that the anodizing voltage approaches the oxide electrical breakdown potential, V_{bd} . However, the breakdown potential is commonly defined as the potential at which the oxide layer cannot grow anymore (electrical breakdown) due to the presence of current leakage through nanoscale defects (as related to the initiation of local sparking in the anodizing process). However, the observed maximum in the measured curves of VPD versus V_{anod} does not correspond to the actual oxide electrical breakdown potential, but rather reflects the maximum anodizing voltage that can be applied for achieving the most dense and compact

barrier oxide layer with the most pronounced residual ionic space charge regions. That the electrical breakdown had not yet reached at the tested potentials is indicated by the fact that thickening of the barrier oxide was still possible at higher potentials.²² Therefore, the observed maximum in VPD versus anodizing current should not be confused with the electrical breakdown potential (V_{bd}) and will be referred to as “ionic charge-recombination-threshold” potential, V_{recomb} , where $V_{\text{recomb}} < V_{\text{bd}}$.

More compact and less defective barrier oxide layers can withstand higher applied electric fields during the anodizing process and thus accumulate more pronounced ionic space charge regions in the oxide prior to electrical-field-induced breakdown. Analogously, redistribution of accumulated ionic charges across the oxide depth should be also more difficult in dense, defect-free oxides. From the SKPFM analysis, highly compact and less-defective barrier oxides with pronounced residual ionic space charge regions are produced on the Al99.5 substrate supporting the observation of lower oxide growth rate of $11.8 \text{ \AA/V}$ on this substrate purity. Besides, for $V_{\text{anod}} > V_{\text{recomb}}$, the barrier oxide formed will become less homogenous and more-defective with less pronounced residual ionic space charge regions, as reflected by the VPD drop. The dissimilar trends in VPD versus V_{anod} for the two substrate purities indicate pronounced differences in the structural defect level of the grown barrier oxides, i.e. the distribution

Figure 4. Surface potentials (VPD) obtained for both purity substrates when anodized at different potentials.

of ionic charges (cation and anion profiles) and the defect concentrations. For crystalline oxide, this could be interpreted in terms of different levels of vacancies and interstitials, but these are concepts that cannot directly be used in the case of the amorphous anodic oxides on aluminum.

Photoelectrochemical and photoluminescence spectroscopies.—Photoelectrochemical (PEC) spectroscopy provides useful knowledge regarding the potential barrier behavior depicted by semiconductors in contact with an electrolyte, which, in turn, should be strongly affected by the presence of impurities, oxide defect concentration, etc.^{34–37} The photoelectrochemical spectra obtained for the anodized Al99.5 and Al99.99 samples are presented in Figure 5A. Oxides grown on both type of substrates exhibited the low photocurrent intensities characteristic of amorphous oxides but still with current maxima close to the mA/cm² range in the case of the Al99.99 anodic samples. Compared to crystalline structures, the lower photocurrent intensities generally displayed by amorphous semiconductors are explained by the different mechanisms through which the charge carriers are transported within the oxide layer and the resulting electron-hole recombination probabilities.³⁸ For crystalline oxides, charge carriers are generated in a continuous energy range and display higher drift mobility and low recombination probabilities. In contrast, charge carriers generated from localized states within the energy gap characteristic of amorphous oxides present poor mobility and are easily recombined.^{38,39}

Although the bandgap (BG) energy of amorphous Al₂O₃ is reported at about 6.5 eV,⁴⁰ the current PEC analysis indicates evident photoresponses at sub-gap energies in the anodically grown barrier oxide layers. For wide bandgap semiconductors, such as Al₂O₃,⁴¹ the observed photocurrents at energy levels below the expected bandgap energy typically originate from internal photoemission of e/h pairs from the metal Fermi level into in-gap states in the oxide layer, following the classical Fowler behavior.^{37,42,43} In fact, both substrate purities display significant photocurrents at excitation energies between 2.5 and 5.5 eV. This implies that optical excitation in this energy range can generate electron-hole pairs,⁴⁴ which are effectively separated and result in the measured photocurrents. The lack of long-order characteristic of amorphous oxides generates located energy states within the forbidden energy region (midgap states) because of the only partial overlapping of the electronic wavefunctions.^{38,39} For both substrate purities, the anodic oxides show lower photocurrent intensities for thicker oxide layers. This could be related to (i) increased effective energy barriers for injection of photoinduced charge carriers from the Al substrate into the oxide layers and/or to (ii) decreased structural defect densities with increasing layer thicknesses.

Based on the experimental findings by ellipsometry, SEM of oxide cross sections and especially AFM-SKPFM, it may be assumed that the lower photocurrent intensities observed at higher anodizing voltages is related to the level of structural defects. A denser, less defective oxide induces a lower density of in-gap states in the barrier oxide layers grown at higher anodizing voltages (up to the previously defined ionic charge recombination threshold potential).²⁷ The relevance of the defect density on the measured PEC photocurrents is indeed highlighted by the equal photocurrents displayed by the Al99.99_150V and Al99.99_200V samples (Figure 5A). Considering the larger layer thickness obtained for Al99.99_200 V, the similar photocurrents observed for both anodizing conditions should be attributed to the different oxide defect amounts within the Al99.99_200V sample. In fact, this is fully consistent with the distinct behavior observed for this sample during the anodic grown and the SKPFM (Figures 1 and 4).

The photoelectrochemical response of the samples can be understood by the relation $(I_{ph}h\nu)^n \propto (h\nu - E_{th})$ where I_{ph} is proportional to the absorption coefficient, $h\nu$ is the photon energy, E_{th} is the threshold energy and indirect electronic transitions characteristic of amorphous materials ($n = 0.5$) are assumed. Figure 5B shows the Tauc's plot obtained for both purities from which E_{th} about 2.1 ± 0.1 and 2.3 ± 0.1 eV were extracted for the Al99.5 and Al99.99 substrates, respectively. The similar onset (E_{th}) energies, similar minimal ener-

Figure 5. A) PEC spectra obtained for Al99.5 and Al99.99 when anodized at different potentials; B) Tauc's plot C) Comparison between both purities when anodized at 100 V and 200 V.

gies for injecting electrons in the oxide energy states, suggest certain similarities between the in-gap states developed on both oxide types. At energies lower than the threshold energies $E < E_{th}$, some differences were observed in the shape of the photocurrent onsets. For the Al99.5 samples, steeper current onsets were observed while the Al99.99 showed certain photocurrent intensities extended until lower energies. According to the Mott and Davis model, amorphous materials exhibit localized states close to the valence and conduction

Figure 6. PL spectra obtained using excitation energy at 260nm: A) Al99.99 samples and B) Comparison between both purities when anodized at 100V and 200V.

mobility edges.³⁸ The accentuated photocurrent tails noted for the anodized Al99.99 samples, which have been associated with optical transitions at $E < E_{th}$ ³⁹ could also represent easier charge carriers mobility for these excitation energies and then, variations in the in-gap states.

Figure 5C compares the PEC spectra obtained for both Al99.5 and Al99.99 when anodized at 100V and 200V. Considering the slightly larger oxide layer thickness of the Al99.99 anodized samples, larger resistances toward charge transfer through the oxide layer are in turn, expected. In contrary, the Al99.99 samples always displayed significantly higher photocurrents than Al99.5 independent of the anodizing voltage (note the different scales used for the different purities in Figure 5A). The observed trend is therefore clearly not related to a thickness effect but accounts for higher structural defect populations developed within the Al99.99 barrier oxides, with respect to the Al99.5. It could then be suggested that, the slower oxide growth rates detected in the oxides growth on the Al99.5 substrate resulted in more compact barrier layers with smaller amounts of point scale defects (e.g. vacancies) and hindered ionic charge carrier transport abilities.

The type and concentration of defect sites embedded in the anodized Al_2O_3 oxides have therefore been further related to the photoluminescent (PL) emissions observed when alumina is exposed to ultraviolet radiation to correlate the defect identification with two different physical phenomena. The photoluminescent emissions are associated with defective sites and, although their origin is not always fully identified, it is known that the oxide defect luminescence behavior is determined by the short-range structural properties and not by the long-range order.⁴⁵ In fact, the local short range order in the amorphous oxides grown by anodizing should resemble the short range order in the crystalline Al_2O_3 polymorphs.⁴⁶ In general, the PL spectra of Al_2O_3 oxides exhibit a broad emission band (260–600 nm) composed of different contributions attributed to defective centers such as oxygen vacancies and/or to impurities.²³ Differences in defective centers concentration in Al_2O_3 oxide films can be directly correlated with emission band intensity. According to the literature, the main intrinsic defects characteristic of Al_2O_3 oxides are F^+ centers and Al^{3+} cations in interstitial positions or distorted local coordination with different oxidation states of Al_2O_3 .^{25,47,48} While F centers and C species related emissions are reported in literature at about 420 nm, PL emissions at about 320 nm (3.8 eV) are mostly ascribed to oxygen vacancies with one electron trapped which emission (F^+ centers) and interstitial Al cations.

Among the identified defects, the higher F^+ centers stability and presence in Al_2O_3 oxides is attributed to the strong repulsion of an electron pair localized in an oxygen vacancy (F centers).⁴⁹ Because of their higher stability and concentration, F^+ centers have been interpreted to be representative for extrapolating the overall defect con-

centrations of the anodic samples. Figure 6A shows the measured PL spectra in the wavelength range from 310–340 nm. For the studied amorphous Al_2O_3 barriers oxides, two different emission edges, centered at 317 and 330 nm are identified being those probably related to locally distorted coordination spheres of interstitial Al cations and F^+ centers, respectively.²⁸ Up to 150V, increasing anodizing voltages for both purities led to emission intensity decrements indicating lowered defective site concentrations embedded within the oxide and correlating with the previous photoelectrochemical current decreasing at higher anodizing voltage.

Also, the oxides grown on both substrate purities showed slight luminescence intensity increase at 200V indicating larger amounts of defect centers. This suggests that $V_{anod} > 150V$ enhances the creation of defects for both substrate purities during the anodizing process. Although this intensity trend is detected for both purities, a much more pronounced luminescence band intensity was measured for the oxide grown on high purity samples. However, for the Al99.5_200V, a slight defect centers increase is uniquely observed by PL spectroscopy, whereas PEC and SKPFM measurements continue to indicate the growth of the dense layer. In this case, it can be postulated that a small structural defect density increase in a dense oxide is insufficient to generate ionic charge recombination until a certain defect threshold is reached. Still, this structural defect level increase is the precursor of the V_{recomb} occurring at higher anodizing voltages. It also shows that the information on the defect level obtained by PL (optical detection) and PEC (electronic charge detection) are slightly different even if the trends are perfectly consistent up the 150V anodizing voltages. For the oxide grown on Al99.99 samples, the increase of the defect concentration level for the anodizing processes at 200V is clearly observable and an overall agreement between the different characterization results is obtained. Indeed, going beyond the V_{recomb} resulted in remarkably higher defect concentrations as evidenced by the significantly larger PL band emissions as well as the relative lower resistance to the ionic and charge carrier transport (AFM-SKPFM and PEC spectroscopy, respectively).

Figure 6B compares the emission bands exhibited for both types of substrate when anodized at voltages of 100 and 200V. It can be observed that the Al99.99 samples showed much higher band intensities compared to the homologous Al99.5 substrates anodized at similar voltages. In agreement with the higher PEC photocurrents and PL emission intensities detected for the Al99.99, it can be confirmed that anodizing processes performed on the high purity substrate induced the formation of higher defective oxides in comparison to the Al99.5 ones. Although the photocurrents displayed by amorphous oxides are lower than those of crystalline structures, the increase of the concentration of defective sites (F^+ centers/ Al_i) in amorphous oxides also leads to larger photocurrent intensities. The higher amount of e-h pairs

Figure 7. A) H profiles for Al99.99 and Al99.5 substrates anodized at different voltages; B) H profiles obtained for Al99.5 and Al99.99 substrates anodized at 100 and 200V; C) C profiles for Al99.99 and Al99.5 substrates anodized at different voltages; D) C profiles obtained for Al99.5 and Al99.99 substrates anodized at 100 and 200V.

effectively separated within the oxides grown on the Al99.99 can be explained by changes in the amount of charge carriers generated and/or on the degree of confinement and probability of recombination.^{38,39} Both possibilities, which could indeed coexist, can explain the higher amounts of e-h pairs effectively separated on the Al99.99 samples. The different defect concentrations detected on the oxides grown on substrates of both purities also provoked changes on the configuration and/or density of midgap states constituted for each oxide. The combination of the two techniques allows possible artefacts of the PEC signal intensity related to larger oxide thickness to be discarded and provides a clear correlation of the measurements with defect density.

RBS, ERDA and FT-IR spectroscopies.—RBS and ERDA measurements along with FT-IR spectroscopy should establish useful relationships between the structural defect population and the H/C species contained within the anodically grown Al_2O_3 oxides.

For both substrate purities, the hydrogen (H) profiles obtained by RBS measurements are presented in Figure 7A. The shape of the H depth-distribution profile in the oxide layers was similar for all cases studied. The H concentration was relatively low and shallow at larger depths within the bulk oxide, but very steadily increased toward

the oxide surface, reaching local H concentrations as high as about 10–12 at.%. Compared to the Al99.99 substrate, the anodized Al99.5 substrates clearly exhibited considerably sharper in depth H profiles, i.e. the drop in the H concentration from the surface was more pronounced, which implies a lower concentration of H in the interior of the barrier oxide. Thus, significantly higher H concentrations were detected in the oxide layers grown on the Al99.99 substrate (for all studied anodizing voltages). Figure 7B shows a comparison of the measured H profiles for the Al99.5 and Al99.99 substrates at two different anodizing voltages of 100 and 200 V, which also clearly shows a broader tail for the Al99.99_100 V substrate as compared to the Al99.5_100 V substrate. Moreover, Figure 7B clearly reflects that the nominal concentration of incorporated the H species decreased with increasing anodizing voltage, in accordance with the lower structural defect concentration of the barrier oxides grown at higher anodizing potentials.

The measured carbon (C) concentration-depth profiles of the anodized Al99.5 and Al99.99 substrates, obtained by ERDA, are presented for the different anodizing potentials in Figure 7C. Lower C amounts were incorporated into the grown oxide barrier as compared to H-species. The decrease of the H and C amounts in deeper positions

Figure 8. FT-IR spectra obtained for the anodic samples: A) Al99.99; B) Effect of the substrate purity when anodized at 100 and 200V.

of the barrier oxides suggests the presence of density and defect concentration gradients from the surface to the bulk of the oxide layer. For higher anodizing voltages, no evident changes on the C concentrations were observed for both purity substrates. However, weak increases of C species with increasing V_{anod} cannot be ignored, especially for the Al99.5. The oxide layer densification and diminution of the structural defect density detected for both purity substrates for increasing V_{anod} is accompanied by a decrease of the H amounts. As for the H concentration, the C impurity concentration in the barrier oxides is also higher for the Al99.99 substrate (Figure 7D).

Concerning the chemical nature of the impurities present in the anodized oxide, Figure 8A shows the FT-IR spectra obtained in reflection mode for the Al99.99 substrate. No spectra could be obtained for the samples anodized at 50V, most probably due to the small oxide layer thicknesses. In terms of observed species in the oxide, similar FT-IR spectra were found for both types of substrate. All the samples exhibited bands typically associated with stretching vibrations of OH ($3700\text{--}3000\text{ cm}^{-1}$) and CH (around 2900 cm^{-1}) species.^{23,50} In addition, additional bands attributed to C=C, C=O ($1200\text{--}1100\text{ cm}^{-1}$) and OCO ($900\text{--}500\text{ cm}^{-1}$) species were observed in the region from 1200 to 500 cm^{-1} .^{51,52} Some bands in the range 800 to 500 cm^{-1} associated with stretching vibrations of Al-O bonds in octahedral ($750\text{--}500\text{ cm}^{-1}$) and tetrahedral coordination ($900\text{--}750\text{ cm}^{-1}$) were also observed. It has to be noted that, although the anodized Al_2O_3 oxides were amorphous, local Al-O short ordered clusters with similar vibrational properties than crystalline compounds are also expected.⁵³ In agreement with the H decrease detected in RBS, the OH and CH band intensities decrease with increasing anodizing voltage. As claimed from ERDA measurements, the trends of the C-containing species

(with edges observed at ca. 1160, 1068, 952, 780 and 677 cm^{-1}) were less clear for the different V_{anod} . Figure 8B compares the measured FT-IR spectra of the Al99.5 and Al99.99 substrates at anodizing voltages of 100 V and 200 V. For both anodizing potentials, the OH-related signals in the range of $3700\text{--}3000\text{ cm}^{-1}$ were significantly higher for the anodized Al99.99 substrates, in accord with the higher H content in the respective barrier oxide layers.

Discussion

An overall picture of the substrate effect on the anodized oxide growth and structural defect distribution is given in the Figure 9 based on the oxide cross sections of Figure 2B. As a general statement, both purity substrates generated barrier oxide layers with thickness determined by the applied voltages: the higher the anodizing voltage, the thicker the oxide layer. Compared to Al99.99 substrate purity, thinner barrier oxides were grown on the Al99.5 substrates on polished as well as electropolished surfaces. This observation points out the impact of the substrate purity on the anodized oxide growth, density, defect structure and ionic transport properties on the oxide under high electrical fields. The main impurities contained in the Al99.5 substrate are 0.2% Fe and 0.2% Si. Enhanced growth rates have been attributed to faster Al ionic migration in (0.2%) Fe-doped Al_2O_3 .⁵⁴ On the other hand, smaller anodic oxide growth rates have been related to the presence of Si in Al-Si alloys³³ where, for larger Si contents starting at 4%, Si-oxide enriched zones at the metal-metal oxide interfaces were observed. The RBS results on oxides grown on Al99.5 substrates showed the presence of a small amount of extra metallic species concentrated close to the metal interface. Similarly, for pure

Figure 9. Schematic description of the of the substrate purity influence on the anodic barrier Al_2O_3 ionic defect structure.

Ti and Ti-Si alloys (6% Si), lower photoelectrochemical currents and higher breakdown potentials were attributed to the presence of Si at the interface and related to highly stoichiometric oxides with lower oxygen vacancies concentration.⁵⁵ Therefore, the lower growth rates observed for Al99.5 could be attributed to the presence of Si as impurities underlining that remarkably different oxide properties can be indeed achieved by incorporating even submonolayer amounts of cationic species within barrier Al₂O₃ layers, also in line with previous findings.⁵³

Related to the different oxide growth rates on the two type of Al purity, a difference in the ionic migration properties resulted in differences on the VPD (dominated by the ionic space charge layer formation in the oxide) measured by AFM-SKPFM. When the anodizing voltages were increased, the progressive increase in the VPD noted for the Al99.5 samples could be explained by anionic and cationic “like” vacancies generated at the M/O and O/electrolyte interphases, respectively. The hindered ionic transport processes, which led to thinner Al99.5 oxide layers with respect to Al99.99 substrates, results in confining more the accumulated ions at the interfaces, impeding the ionic charge recombination and inducing an increased VPD. In contrast, easier ionic mobility and charge recombining processes within a more structural defective oxide matrix accounts for the lower measured VPD and strong decrease observed for Al99.99_200V. When higher voltages were applied on the Al99.99 substrates, favored driving force for ionic migrations allowed for recombination processes in the presence of larger amount of structural defects and led to the observed VPD decrease. Thus, although the oxide was in an overall charge neutrality condition, different oxide density and defect levels were generated depending on the migration mechanisms. In case of a denser oxide, this will result in pronounced ionic space charge localization at interfaces identified by AFM-SKPFM.

For compact barrier oxides, migration processes occurring under high electrical fields will determine the defect and impurity concentrations within the oxide and consequently, the structural and electronic properties. The electronic charge transport capability through the oxide, i.e. the displayed decreasing photocurrents as a function of anodizing voltage in PEC spectroscopy, is correlated to the higher layer thickness and to the lower defect density, which will determine the electron-hole pair generation and annihilation. For similar substrates and conditions, Evangelisti et al.²² experimentally observed anodic Al₂O₃ oxide densification, supported by DFT modelling of amorphous oxide, when the anodizing voltages were increased. In agreement to the density decrease with the V_{anod} , higher anodizing voltages also led to lower emission intensities in PL spectroscopy indicating defect concentration decrease. In terms of extrinsic species, no significant C content variations were measured in ERDA while FT-IR and RBS undoubtedly indicated that larger anodizing voltages also decreased the amount of H species present in the Al₂O₃ barrier layers for both purity substrates. It should be highlighted that, although the C species affect the oxide luminescence emissions, considering the absence of significant changes of the C contents with anodizing voltage and the luminescence emission range measured (C species emit around 420 nm), the large changes observed on the PL band intensities should be uniquely correlated to variations on the H and/or defect concentrations.

The impact of the substrate purity in the obtained oxide properties can also be clearly established. Indeed, qualitative and clear differences were detected between both Al purities for the entire anodizing voltage range considered. The higher photocurrents and band intensities displayed by the Al99.99 samples for PEC and PL spectroscopies clearly indicated higher structure defect site concentrations. The higher ionic migration rate that led to larger oxide thicknesses exhibited by the Al99.99 substrate resulted in lower density and highly disordered oxides with higher defect populations. Larger electronic charge generation and ionic transport processes as well as integration of extrinsic species within the oxide layer then resulted for the oxide grown on Al99.99 substrate. This statement is, in fact, strongly supported by the larger amount of H and C species detected in the Al99.99 samples. In contrast, the slower oxide growth rate obtained

for the Al99.5 substrate could be related to the lower effective electrical field caused by the accumulation of the Si species at the M/O interface and resulted in the constitution of highly ordered barrier layers with lower defect sites and lower amount of H and C in the bulk of the oxide. The differences observed in oxide structural defect levels between these two substrate purities anodized in the same electrolyte and conditions, indicates that H integration is a consequence of the oxide defect formed during anodizing. Often in the literature, the impurities from the electrolyte integrated in the oxide are considered to be responsible for the generation of defects in the grown oxide. The outcomes obtained in this study underline the opposite: highly defective oxides favor the incorporation of extrinsic species coming from the electrolyte.

Conclusions

In this work, two different aluminum metal purities, 99.5% and 99.99%, have been used as substrates for growing barrier Al₂O₃ layers via anodizing processes performed at different voltages in citric acid. The metallic substrate strongly determined the properties the barrier oxides even for this slight impurity level difference. In fact, the importance of the substrate purity on the anodized oxide structure was reflected by the different ionic charge recombination voltages, layer thicknesses, structural defect concentration and extrinsic impurity integration. Compared to Al99.5 substrate, the Al99.99 ones exhibited faster oxide growth rates, larger layer thicknesses and lower ionic charge recombination threshold potentials (V_{recomb}). In concordance to the more disordered and rough oxide layers, larger amounts of defects sites and easier incorporation of extrinsic species coming from the electrolyte were also detected for the higher purity substrate.

Potential mapping by AFM-SKPFM indicated larger lateral variations of the measured VPD for the Al99.99 substrates as compared to the Al99.5 substrate which indicated the formation of less homogeneous oxide layers on the Al99.99 substrate. The considerably lower V_{recomb} noted for the Al99.99 substrate with respect to the Al99.5 one, was associated with a less dense, more defective oxide formation and consequent easier ionic space charge recombination. In agreement, compared to the Al99.5 purity substrate, larger PEC photocurrents and PL emission intensities observed for the anodic oxide grown on the Al99.99 substrate further point out the higher structural defect amount. RBS and ERDA measurements indicated the incorporation of light impurities species (C and H) from the electrolyte during the oxide growth. The total H and C content within the oxide barrier layer was considerably higher for the oxides grown on Al99.99 substrates.

The experimental findings emphasize the significant effect of substrate impurities on the resulting barrier oxide properties of anodized oxides. They also indicate that very different oxide structural defect levels can be obtained during anodizing with the substrate considered to play a larger role compared to the electrolyte species that are integrated as a consequence of formed defects. The present study represents a step forward toward the fundamental understanding of why, contrary to the intuition, purer Al substrates induce highly defective barrier oxides. A significant contribution to this understanding can be obtained by the new combination of employed characterization techniques (AFM-SKPFM, PEC and PL) which constitutes a promising methodology for investigating very fine oxide structural differences affecting the Al₂O₃ barrier properties.

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ORCID

Miriam González-Castaño <https://orcid.org/0000-0003-2575-8398>Claudia Cancellieri <https://orcid.org/0000-0003-4124-4362>

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