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Band gap structure modification of amorphous anodic Al oxide film by Ti-alloying

S. Canulescu,[1,a)] K. Rechendorff,[2] C. N. Borca,[3] N. C. Jones,[4] K. Bordo,[5] J. Schou,[1] L. Pleth Nielsen,[2] S. V. Hoffmann,[4] and R. Ambat[5]

[1]*Department of Photonics Engineering, Technical University of Denmark, 4000 Roskilde, Denmark*
[2]*Danish Technological Institute, Kongsvang Alle 29, 8000 Aarhus, Denmark*
[3]*Paul Scherrer Institute, 5232 Villigen, Switzerland*
[4]*ISA, Department of Physics and Astronomy, Aarhus University, 8000 Aarhus, Denmark*
[5]*Department of Mechanical Engineering, Technical University of Denmark, 2800 Kongens Lyngby, Denmark*

The band structure of pure and Ti-alloyed anodic aluminum oxide has been examined as a function of Ti concentration varying from 2 to 20 at. %. The band gap energy of Ti-alloyed anodic Al oxide decreases with increasing Ti concentration. X-ray absorption spectroscopy reveals that Ti atoms are not located in a TiO_2 unit in the oxide layer, but rather in a mixed Ti-Al oxide layer. The optical band gap energy of the anodic oxide layers was determined by vacuum ultraviolet spectroscopy in the energy range from 4.1 to 9.2 eV (300–135 nm). The results indicate that amorphous anodic Al_2O_3 has a direct band gap of 7.3 eV, which is about $\sim$1.4 eV lower than its crystalline counterpart (single-crystal Al_2O_3). Upon Ti-alloying, extra bands appear within the band gap of amorphous Al_2O_3, mainly caused by Ti 3d orbitals localized at the Ti site. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4866901]

Amorphous anodic aluminum oxides (AAO) have received large interest in materials science as they are key materials in many applications such as metal-oxide semiconductor devices,[1] dye-sensitized solar cells,[2] or corrosion protection. Due to the possibility of tuning the band gap, dielectric constant, conductivity, and even optical appearance by alloying,[3] amorphous anodic oxides are interesting from both theoretical and practical viewpoints. However, studies on the modification of the band gap structure of the amorphous anodic layers upon alloying are rather limited. Semi-empirical correlation between the electronegativity and band gap of oxides has been used recently to estimate the band gap of mixed metal oxides.[4,5] While anodic Al oxide layers are widely used, few studies on band gap structure of anodic oxide films have been reported.[5]

In this Letter, we study the effect of Ti alloying on the electronic structure and band gap states of amorphous anodic aluminum oxide. We analyze the local environment of Ti atoms in the mixed Ti-Al oxide films by means of X-ray absorption spectroscopy (XAS), and we determine the band gap energy of Ti-alloyed anodic aluminum oxide by vacuum ultraviolet (VUV) spectroscopy.

Thin films of Ti-Al alloys, with Ti concentration ranging from 2 to 20 at. %, were deposited at room temperature by DC magnetron sputtering on double-side polished sapphire substrates. The deposition was carried out using two Al and two Ti targets (99.99% purity). The film composition was adjusted by changing the relative power on the Al and Ti targets, keeping the total power constant, while the sputtering time was appropriately set in order to deposit films of similar thickness $\sim$130 nm. The anodizing was performed in a dual-electrode cell, where an Al-Ti film on sapphire served as the anode and a Pt mesh served as the cathode. All films were anodized in 20% sulphuric acid at a constant voltage of 20 V at 18 °C. The anodizing was stopped when the observed current density was stabilized at 0.1 mA/cm^2. All anodized samples show high transparency in the visible spectra range. The films were not sealed after anodizing, such that the anodized layer consists of a porous structure with open pores.

X-ray absorption spectra at the Ti K-edge were measured at the microXAS beamline at the Swiss Light Source (Switzerland) using a Si (111) double-crystal monochromator with an energy resolution close to the intrinsic (111) crystal reflection. The X-ray beam size was 500×500 μm^2. The films were measured in fluorescence mode, while powder references were measured in transmission mode. The energy shifts between the various spectra were established by comparison with spectra obtained from the appropriate reference compounds. After background subtraction, all spectra were normalized to unity at 400 eV above the Ti K-edge.

VUV spectroscopy in the energy range from 4.1 to 9.2 eV (300–135 nm) was used to probe the valence to conduction band transitions. Transmittance measurements were carried out at the CD1 beamline of the ASTRID Synchrotron Light Source (Denmark) in a N_2 purged chamber to avoid absorption of the UV light by air molecules. A baseline was acquired each time before and after the measurement. The measurements from 6.2 to 2.1 eV (200–600 nm) were taken using a UV-visible spectrometer (model Cary 50). The results from the VUV and UV-visible spectrometer agreed well in the overlapping energy region from 200 to 300 nm, and the data were spliced together without the need to use a multiplicative scaling factor.

The local electronic structure of anodized Ti-alloyed Al oxides (2, 10, and 20 at. % Ti) and reference compounds was investigated using XAS at the Ti K-edge, and the results are shown in Fig. 1(a). The XAS measurements were performed in fluorescence mode, in which the emitted Ti K$\alpha_{1,2}$ photons
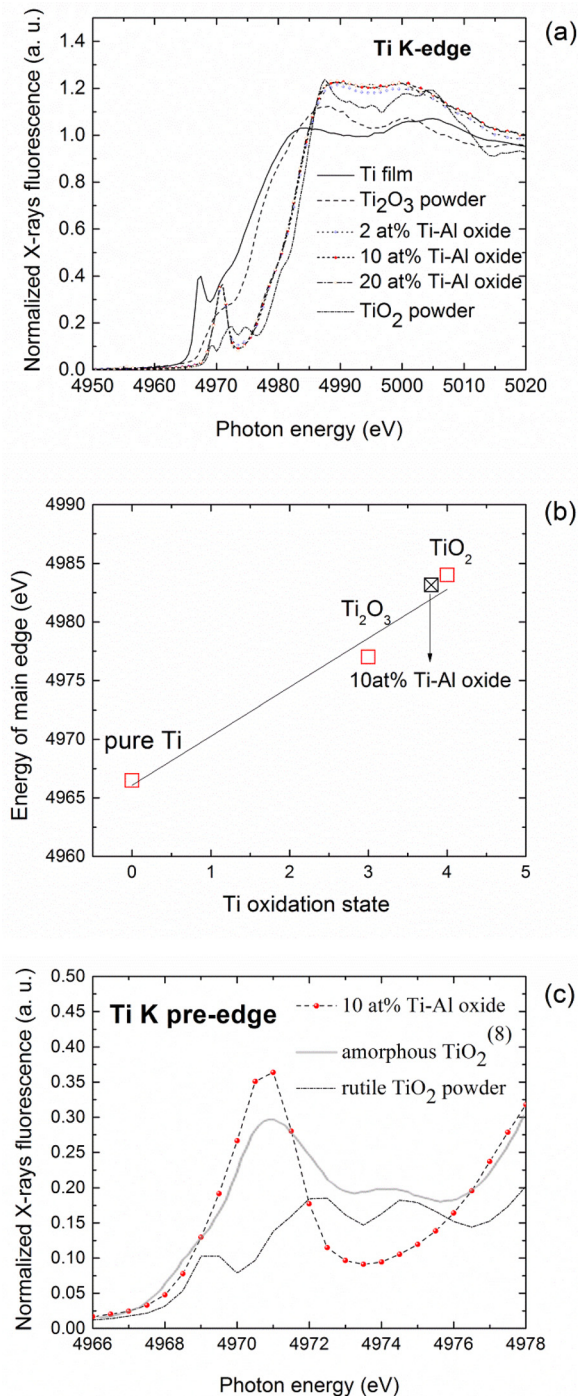
a)Electronic mail: stec@fotonik.dtu.dk.

FIG. 1. (a) XAS spectra of sputter-deposited Ti film, Ti_2O_3 powder, TiO_2 rutile powder, and 2, 10, and 20 at. % Ti-Al oxide at the Ti K-edge; (b) the position of the Ti K-edge as a function of Ti oxidation state, as determined from the XAS spectra; (c) XAS spectra at the Ti K pre-edge for 10 at. % Ti-Al oxide together with reference spectra of rutile and amorphous TiO_2. Reproduced by permission from Borghols *et al.*, J. Electrochem. Soc. **157**, A582 (2010). Copyright 2010 by The Electrochemical Society.[8]

were collected along the X-ray probing depth (at 5 keV) of several tens of microns. As the average thickness of films is 130 nm, the XAS analysis reveals the bulk electronic structure of the film, and surface effects can be neglected. The main absorption edge of the anodized Ti-Al oxide alloy is located at lower energy compared to the one of rutile TiO_2 (Fig. 1(a)). The energy of the main absorption edge is very sensitive to the actual chemical valence of the excited

atom,[6,7] and a systematic shift to higher energy corresponds to an increase of the oxidation state. In Fig. 1(b), the energy of the main edge of 10 at. % Ti-alloyed Al oxide is compared to the well-known titanium reference compounds, i.e., Ti foil (Ti^0), Ti_2O_3 (Ti^{3+}), and rutile TiO_2 (Ti^{4+}). An average valence of Ti of 3.8 was estimated based on the linear interpolation, indicating that Ti atoms have a mixed valence state between 3+ and 4+ in the anodized layer. No change of the Ti K-edge spectra was observed with increasing Ti alloying from 2 to 20 at. %. This suggests that the valence state and local atomic environment around the Ti atoms do not change with the amount of Ti alloying.

The pre-edge features of the Ti K-edge shown in Fig. 1(c) represent the discrete electronic excitations into unoccupied (bound) states. The pre-edge features of Ti-Al oxides are compared with those of rutile and amorphous TiO_2.[8] X-ray diffraction analyses reveal that the anodized Ti-Al oxide layers have an amorphous structure (not presented here), so the spectrum of amorphous TiO_2 is also included for comparison. Three pre-edge peaks of the TiO_2 rutile indicate the presence of the TiO_6 octahedron, which is characteristic to all crystalline forms of TiO_2.[8] The first two pre-peaks are associated with transitions of the excited core electrons to the $3d$–t_{2g} non-bonding bands, whereas the third peak is a signature of the transition to the $3d$–e_g anti-bonding band. Amorphous TiO_2 resembles a strongly deformed octahedron which modifies the local atomic distribution of ions around the Ti, and thus, the shape and the intensity of the pre-edge peaks are completely modified compared to the crystalline form. The pre-edge spectra of the amorphous Ti-Al oxides resemble neither a rutile nor an amorphous TiO_2 spectrum suggesting that the Ti atoms are not located in a TiO_2 unit but rather in a mixed Ti-Al oxide matrix. Previous results on anodic films on Al-25 at. % Ti[9] and Al-51 at. % Ti[10] indicate that the anodized layer contains units of TiO_2 and Al_2O_3. However, the XAS analysis in this work does not reveal the presence of TiO_2 units. A possible explanation of this discrepancy could be the lower amount of Ti (up to 20%) in the samples used in this study.

VUV spectroscopy has been employed to study the electronic structure of pure and Ti-alloyed anodic aluminum oxide.

The theoretical expression of the absorption coefficient, α, for direct optical transitions is related to the incident photon energy ($h\nu$) by the relation[11,12]

$$(\alpha E)^2 \sim A(E - E_g),\qquad(1)$$

where A is a constant depending on the transition probability. The band gap energy can then be determined by extrapolating $(\alpha E)^2$ to zero. The optical band gap plot of anodized aluminum oxide film on sapphire is shown in Fig. 2, together with the band gap plot for sapphire included for comparison in the inset. Here, we assumed that all incident light is either transmitted or absorbed, with reflection or scattering being negligible.[13]

Sapphire (single-crystal Al_2O_3) shows a dramatic cut-off in transmittance at around 8.7 eV, corresponding to the optical band gap energy (see inset in Fig. 2). The measured band gap energy is in close agreement with the reported value of
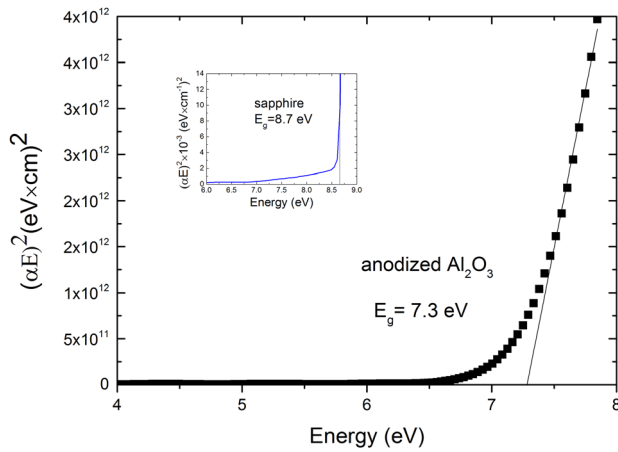
FIG. 2. Optical band gap plot of the anodized Al_2O_3 film on sapphire. Inset represents the band gap plot of sapphire (single crystal of Al_2O_3).

single-crystal Al_2O_3, i.e., 8.8 eV.[11] Anodic Al oxide has a band gap value of 7.3 eV, as determined assuming direct optical transitions, which matches the experimental values of γ-Al_2O_3 (7.2 eV) (Ref. 11) well. Our results indicate a decrease in the band gap energy as one goes from a crystalline to amorphous Al_2O_3. The reduction in the band gap energy of amorphous oxide is attributed to the presence of unoccupied states within the band gap. These unoccupied states have been associated with oxygen vacancies that act as electron and hole traps[14] in amorphous Al_2O_3 grown by Atomic Layer Deposition (ALD). A band tail of 6.4 eV is observed. Anodized aluminum oxide has an amorphous structure (similar to ALD-deposited Al_2O_3), but with pores of 15 nm and with a typical inter-pore distance around 100 nm.[15] The degree of lattice distortion is therefore likely to be higher for these nano-porous anodic films, thus causing aggregation of vacancies acting as trap states along the walls of the pores and leading to lower band-to-band transition energy.[13]

Upon alloying with Ti, modifications of the microstructure, as well of the electronic structure of the amorphous anodic films are produced. Fig. 3 shows the variation of the absorption at the band gap for thin films of Ti-alloyed Al oxide. The band gap energy of anodic Ti-Al oxide decreases with increasing Ti content. The determined experimental
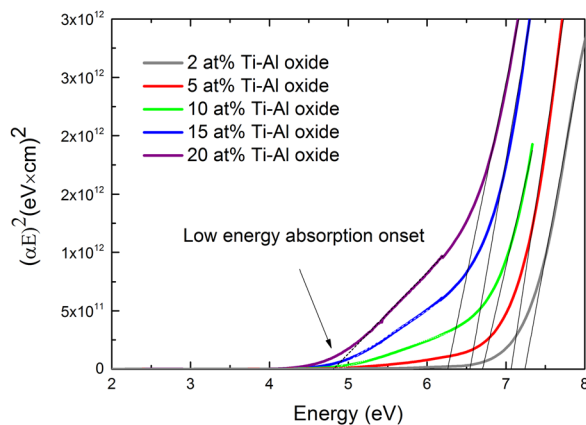
values of band gap energy are given in Table I. The valence band consists of occupied O 2p orbitals and the conduction band of Al 3s−3p empty orbitals,[11] therefore the optical band gap in Al_2O_3 originates from O 2p to Al 3s transitions. When the Ti ions are present at the Al site, extra bands appear within the band gap of Al_2O_3 below the conduction band. First principle pseudopotential calculations have shown that these bands are mainly composed of Ti 3d orbitals localized around the Ti sites.[16] The interaction between the Al_2O_3 band electrons and localized 3d-electrons associated with Ti atoms leads to a change in the conduction band (CB) and valence band (VB) energy levels, causing the band gap to shrink. The experimentally determined band gap energy decreases by about 1.1 eV from the pure to 20 at. % Ti alloyed Al oxide (Table I). The reduction in the band gap energy of Al_2O_3 was also reported experimentally for other transition metal-alloyed Al_2O_3, such as Nb and Zr. A reduction in the band gap energy of 2.3 eV and 0.8 eV was estimated for 6.25 at. % Nb- and Zr-alloyed Al_2O_3, respectively.[3] Thus, we have confirmed experimentally the decrease in the band gap upon Ti-alloying, which is in agreement with the introduction of extra Ti 3d bands within the band gap of Al_2O_3.

A low-energy absorption feature for the highest Ti-alloyed Al oxide films can be observed in Fig. 3. The onset of low-energy absorption is rather similar ($\sim$4.8 eV) suggesting that the origin of the optical transitions is the same. However, the area under the low-energy absorption region increases linearly with Ti content due to the replacement of Al states with Ti states. This feature could indicate the formation of Ti-derived band states near the conduction band gap edge. States introduced by Ti alloying overlap at high titanium concentration and evolve as an impurity band. Therefore, the low-energy absorption onset is most likely caused by electron transitions from the valence band to Ti-derived impurity states located within the band gap of amorphous anodic aluminum oxide.

In summary, we have studied the optical and electronic structure properties of anodized Al oxide and Ti-alloyed Al oxide over a wide Ti composition range (up to 20 at. %). X-ray absorption spectroscopy at Ti K-edge reveals that Ti atoms are not located in a TiO_2 unit, but in an Al-Ti oxide with mixed Ti^{3+}/Ti^{4+} valence states and an effective valence of 3.8. Vacuum ultraviolet spectroscopy of these films shows that the band gap structure is closely related to the crystal structure of the films, such that amorphous anodized Al oxide

FIG. 3. Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the Ti-alloyed Al oxide films with Ti concentrations varying from 2 to 20 at. %.

TABLE I. Band gap energy values of Al oxide and Ti-alloyed Al oxide.

Alloy	Band gap energy, E_g^{opt}(eV)
Single crystal Al_2O_3 (sapphire)	8.7 eV
Anodised Al_2O_3	7.3 eV
2 at. % Ti-alloyed Al_2O_3	7.2 eV
5 at. % Ti-alloyed Al_2O_3	7 eV
10 at. % Ti-alloyed Al_2O_3	6.7 eV
15 at. % Ti-alloyed Al_2O_3	6.5 eV
20 at. % Ti-alloyed Al_2O_3	6.2 eV
Anodised TiO_2[a]	3.4 eV

[a]Reference 13.

has a direct band gap energy which is about 1.4 eV lower than its crystalline counterpart. Upon Ti-alloying, extra bands appear within the band gap of amorphous anodized Al oxide, mainly composed of Ti 3d orbitals localized at the Ti site. This results in a linear decrease of the direct band gap from 7.3 eV of anodic Al oxide to 6.2 eV for 20 at. % Ti-alloyed Al oxide. Furthermore, a low-energy absorption feature induced by Ti-derived impurity states was observed for the highest Ti-alloyed oxide films. The present results demonstrate the possibility of tuning the band gap by tailored alloying with Ti and provide a detailed study of the alloy-induced modification of the electronic structure of Al oxide.

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