Effect of Composition on the Photoelectrochemical Behavior of Anodic Oxides on Binary Aluminum Alloys

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The photoelectrochemical behavior of anodic films on Al alloys, containing titanium, tantalum, and tungsten (valve metals), has been studied as a function of alloy composition and anodizing conditions. Photocurrent spectroscopy has been used to get information on bandgap and the flatband potential values of different mixed oxides. Both insulator-like and semiconducting behavior has been observed for anodic oxides grown on Al-W and Al-Ti alloys dependent on alloy initial composition. Optical bandgap values, $E_g$, of different oxides are in accordance with predictions based on the correlation between $E_g$ and the difference of electronegativities of the oxide constituents, indicating potential for tailoring solid state properties of ternary oxides.

Anodic films on valve metals alloys are of interest for investigating mechanisms of oxide growth; different works have mainly focused their attention toward their morphology, structure, and composition to get insights on mechanism of anodic oxidation and ionic transport in “mixed oxides.” Because these films are also of interest for possible application in electronics, for instance in metal-oxide-semiconductor junctions or in dye-sensitized photoelectrochemical and solid-state solar cells, the possibility of controlled modification of the solid-state properties, such as bandgap, flatband potential, and dielectric constant, by use of “mixed oxides,” is appealing from both practical and theoretical viewpoints. This aspect becomes more important if we consider the prominent role of the solid-state properties of passive layers in controlling also the pitting behavior of metals and alloys. Notably, it has been proposed that the bandgaps of crystalline binary oxides correlate with the electronegativities of their constituents, thus suggesting the possibility to predict the bandgaps of ternary oxides using an average electronegativity parameter for the cationic group and hence, tailoring of oxide properties. The correlation can apply also to amorphous oxides if account is taken of the influence of disorder on the optical bandgap value.

In the present work, a study of the solid-state properties of anodic films on several Al alloys was carried out by using photocurrent spectroscopy (PCS) to measure their bandgap and flatband potential. The validity of the above mentioned correlation was tested to get information about its applicability and limits.

Experimental

Al-23 atom % Ti, Al-53 atom % Ti, and Al-34 atom % Ta alloys, prepared by physical vapor deposition, and Al-W alloys, containing 15, 23, and 77 atom % W, prepared by dc magnetron sputtering, were anodized either potentiodynamically, at 100 mV s−1, or galvanostatically, at 5 mA cm−2 in either 0.1/0.01 M ammonium pentaborate electrolyte or 0.01 N H2SO4 solution protected at 165° to the direction of the incident beam. Data were interpreting by the RUMP program. Anodizing, were anodized either potentiodynamically, at 100 mV s−1, or galvanostatically, at 5 mA cm−2 in either 0.1/0.01 M ammonium pentaborate electrolyte or 0.01 N H2SO4 solution protected at 165° to the direction of the incident beam. Data were collecting by the RUMP program.

The photoelectrochemical setup and PCS have been described elsewhere. Briefly, a 450 W UV-vis xenon lamp, coupled with a monochromator, irradiates the specimen through a quartz window in the anodizing cell. A two-phase, lock-in amplifier, with a mechanical chopper (chopping frequency 13 Hz), enables separation of the photocurrent from the total current. Photocurrent spectra are corrected for the relative photon efficiency of the light source at each wavelength so that the photocurrent yield in arbitrary current units is represented in the $y$ axis.

Results

Kinetic behavior.—Potentiodynamic anodizing to 8 V of Al-Ti and Al-Ta alloys in ABE revealed usual behavior for growth of barrier oxide: an initial oxidation peak (or two peaks for Al-77 atom % W and Al-23 atom % W alloys) followed by a region of constant current density (Table I), between values for the similarly anodized relevant high purity metals (21–24), as shown for the Al-53 atom % Ti alloy (Fig. 1).

Under galvanostatic conditions, the voltage rose linearly with time for anodizing the alloys to 100 V in ABE (Table II), with films growing at high efficiency, except for the Al-53 atom % Ti alloy that evolved oxygen above 20 V, as occurs with titanium and similar Al-Ti alloys. For Al-W alloys, the voltage rose more slowly in H2SO4 solution than in ABE, due to loss of Al3+ ions to solution.

From previous work, anodic films on Al-25 atom % Ti and Al-Ta alloys containing more than 32 atom % tantalum are relatively uniform amorphous oxides, based on units of alumina and the partner oxide. Furthermore, in Ref. 21 anodic films on Al-51 atom % Ti alloys are described as oxides, where the alloy components are distributed over the width virtually uniformly with a ratio Al14/Ti17 close to unity. According to Ref. 21, X-ray photoelectron spectroscopy (XPS) data show that electrochemical oxidation of the alloy components is accompanied by formation of oxides, in which the chemical bond of Ti and Al with oxygen corresponds to the TiO2 and Al2O3.

In Table III we compare the results of RBS analysis performed on anodic oxides on Al-W alloys. The composition depth profile revealed that thick anodic films grown in ammonium pentaborate electrolyte show a bilayered structure with an almost pure Al2O3.

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Table I. Current density relating to the anodizing of different Al alloys in 0.1 M ABE at 100 mV $s^{-1}$ to $U_f = 8$ V (SCE).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al-23 atom % Ti</th>
<th>Al-53 atom % Ti</th>
<th>Al-34 atom % Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>i (mA cm$^{-2}$)</td>
<td>0.30 ± 0.05</td>
<td>0.40 ± 0.05</td>
<td>0.28 ± 0.05</td>
</tr>
</tbody>
</table>
layer at the oxide/electrolyte interface, due to higher relative \textit{Al}\textsuperscript{16} migration rate with respect to \textit{W}\textsuperscript{6+}. By anodizing in 0.01 N \textit{H}\textsubscript{2}\textit{SO}\textsubscript{4}, the outer layer is absent, due to higher solubility of alumina in acidic electrolyte, with the formation of a mixed \textit{Al}-\textit{W} oxide with the same composition of the inner layer of the anodic films grown in ABE. For each investigated alloy a \textit{W} enrichment into the mixed oxide with respect to the base alloy has been revealed by RBS.

For each investigated alloy \textit{W} enrichment into the mixed oxide with respect to the base alloy has been revealed by RBS.

**Photocurrent spectra** were obtained for alloys anodized potentiodynamically to 8 V in 0.1 M ABE, with subsequent polarization at reduced voltage, \textit{U}\textsubscript{fb}, except for the \textit{Al}-15 atom \% \textit{W} alloy for which no photocurrent was detected. The example of the \textit{Al}-53 atom \% \textit{Ti} alloy at 100 mV s\textsuperscript{-1} in 0.1 M ABE at room temperature.

The external electron photoemission (from the alloy Fermi level to the electrolyte) is excluded owing to the large film thickness.

The knowledge of the bandgap and of the cathodic photoemission threshold for the \textit{Al}-\textit{Ta} mixed oxide allows to get the energetic sketch of Fig. 8, which has been derived by assuming for...
Al-34 atom % Ta a work function between those reported for Al and Ta (according to Ref. 26, 4.20 and 4.15 eV, respectively). A cathodic photocurrent tail at long wavelengths is usually observed with insulating wide bandgap oxides such as ZrO₂, Al₂O₃, and Ta₂O₅ at electrode potentials near $V_{FB}$27-29 and it has been reported also for passive Mo-79 atom % Ta.21

To get further information on the semiconducting or insulating behavior of the investigated films, photocurrent vs electrode potential curves (photocharacteristics) under monochromatic light have been recorded. By polarizing toward the cathodic direction at a scan rate, $v_{scan}$, of 10 mVs⁻¹, an inversion of the photocurrent sign was revealed for anodized Al-23 atom % Ti (Fig. 9), Al-34 atom % Ta and Al-23 atom % W alloys, thus confirming the formation of insulating oxides. The inversion potentials, which are a rough estimate of the flatband potential for insulating layers,19 are summarized in Table V. In contrast, no inversion of photocurrent sign was evidenced for anodic films on Al-53 atom % Ti and Al-77 atom % W alloys in agreement with a n-type semiconducting behavior of mixed oxides (Fig. 10), reminiscent of the behavior of TiO₂ and WO₃, respectively.

For these films a different approach has been followed to estimate their flatband potential. For the n-type oxide on Al-77 atom % W alloy, a $V_{FB} = 0.05 \pm 0.1$ V (SCE) at pH 2 is assumed (see Fig. 10), coincident with average potential of the zeroing of photocurrent in the photocharacteristics recorded at different wavelengths in 0.01 N H₂SO₄ solution, where a chemically stable film is formed. The $V_{FB}$ value could be adjusted to pH 8.5 using the relationship

$$V_{FB} = \text{const.} - 0.059 \ \text{pH}$$

usually reported to hold for oxide semiconductors.30 After correction for the solution pH, a $V_{FB} = -0.28 \pm 0.1$ V (SCE) was estimated for the mixed oxide on Al-77 atom % W in ABE solution. The presence of units of alumina in mixed oxide on both the investigated Al-W alloys shifts $V_{FB}$ toward the cathodic direction with respect to the flatband potential of a-WO₃, for which a $V_{FB} = 0.40 \pm 0.1$ V (SCE) at pH 0 is reported in Ref. 31, which becomes −0.10 V (SCE), once corrected by Eq. 3 at pH 8.5. The larger shift of $V_{FB}$ value toward cathodic potentials for film grown on lower alloyed Al-W sputtered layer is also in agreement with the theoretical expectation.

In the case of anodized Al-53 atom % Ti alloy the beginning of

![Figure 2](image.png)

**Figure 2.** (a) Photocurrent spectrum relating to an anodic film grown to 8 V (SCE) on Al-53 atom % Ti at 100 mV s⁻¹ in 0.1 M ABE and polarized in the same electrolyte at $E_g = 2$ V (SCE). (b) $I_{ph}(hv)^{1/2}$ vs $hv$ plot and (c) Urbach tail.

<table>
<thead>
<tr>
<th>Sample/atom %</th>
<th>Anodizing electrolyte</th>
<th>$E_g^{opt}$/eV</th>
<th>$\chi_M$</th>
<th>$\Delta E_{num}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-23 atom % Ti</td>
<td>0.1 M ABE</td>
<td>3.86</td>
<td>1.536</td>
<td>0.14</td>
</tr>
<tr>
<td>Al-53 atom % Ti</td>
<td>0.1 M ABE</td>
<td>3.55</td>
<td>1.583</td>
<td>0.08</td>
</tr>
<tr>
<td>Al-34 atom % Ta</td>
<td>0.1 M ABE</td>
<td>4.30</td>
<td>1.50</td>
<td>0.39</td>
</tr>
<tr>
<td>Al-15 atom % W</td>
<td>0.01 N H₂SO₄</td>
<td>—</td>
<td>1.53</td>
<td>—</td>
</tr>
<tr>
<td>Al-23 atom % W</td>
<td>0.01 N H₂SO₄</td>
<td>4.05</td>
<td>1.546</td>
<td>0.38</td>
</tr>
<tr>
<td>Al-77 atom % W</td>
<td>0.01 N H₂SO₄</td>
<td>3.68</td>
<td>1.654</td>
<td>0.57</td>
</tr>
</tbody>
</table>

![Figure 3](image.png)

**Figure 3.** Total current vs time for an anodic film grown to 8 V (SCE) on Al-23 atom % Ti at 100 mV s⁻¹ in 0.1 M ABE, in the dark (off) and under irradiation (on) at different wavelengths. Sol: 0.1 M ABE.
a cathodic process at electrode potentials more positive than $V_{FB}$ hampered to get the region of zeroing photocurrent. Thus, in this case, to estimate the flatband potential of the oxide the photocharacteristics were fitted according to a power law, $I_{ph} \propto U_{E}^{n}$ (see Fig. 11), and a $V_{FB}$ coincident with the extrapolated potential of zero photocurrent, $V^{*}$, has been assumed.\(^{19}\) The values of $n$ and $V^{*}$ obtained at each wavelength are reported in Table VI. The disclosed supralinear behavior in a large potential range (Fig. 11), as well as the dependence of $n$ on the wavelength, has been attributed to the presence of initial (geminate) recombination effects of injected photocarriers. Geminate recombination effects can occur if the thermalization length of the photogenerated electron-hole pairs is too short to prevent some recombination of photocarriers, and it is typical in amorphous material, owing to a low mobility of electron carriers in localized states near the mobility gap.\(^{19}\)

By averaging the $V^{*}$ values for different wavelengths, a $V_{FB} \approx -0.55 \pm 0.05 \text{ V (SCE)}$ has been assumed for the anodic oxide on the Al-53 atom % Ti alloys. $V_{FB}$ estimated for the anodic film on Al-53 atom % Ti alloy is more cathodic than that reported for thin anodic films on a Al-50 atom % Ti alloy,\(^{32}\) obtained by fitting the photocharacteristics in a rather limited region of electrode potentials with $n = 2$. Such a value of $n$, usually predicted for crystalline semiconductors, occurs with amorphous semiconductors with appropriate distributions of states within the gap and collection lengths.\(^{19}\) However, reliable information from photocharacteristics is best achieved from a full investigation of the dependence of $I_{ph}$ on both $U_{E}$ and $\lambda$, accounting for the possible amorphous nature of oxides. For comparison with results pertaining Al-Ti alloys, photocharacteristics relating to anodic films formed to $8 \text{ V (SCE)}$ on pure cast titanium in $0.1 \text{ M ABE}$ has been recorded. The best fitting procedure indicated $V^{*} = -0.35 \pm 0.05 \text{ V (SCE)}$ (see Table VI), thus suggesting that the presence of units of alumina in the mixed oxide causes shifts $V_{FB}$ toward the cathodic direction with respect to $V_{FB}$ of TiO$_2$. Moreover, the trend of the exponent $n$ suggests an increase in the amorphous nature of the mixed film, owing to the presence of the partner oxide.

For anodized Al-34 atom % Ta alloy the estimated $V_{fb} \approx -0.60 \text{ V (SCE)}$ (see Table V) is more positive than that reported for thin films of anodic tantalum at the same pH ($V_{FB} \approx -1.05 \text{ V (SCE)}$ from data in Ref. 27). On the other hand, for the Al/Al$_2$O$_3$ in ammonium tartrate electrolyte at pH 6.7, a zero anodic photocurrent potential of $-0.70 \text{ V (SCE)}$ has been estimated for anodic alumina film grown in such an electrolyte.\(^{33}\) Thus, by means of Eq. 3 a

Figure 4. Photocurrent spectrum relating to an anodic film grown to $8 \text{ V (SCE)}$ on Al-23 atom % Ti at $100 \text{ mV s}^{-1}$ in $0.1 \text{ M ABE}$ and polarized in the same electrolyte at $U_{E} = -1.0 \text{ V (SCE)}$. Inset: estimation of the optical bandgap by assuming nondirect optical transitions.

Figure 5. Photocurrent intensity and its phase angle vs wavelength for an anodic film grown to $8 \text{ V (SCE)}$ on Al-34 atom % Ta at $100 \text{ mV s}^{-1}$ in $0.1 \text{ M ABE}$, recorded by polarizing the electrode in $0.1 \text{ M ABE}$ at $U_{E} = -0.5 \text{ V (SCE)}$. Inset: total current in the dark and under irradiation.

Figure 6. Total current vs time for an anodic film grown to $8 \text{ V (SCE)}$ on Al-34 atom % Ta at $100 \text{ mV s}^{-1}$ in $0.1 \text{ M ABE}$, in the dark (off) and under irradiation (on) at different wavelengths at $U_{E} = -0.8 \text{ V (SCE)}$. Sol: $0.1 \text{ M ABE}$.

Figure 7. Fowler plot at $U_{E} = -1.3 \text{ V (SCE)}$ for the anodic film of Fig. 5. Sol: $0.1 \text{ M ABE}$.
flatband potential of −0.80 V/SCE can be tentatively attributed to anodic oxide film in ABE solution at pH 8.5. It comes out that the flatband potential of anodic oxide grown on Al-34 atom % Ta is more anodic than that of both pure partner oxides. The results show that $V_{FB}$ has a complex dependence on the oxide composition, which is expected by considering that $V_{FB}$ depends not only on the nature of the oxide but also on the nature (n- or p-type) and concentration of doping. Thus, it is really difficult to relate quantitatively the flatband potential to the oxide composition.

In Ref. 16, a correlation was proposed between $V_{FB}$, isoelectric point and bandgap of metal oxides. Accordingly, a more cathodic $V_{FB}$ is expected with increasing $E_g$ and pH of zero charge. Because increased presence of units of alumina increases the bandgap of mixed oxides with respect to the corresponding partner oxide, and is also

**Table V.** Photocurrent sign inversion potentials of anodic films grown to 8 V/SCE in 0.1 M ABE at 100 mV s$^{-1}$. Sol: 0.1 M ABE and $v_{scan} = 10$ mV s$^{-1}$.

<table>
<thead>
<tr>
<th>Base alloy</th>
<th>Al-23 atom % Ti</th>
<th>Al-34 atom % Ta</th>
<th>Al-23 atom % W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{inv}/$V(SCE)</td>
<td>$-0.57 \pm 0.03$</td>
<td>$-0.60 \pm 0.05$</td>
<td>$-0.37 \pm 0.03$</td>
</tr>
</tbody>
</table>

**Figure 8.** Energy scheme of metal/anodic film/electrolyte junction for anodized Al-34 atom % Ta.

**Figure 9.** $I_{ph}$ vs $U_E$ curves recorded by irradiating at different wavelengths anodic films grown to 8 V/SCE at 100 mV s$^{-1}$ in 0.1 M ABE on different Al-23 atom % Ti. Sol: 0.1 M ABE and $v_{scan} = 10$ mV s$^{-1}$.

**Figure 10.** $I_{ph}$ vs $U_E$ curves recorded by irradiating at different wavelengths an anodic film grown to 8 V/SCE at 100 mV s$^{-1}$ in 0.01 N H$_2$SO$_4$ on Al-77 atom % W. Sol: 0.01 N H$_2$SO$_4$ and $v_{scan} = 10$ mV s$^{-1}$.

**Figure 11.** $(I_{ph})^p$ vs $U_E$ for an anodic film grown to 8 V(SCE) on Al-53 atom % Ti at 100 mV s$^{-1}$ in 0.1 M ABE. Sol: 0.1 M ABE and $v_{scan} = 10$ mV s$^{-1}$.
expected to increase the pH$pzc$; the estimated $V_{FBR}$ for Al-Ti, Al-W alloys follow the proposed trend, while the estimated $V_{FBR}$ for anodized Al-34 atom % Ta alloys does not show the predicted dependence.

**Photocurrent spikes occur for thicker films as formation voltage of 100 V.** For both anodized Al-Ti alloys, anodic the same Fowler threshold. The current-voltage response at film grown at 100 mV s$^{-1}$ to 90 V. Nevertheless, the effect of increasing formation voltage, reaching a value of 3.34 eV for anodizing voltage equal to 100 V in H$_2$SO$_4$ solution. Analogously to thin film the thicker oxide film on Al-23 atom % W and Al-77 atom % W alloys behave like insulators and n-type semiconductors, respectively.

**Discussion**

The experimental findings suggest that anodizing of aluminum-valve metal alloys produces insulating or semiconducting oxides, depending on the nature and relative amounts of the alloy constituents. Amorphous anodic oxides on electropolished aluminum are insulating with a wide ($E_g \approx 6.3$ eV) bandgap, while thin hydroxide layers having lower bandgap ($E_g \approx 3.0$ eV) can also be formed on mechanically treated Al surface. Anodic films on Al-23 atom % Ti, Al-23 atom % W, and Al-34 atom % Ta alloys are insulators, while anodic films on the more highly alloyed Al-53 atom % Ti and Al-77 atom % W alloys are n-type semiconductors, correlating with the n-type nature of TiO$_2$ and WO$_3$, having bandgaps of 3.2 eV$^{24}$ and 2.7 eV$^{35}$, respectively.

Previous work$^{35}$ proposed that the optical bandgaps of crystalline oxides, M$_2$O$_3$, are proportional to the square of the electronegativity difference of their constituents, based on the assumption of a direct relation between the bandgap and the single M-O bond energy, obtained from the Pauling equation for the single bond energy.

The following fitting equations have been suggested to apply$^{16-20}$ to amorphous sp and d metal oxides, respectively, with few exceptions:

\[ E_{opt}^{sp} - \Delta E_{eV}(eV) = 2.17(\chi_M - \chi_O)^2 - 2.71 \]  
\[ E_{opt}^{d} - \Delta E_{eV}(eV) = 1.35(\chi_M - \chi_O)^2 - 1.49 \]

The rare earth metal oxides seem to follow the d-metal oxide correlation.$^{20}$ $\chi_M$ and $\chi_O$ are the electronegativities of metal and oxygen, respectively, and $\Delta E_{eV}$ is a parameter which takes into account the influence of amorphous nature on the bandgap of the oxides. $E_{opt}$ is the mobility gap in amorphous oxide according to Fig. 12. The term $\Delta E_E$ and $\Delta E_{eV}$ are a measure of the extent of localization of electronic states near the conduction and valence band mobility edges, respectively. A value of 0.20 eV has been suggested as typical for $\Delta E_E$ and $\Delta E_{eV}$, owing to lattice disorder in otherwise stoichiometric crystal. According to Fig. 12, $\Delta E_{eV} = 0$ for crystalline oxides, when $E_{opt} = E_{FBR}$, while increasing values are expected (up to $-0.5$ eV) if the lattice disorder affects both the mobility edges in a similar manner.

For mixed oxides $\text{A}_x\text{B}_{1-x}\text{O}_3$, it has been suggested that the previous correlation is still valid provided that the average single bond energy is estimated taking into account the contributions of both, $A$ and $B$, cations of the oxide through an average cationic electronegativity parameter, $\chi_M$, given by

### Table VI. Exponent $n$ and extrapolated zero photocurrent potential, $V^*$, obtained for anodic films on Ti and Al-53 atom % Ti grown to 8 V (SCE) in 0.1 M ABE at 100 mV s$^{-1}$. Sol: 0.1 M ABE and $v_{max} = 10$ mV s$^{-1}$.

<table>
<thead>
<tr>
<th>Base alloy</th>
<th>$\lambda$ / nm</th>
<th>$n$</th>
<th>$V^*/$V(SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>230</td>
<td>1.35</td>
<td>-0.38</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>1.125</td>
<td>-0.35</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.95</td>
<td>-0.31</td>
</tr>
<tr>
<td>Al-53 atom % Ti</td>
<td>230</td>
<td>0.95</td>
<td>-0.63</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>0.90</td>
<td>-0.62</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>0.80</td>
<td>-0.59</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>0.70</td>
<td>-0.61</td>
</tr>
</tbody>
</table>

### Table VII. Bandgap and Fowler thresholds of oxide films grown on Al-34 atom % Ta alloys. Polarizing electrolyte: 0.1 M ABE.

<table>
<thead>
<tr>
<th>Formation voltage</th>
<th>Growth conditions</th>
<th>$E_{opt}$/eV</th>
<th>$E_{FBR}$/eV</th>
<th>$E_{FB}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air formed film</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8 V (SCE)</td>
<td>100 mV s$^{-1}$</td>
<td>4.35</td>
<td>1.45</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>in 0.1 M ABE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 V</td>
<td>100 mV s$^{-1}$</td>
<td>4.25</td>
<td>1.55</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>in 0.1 M ABE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 V</td>
<td>100 mV s$^{-1}$</td>
<td>4.15</td>
<td>1.64</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>in 0.1 M ABE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>—</td>
<td>Thermal treatment</td>
<td>3.96</td>
<td>1.56</td>
<td>1.59</td>
</tr>
<tr>
<td>(3.5 h at T = 600°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table VIII. Bandgap values of anodic oxide grown on Al-53 atom % Ti as a function of the anodizing conditions. Polarizing electrolyte: 0.1 M ABE.

<table>
<thead>
<tr>
<th>Formation voltage</th>
<th>Anodizing conditions</th>
<th>$E_{opt}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 V (SCE)</td>
<td>100 mV s$^{-1}$ in 0.1 M ABE</td>
<td>3.55</td>
</tr>
<tr>
<td>15 V</td>
<td>100 mV s$^{-1}$ in 0.1 M ABE</td>
<td>3.54</td>
</tr>
<tr>
<td>40 V</td>
<td>100 mV s$^{-1}$ in 0.1 M ABE</td>
<td>3.48</td>
</tr>
<tr>
<td>80 V</td>
<td>100 mV s$^{-1}$ in 0.1 M ABE</td>
<td>3.38</td>
</tr>
<tr>
<td>100 V</td>
<td>5mA cm$^{-2}$ in 0.01 M ABE</td>
<td>3.25</td>
</tr>
</tbody>
</table>

Similar to thinner films photocurrents were absent for thicker films formed up to 50 V in either ABE or H$_2$SO$_4$ for anodized Al-15 atom % W alloy. For the Al-23 atom % W alloy, $E_{opt}$ values of 4.0 ± 0.05 eV were determined for films formed to $V_{FBR} \leq 60$ V in H$_2$SO$_4$ solution and to 100 V in ABE, with higher $E_{opt}$ values pertaining to the thinner film.

For the Al-77 atom % W alloy, $E_{opt}$ decreases with increasing formation voltage, reaching a value of 3.34 eV for anodizing voltage equal to 100 V in H$_2$SO$_4$ solution. Analogously to thin film the thicker oxide film on Al-23 atom % W and Al-77 atom % W alloys.

The experimental findings suggest that anodizing of aluminum-valve metal alloys produces insulating or semiconducting oxides, depending on the nature and relative amounts of the alloy constituents. Amorphous anodic oxides on electropolished aluminum are insulating with a wide ($E_g \approx 6.3$ eV) bandgap, while thin hydroxide layers having lower bandgap ($E_g \approx 3.0$ eV) can also be formed on mechanically treated Al surface. Anodic films on Al-23 atom % Ti, Al-23 atom % W, and Al-34 atom % Ta alloys are insulators, while anodic films on the more highly alloyed Al-53 atom % Ti and Al-77 atom % W alloys are n-type semiconductors, correlating with the n-type nature of TiO$_2$ and WO$_3$, having bandgaps of 3.2 eV$^{24}$ and 2.7 eV$^{35}$, respectively.

The rare earth metal oxides seem to follow the d-metal oxide correlation.$^{20}$ $\chi_M$ and $\chi_O$ are the electronegativities of metal and oxygen, respectively, and $\Delta E_{eV}$ is a parameter which takes into account the influence of amorphous nature on the bandgap of the oxides. $E_{opt}$ is the mobility gap in amorphous oxide according to Fig. 12. The term $\Delta E_E$ and $\Delta E_{eV}$ are a measure of the extent of localization of electronic states near the conduction and valence band mobility edges, respectively. A value of 0.20 eV has been suggested as typical for $\Delta E_E$ and $\Delta E_{eV}$, owing to lattice disorder in otherwise stoichiometric crystal. According to Fig. 12, $\Delta E_{eV} = 0$ for crystalline oxides, when $E_{opt} = E_{FBR}$, while increasing values are expected (up to $-0.5$ eV) if the lattice disorder affects both the mobility edges in a similar manner.

For mixed oxides $\text{A}_x\text{B}_{1-x}\text{O}_3$, it has been suggested that the previous correlation is still valid provided that the average single bond energy is estimated taking into account the contributions of both, $A$ and $B$, cations of the oxide through an average cationic electronegativity parameter, $\chi_M$, given by
With increased formation voltage, $E_{\text{opt}}^{\text{th}}$ for the Al-Ta mixed oxide decreases which, according to Eq. 5 and 6, can only be related to a reduced $\Delta E_{\text{am}}$, as the Pauling electronegativities of aluminum and tantalum are equal. 27 This suggestion is further supported by a low $E_{\text{opt}}^{\text{th}}$ of the thermal oxide on the Al-34 atom % Ta alloy (Table VII), which is very near to that calculated from Eq. 5 for crystalline $\text{Ta}_2\text{O}_5$. 29 A further support to this suggestion comes from the dependence of the Fowler’s threshold value on the film thickness. As reported in Table VII a steadily increasing $E_{\text{opt}}$ with increasing film thickness was measured at constant cathodic polarizing voltage. This increase is compatible with the effect of lowering of Schottky barrier, $\Delta \phi_B$, at the metal/oxide interface, due to the image force, which is dependent on the electric field, $E$, according to 33

$$\Delta \phi_B = \phi(E = 0) - \phi(E) = 3.84 \times 10^{-4} \sqrt{\frac{E}{E_{\text{opt}}}}$$

where $\Delta \phi_B$ is in eV and $E$ is in V cm$^{-1}$. $e_{\text{opt}}$ is the dielectric constant at high frequency, assumed equal to the squared refractive index, $n_{\text{am}}^2$. The electric field can be estimated as a function of the anodizing ratio, $A$, and formation voltage, $U_f$, as

$$E = \frac{U_f - V_{\text{th}}}{A \phi}$$

By assuming $n_{\text{am}} = 1.70$ 27 and for the mixed oxide an anodizing ratio of $A = 14$ Å V$^{-1}$, averaged between those reported for pure alumina and tantalum, 25 we estimated the zero field Fowler thresholds at different thickness reported in Table VII for electron photoemission from the alloy Fermi level to the conduction band mobility edge of mixed oxide. After correction, we still observed a difference of about 0.1 eV in the cathodic photoemission threshold values, at different thickness, which could be attributed to the lack of a sharp mobility edge typical of amorphous material.

On the other hand, note that the difference in $E_{\text{opt}}^{\text{th}}$ values of 80 V anodic film and corresponding thermal oxide is still about twice the difference in photoemission threshold. This finding agrees with $\Delta E_{\text{am}} = \Delta E_C + \Delta E_V$ and $\Delta E_C \approx \Delta E_V \approx 0.1$ eV, as sketched in Fig. 12. The decrease of $E_{\text{opt}}^{\text{th}}$ with increasing thickness agrees with the hypothesis that anodic thicker films display a reduction in the extent of localized DOS near the mobility edges. This is also confirmed by the dependence of the photocurrent from energy in the Urbach region, i.e., for energy lower than the optical bandgap of the films, where the photocurrent can be generated by absorption involving one or both the band tails. In this region the dependence of light absorption coefficient, $\alpha$, follows

$$\alpha = \alpha_0 e^{\frac{\hbar \omega}{E_{\text{opt}} - \hbar \omega}}$$

where $\alpha_0$, the Urbach mobility gap, marks the end of linearity in the ln $\alpha$ vs $\hbar \omega$ plot and $E_{\text{opt}}$ is a measure of the width of band tails, i.e., the extent of DOS localization near the mobility edge. $E_I$, ranging between 0.094 and 0.055 eV were obtained for thin (8 V SCE) and thick (80 V) film on Al-34 atom % Ta, respectively, thus suggesting larger tails for thinner film.

It comes out that the tendency of anodic $\text{Ta}_2\text{O}_5$ to become more ordered with increasing anodizing voltage, although still present in mixed oxide, is strongly counteracted by the amorphous nature of aluminum oxide. In fact $E_{\text{opt}}^{\text{th}}$ values of mixed oxide appreciably larger (>$0.2$ eV) than that measured for pure anodic oxide on Ta metal 27 agrees with the suggested amorphizing influence of aluminum oxide. Moreover by comparing the bandgap value of thermal $\text{Ta}_2\text{O}_5$ with the $E_{\text{opt}}^{\text{th}}$ values in Table VII we suggest that amorphous mixed oxide is formed at any thickness during anodic oxidation of Al-34 atom % Ta alloy while a quasi-crystalline mixed oxide is formed by thermal oxidation in analogy with similar finding on pure Ta metal. 29

As for the estimate of flatband potential, it seems evident that the inversion photocurrent potential is more anodic than any expected value if we consider that both $\text{Ta}_2\text{O}_5$ and $\text{Al}_2\text{O}_3$ display more ca-

$$\Delta E_{\text{am}} = \Delta E_C + \Delta E_V$$

where $\Delta E_{\text{am}}$ has been estimated assuming an Al-partner metal ratio equal to that of the base alloy. Nevertheless, the composition of films on valve metal alloys depends on the relative migration rates of the cation species of the oxides as well as on the stability of surface layer in the different electrolyte used in the formation process. For Al-23 atom % Ti, Al-53 atom % Ti, and Al-34 atom % Ta alloys, similarity of rates and good stability of surface layer in ABE solution result in uniform oxides with cation fractions approximating to the alloy composition, allowing a direct estimation of $E_{\text{opt}}^{\text{th}}$ from Eq. 5 and 6. For such oxides formed to 8 V (SCE), the calculated $\Delta E_{\text{am}}$ values (see Table IV) agree with the theoretical expectations. 36 The larger value measured for the Al-Ta alloy is unsurprising, as amorphous alumina and tantalum films form under the current growth conditions, while partially crystalline oxides occur for titanium. 38
thodic $V_{FB}$ values than the inversion photocurrent potential of the mixed oxide. A rationale for this discrepancy could be traced to the fact that under illumination a surface trapping of photogenerated hole could occur in localized states near the valence band mobility edge with a consequent shift of the bandedges. Such a finding, previously observed on other amorphous anodic oxides (NbO$_x$ and TiO$_2$), deserves further investigation to get reliable information on $V_{FB}$ of anodized Al-34 atom % Ta.

Increased film thickness has the same effect for the Al-23 atom % Ti alloy, with respective $E_{g}^{opt}$ values of 3.86 and 3.75 eV for thin and thick films formed at 100 mV s$^{-1}$. The increased thickness increases the crystallinity of the oxide as confirmed by the higher bandgap value (3.85 eV) measured for thick ($V_0 = 90$ V) films formed at higher growth rate (1.9 V s$^{-1}$). The value of $\Delta E_{am}$ for thin film is comprised between 0.11 eV and 0.16 eV depending on the value of electronegativity parameter we choose for titanium ($\chi_{Ti} = 1.676$ for rutile, $\chi_{Ti} = 1.636$ for anatase). This value is lower than the previous one and is in agreement with the tendency of TiO$_2$ film to crystallize during the anodizing process since low voltages and more easily as lower the growth rate is.$^{15}$

For the Al-53 atom % Ti alloy, $E_{g}^{opt}$ decreases with increase of forming voltage (Table VIII). In this case a decrease in $\Delta E_{am}$ cannot explain the photocurrent spectra behavior of the films, since $\Delta E_{am} \leq 0$ is required to fit results using Eq. 5 and 6, as the formation voltage increases. In this case, lower $E_{g}^{opt}$ values can arise from the formation of anodic films enriched in Ti in respect to the base alloy, more pronounced as the formation voltage increases with the formation of titania outer layer, with $E_{g}^{opt}$ of 3.25 eV, at high voltages. The presence of an almost pure TiO$_2$ outer layer on anodized Al-74 atom % Ti has been reported in Ref. 22 due to a faster migration rate of Ti$^{4+}$ with respect to Al$^{3+}$.

For the Al-W alloys, RBS indicates an outer alumina layer forms during the anodizing in ABE, but not in H$_2$SO$_4$ solution of low pH. Using RBS data compositions (Table III) together with Eq. 5 and 6, for thick films $\Delta E_{am}$ values of 0.38 and 0.30 eV were obtained for mixed oxides with tungsten fractions of 0.29 and 0.86, respectively, in agreement with theoretical expectation and higher than those estimated for other thick mixed oxides. Such finding agrees with the above mentioned suggestion based on the tendency to crystallize of each partner, the scarce tendency to crystallize of anodic WO$_3$ and Al$_2$O$_3$ being well known.

Finally, the mechanism of growth of mixed film and the relative mobility of different cations as a function of metal-oxygen bond$^{41}$ can help to explain the differences in $E_{g}^{opt}$ values measured for thin and thick films on such alloys. In fact, the measured $E_{g}^{opt}$ of thin film formed on Al-77 atom % W is noticeably higher than the theoretical one ($E_{g}^{opt} = 3.11$ eV) estimated by assuming the same cationic ratio in the alloy and into the film. According to this, a $\Delta E_{am} = 0.57$ eV, larger than the theoretical expectation as well as that of thick film, is obtained. It seems reasonable to assume that, in the thin film range, when the anodizing process is still far from reaching the steady-state condition, the tungsten enrichment of inner mixed oxide, with respect to the base alloy, occurs at expenses of an alumina enrichment of the outer layer due to faster (than W$^{6+}$ ions) Al$^{3+}$ migrating ions. According to this interpretative hypothesis higher $E_{g}^{opt}$ value for thin film could be attributed to an excess of aluminium ions in outer mixed layer with respect to the thicker film formed at longer anodizing times. The decrease of $E_{g}^{opt}$ with increasing polarization time further confirms this hypothesis.

Finally, we want to stress that the experimental bandgap values of the investigated Al-mixed oxides confirm that the correlation proposed for d metal oxides also holds for mixed oxides containing both sp and d metals. The absence of a photoeffect for the anodized Al-15 atom % W alloy may be explained by the lower d metal content into the film, with its bandgap value then following Eq. 4. In this case, the predicted $E_{g}^{opt}$ value ($\approx 5.60$ eV) is above the accessible range of our experimental setup. If this interpretation is confirmed it could be inferred that a percolation threshold is necessary for using the d-metal correlation in mixed sp-d-metals oxides. Further investigation seems necessary to highlight such aspects.

**Conclusions**

“Mixed oxides” are formed on valve metal alloys with optical bandgap, the flatband potential and semiconductor or insulator behavior depending on the nature and relative amount of the partner oxides in the film. Thus, their solid-state properties can be controlled within a reasonably large range of values by a selection of the alloy and the anodizing process. The reported semiconducting behavior of mixed oxide grown on Al-Ti, W alloys richer in d-metal cation is appealing for tailoring transparent semiconducting oxides recently proposed in microelectronics applications.$^{42}$

The measured bandgaps agree well with the proposed correlation with the electronegativities of the oxides constituents. Moreover, it is confirmed that the correlation proposed for d-metal oxides applies also to “mixed oxides” containing both sp and d metals provided that a minimum d metal content ($\approx 25$ atom %) is present in the mixed oxide.

Concerning the $V_{FB}$ estimate of mixed oxides, this study suggests that photocurrent spectroscopy, if correctly used, offers some advantages over Mott-Schottky plots for estimation of flatband potentials. In fact, for insulating materials (crystalline or amorphous) Mott-Schottky analysis is not accessible while for anodic films on valve metals, usually behaving as amorphous semiconductors, the frequently reported Mott-Schottky plots display a strong frequency dependence which hampers a reliable determination of flatband potential value.$^{43}$

The Università di Palermo assisted in meeting the publication costs of this article.

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