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<th>Instructions for use</th>
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<td>Author(s)</td>
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<tr>
<td>Citation</td>
<td>Journal of the Electrochemical Society, 159(1), C33-C39</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2012</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/48149">http://hdl.handle.net/2115/48149</a></td>
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<td>File Information</td>
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Characterization of the Solid State Properties of Anodic Oxides on Magnetron Sputtered Ta, Nb and Ta-Nb Alloys

F. Di Franco, G. Zampardi, M. Santamaria, F. Di Quarto, and H. Habazaki

Abstract

Tantalum oxide, niobium oxide and Ta-Nb containing mixed oxides were grown by anodizing sputter-deposited Ta, Nb and Ta-Nb alloys of different compositions. A photoelectrochemical investigation was performed in order to estimate the band gap and the flat band potential of the oxides as a function of their composition. The band gap of the investigated Ta-Nb containing mixed oxides changed monotonically between those estimated for Ta₂O₅ (4.1 eV) and Nb₂O₅ (3.4 eV) and in agreement with a proposed correlation between the Band gap of an oxide and the difference of electronegativity of the oxide constituents. From the differential capacitance curves recorded in a wide range of electrode potential and for several frequencies of the alternative signal, the dielectric constant of the investigated oxides were estimated.

Microelectronics is very important for almost all kinds of technology evolutions in the past four decades. In this area, the dielectrics science occupies a prominent place in providing the dominant technology in integrated capacitors or gate insulators. In the last years the main challenge has been to scale down the insulating oxide thickness keeping low values of the leakage current. This task has been partially achieved for metal-oxide-semiconductor field effect transistor thanks to the use of hafnium based dielectrics, while less has been done for dynamic random access memory and metal-insulator-metal capacitors (DRAM MIMCAP). To the last generation DRAM, very low (from 0.5 to 0.35 nm) equivalent thickness is required with the constraint to maintain a very low leakage current. This implies the use of material having high dielectric constant (~50) and high band gap (>4 eV), which can be obtained by post formation thermal treatment and tuning of the oxide composition. Owing to their high value of dielectric constant, Ta₂O₅ and Nb₂O₅ are quite attractive oxides for the development of the next generation of DRAM. Tantalum oxide is a wide band gap (~4 eV) material with a high dielectric constant (ε = 27 ~ 30) if properly crystallized (T > 750°C). Niobium oxide has a higher dielectric constant (ε = 53) with respect to Ta₂O₅ but a lower band gap (~3.3 eV). In recent papers, it has been shown that the addition of small amount of Nb in tantalum based oxide decreases the crystallization temperature with small effect on the band gap value of the material. Thus, (Nb₁₋ₓTaₓ)₂O₅ have been introduced in the International Technology Roadmap for Semiconductors (ITRS).

Experimetal

Ta, Nb and Ta–Nb alloy films were prepared by dc magnetron sputtering. Targets consisted of a 99.9% niobium disk, of 100 mm diameter, with an appropriate number of 99.9% tantalum disks, of 20 mm diameter, located symmetrically on the erosion region for preparation of the alloys. Substrates were glass plates. Thickness of metallic layer was 300 nm. In order to obtain alloy films of uniform thickness and composition, the substrate holders were rotated around the central axis of the chamber, as well as about their own axes, during sputter deposition. As reported in ref. 8, tantalum and Ta-Nb alloys containing up to 22 at.% niobium comprised the β-Ta phase, with a tetragonal structure. Further increase in the niobium content resulted in the formation of a body centered cubic phase. All the alloys appear to be mainly single-phase solid solutions, whose compositions were determined by Rutherford backscattering spectroscopy.

Anodizing was undertaken in 0.1 M sodium hydroxide (NaOH) at 298 K potentiodynamically at 10 mV s⁻¹. Sodium hydroxide was chosen to avoid incorporation of species from the anodizing bath that can influence the solid state properties of the anodic films.

A saturated silver/silver chloride electrode (0 V vs Ag/AgCl = 0.197 V vs SHE) was employed as reference electrode for all the electrochemical and photoelectrochemical experiments. The experimental set-up employed for the photoelectrochemical investigations is described elsewhere; it consists of a 450W UV–VIS xenon lamp coupled with a monochromator (Kratos), which allows monochromatic irradiation of the specimen surface through the electrochemical cell quartz windows. A two-phase lock-in amplifier (EG&G) was used in connection with a mechanical chopper (frequency: 13 Hz) in order to separate the photocurrent from the total current circulating in the cell due to the potentiostatic control. Photocurrent spectra reported below are corrected for the relative photon flux of the light source at each wavelength, so that the photocurrent yield in arbitrary current units is represented in the Y axis. All the experiments were performed in air at room temperature.

Differential capacitance curves were recorded in 0.5 M H₂SO₄ solution by using a Parstat 2263 (PAR), connected to a computer for the data acquisition. For all the experiments, a Pt net having a very high surface area was used as counter electrode and a silver/silver chloride electrode was employed as reference electrode.

Results and Discussion

Anodic film growth.— Anodic films were grown to 5 V at 10 mV s⁻¹ on all investigated materials. In Fig. 1 we report the growth curves relating to the anodizing of Ta, Nb and Ta-66at.%Nb. As typical of valve metals, after an abrupt increase, the current density reaches an almost constant value, which is a function of the metallic
substrate composition. The current density is sustained by the oxidation of metals, according to the following half cell reaction:

\[
2\text{Me} + 5\text{H}_2\text{O} \rightarrow \text{Me}_2\text{O}_5 + 10\text{H}^+ + 10\text{e}^-
\]

where Me is Ta or Nb or one of the investigated alloys. According to Faraday’s law in the case of high field growth of anodic films, it is possible to relate the electric field strength, \(E_d\), to the growth rate, \(dV/dt\), according to eq.:

\[
\frac{dV}{dt} = \eta \frac{iE_d M}{2F\rho}
\]

in which \(i\) is the measured current density, \(M\) is the molecular weight of the growing oxide, \(z\) the number of electrons circulating per mole of formed oxide (i.e. 10), \(F\) the Faraday constant, \(\rho\) the film density and \(\eta\) the growth efficiency.

\[
\eta = \frac{i_{\text{form}}}{i_{\text{tot}}} = \frac{i_{\text{form}}}{i_{\text{form}} + i_{\text{diss}} + i_{\text{el}}}
\]

where \(i_{\text{form}}\) is the current density effectively employed for the film formation, \(i_{\text{diss}}\) is the current density fraction due to dissolution phenomena, expected to be negligible for all the investigated samples according to the Pourbaix diagrams relating to Ta and Nb, and \(i_{\text{el}}\) is the electronic current which is negligible due the blocking character of the oxides, as confirmed by the very low current circulating during the reverse scan.

In Table I we report the electric field strengths and the anodizing ratios, \(\tilde{A}\), (i.e. the reciprocal of \(E_d\)) calculated by eq. 1 from the current density measured during the forward scan. We have assumed for the mixed oxides a density and a molecular weight obtained by averaging according to the alloy composition the corresponding data pertaining to pure Nb\(_2\)O\(_5\) and Ta\(_2\)O\(_5\). Rutherford back scattering analysis revealed that the oxide composition is almost coincident with the base alloy composition due to comparable migration rate of Nb\(^{5+}\) and Ta\(^{5+}\) during the anodizing process. It is interesting to mention that the \(E_d\) (and thus \(\tilde{A}\)) values estimated for mixed oxides changes monotonically as a function of the base alloy composition. In Table I we also report the oxides’ thickness for all the investigated anodized alloys, estimated from the measured total circulated charge during the anodizing process, according to the integrated version of eq. 1. The films become thicker with increasing the Nb content and their value compares well with those reported in ref. 8, estimated for thicker anodic films by the direct observation of the transmission electron micrographs of their ultramicrotomed cross section, taking into account the different formation voltage and the higher formation rate.8

**Photoelectrochemical study**— In Fig. 2 we report the photocurrent spectra (photocurrent vs irradiating wavelength curves at constant potential) recorded by polarizing the anodic films grown on all the investigated alloys at 2 V in 0.5 M H\(_2\)SO\(_4\). By recording the total current circulating in the dark and under irradiation, we verified that the photocurrent was anodic at all the investigated wavelengths, as shown in Fig. 3 for anodic films grown on Ta-66at.%Nb alloys. For photon energy in the vicinity of the band gap the following equation holds:

\[
(I_{\text{ph}}h\nu)^n \propto (h\nu - E_{\text{opt}}^g)^3
\]

### Table I. Kinetic parameters estimated for the anodizing of Ta, Nb and Ta-Nb alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(E_d/\text{MV cm}^{-1})</th>
<th>(\tilde{A}/\text{Å V}^{-1})</th>
<th>Oxide thickness/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>4.8</td>
<td>21</td>
<td>114</td>
</tr>
<tr>
<td>Ta-10at.%Nb</td>
<td>4.30</td>
<td>23</td>
<td>121</td>
</tr>
<tr>
<td>Ta-19at.%Nb</td>
<td>4.2</td>
<td>24</td>
<td>130</td>
</tr>
<tr>
<td>Ta-39at.%Nb</td>
<td>4.0</td>
<td>25</td>
<td>134</td>
</tr>
<tr>
<td>Ta-66at.%Nb</td>
<td>3.8</td>
<td>26</td>
<td>140</td>
</tr>
<tr>
<td>Ta-85at.%Nb</td>
<td>3.4</td>
<td>29</td>
<td>163</td>
</tr>
<tr>
<td>Nb</td>
<td>3.2</td>
<td>31</td>
<td>185</td>
</tr>
</tbody>
</table>

**Figure 1.** Current density vs potential curves recorded during the potentiodynamic anodizing of Ta, Nb and Ta-66at.%Nb at 10 mV s\(^{-1}\) in 0.1 M NaOH.

**Figure 2.** Raw photocurrent spectra relating to anodic films grown on all investigated alloys to 5 V, recorded by polarizing the electrodes at 2 V in 0.5 M H\(_2\)SO\(_4\).

**Figure 3.** Total current circulating in the dark (off) and under irradiation (on) for anodic films grown on Ta-66at.%Nb, recorded by polarizing the electrode at \(U_E = 2\) V and \(\lambda = 270\) nm in 0.5 M H\(_2\)SO\(_4\).
where I_ph is the photocurrent yield, assumed proportional to the light absorption coefficient, hν is the photon energy, \( E_{opt}^{\text{diff}} \) the optical band gap and the exponent n is 0.5 for indirect (non direct for amorphous materials) optical transitions.\(^{11}\) As shown in Fig. 4 for the anodic film grown on Ta-66at.%Nb, from the photocurrent spectra corrected for the efficiency of the lamp–monochromator system,\(^9\) according to eq. 3 we can estimate the optical band gap of the investigated oxides by extrapolating to zero the \( I_{ph}(hν)^{0.5} \) vs hν plot. In Fig. 5 we report the \( E_{opt}^{\text{diff}} \) values estimated with the same procedure for all the investigated oxides. These data clearly show that the band gap value monotonically changes between those estimated for the corresponding pure oxides. This finding suggests that it is possible to tailor the band gap of an oxide by properly selecting the composition of the base alloy to be anodized.

Previous work\(^{12}\) proposed that the optical band gaps of crystalline oxides, \( M_{x}O_{y} \), are proportional to the square of the electronegativity difference of their constituents, \( (\chi_{M} - \chi_{O})^2 \), based on the assumption of a direct relation between the band gap and the single M-O bond energy, obtained from the Pauling equation for the single bond energy.

The following equation has been suggested to apply\(^{13, 14}\) to amorphous d metal oxides:

\[
E_{g}^{\text{opt}} - \Delta E_{\text{am}}(eV) = 1.35(\chi_{M} - \chi_{O})^2 - 1.49
\]  

[4]

\( \Delta E_{\text{am}} = 0 \) for crystalline oxides, when \( E_{g}^{\text{opt}} = E_{g} \), whilst increasing values are expected (up to around 0.5 eV) if the lattice disorder affects both density of states distribution (DOS) near the valence and conduction band edges.\(^{11}\)

For d-metal mixed oxides \( A_{x}B_{y}O_{z} \), 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 trough an average cationic electronegativity parameter, \( \chi_{M} \), given by:

\[
\chi_{M} = x_{A}\chi_{A} + x_{B}\chi_{B}
\]  

[5]

where A and B are the metals of the oxide, and \( x_{A, B} \) their cationic fractions.

In order to use eqs. 4 and 5 to fit the experimental band gap values of the investigated Ta-Nb mixed oxides, we assume \( x_{Ta} = 1.50 \pm 0.05 \) and \( x_{Nb} = 1.60 \pm 0.05 \), which are in the range of uncertainty accepted by Pauling.\(^{15}\) As Fig. 5 shows \( E_{g}^{\text{opt}} \) differs from the values calculated by means of eqs. 4 and 5, of a quantity which is less than 0.15 eV and in the range foreseen by the taking into account the amorphous nature of the investigated layers.

The good agreement between the experimental \( E_{g} \) values of Ta-Nb mixed oxides and those predicted by eq. 4 is a further evidence of the validity of the correlation between the electronegativity of the oxides’ constituents and their band gap. This correlation is a powerful tool for the prediction of the band gap of a material starting from the knowledge of its composition. This statement becomes more convincing if we consider the large approximation provided by Density Functional Theory based methods for \( E_{g} \) estimation. This is the case of the band gap value calculated in ref. 16 in the Low Density Approximation for TaNbO\(_{x}\) (\( E_{g} \approx 1.82 \) eV), that the authors report to be underestimated and that appears really far from the expected value according to the experimental results of Fig. 5.

For a possible technological application, it is very important that the band gap of the mixed oxides are between those calculated for Ta\(_{2}\)O\(_{5}\) and Nb\(_{2}\)O\(_{5}\), if we consider that oxides with the band gaps over 3–4 eV meet the specifications defined by ITRS. However, the band offset with the metal electrode is also a critical factor that may define the leakage current. Therefore, the knowledge of the energetics of the metal/oxide interface is crucial.

Photocurrent vs electrode potential curves under constant irradiating wavelength (photocharacteristics) were recorded for all the investigated oxides, by scanning the polarizing voltage toward the cathodic direction at 10 mV s\(^{-1}\). As typical of n-type semiconducting materials, the photocurrent decreases by decreasing the polarizing voltage, i.e. the electric field strength across the film. Due the very low thickness of the investigated films, the contribution to the measured photocurrent coming from the field free region is negligible. The zero photocurrent potential, \( V_{on} \), which can be assumed as a rough estimate of the flat band potential, changes sensitively on going from Nb\(_{2}\)O\(_{5}\) (\( V_{on} = -0.25 \) V) to Ta\(_{2}\)O\(_{5}\) (\( V_{on} = -1.0 \) V).

In Fig. 6 we report the \( I_{ph} \) vs polarizing voltage curves relating to 5 V anodic films grown on Ta, Ta-10at.%Nb and Ta-19at.%Nb. It is interesting to stress that the addition of a small amount of Nb shifts sensitively the zero photocurrent potential toward more anodic values with respect to Ta\(_{2}\)O\(_{5}\). Owing to the amorphous nature of all the investigated anodic films, we expect an influence of the irradiating photon energy as well as of the electric field strength on the photocurrent. The lack of the long range order for the amorphous oxides is responsible of a reduced mobility of the generated photocarriers, which do not cover during their thermalization time a distance long enough to prevent their recombination. Thus, for amorphous oxides it is not possible to assume as unit the efficiency of free carriers generation even for photon energies higher than the band gap of the material (geminate

**Figure 4.** Photocurrent spectrum relating to anodic film grown on Ta-66at.%Nb to 5 V, recorded by polarizing the electrode at 2 V in 0.5 M H\(_{2}\)SO\(_{4}\). Inset: band gap estimate by assuming non direct optical transitions.

**Figure 5.** Experimental band gap values for Ta and Nb containing mixed oxides as a function of the Nb atomic fraction, \( x_{Nb} \). Continuous line represents the theoretical prediction for amorphous oxides according to eqs 4 and 5 with \( \Delta E_{\text{am}} = 0.15 \) eV.
Figure 6. Photocurrent vs potential curves relating to 5 V anodic films grown on Ta, Ta-10at.%Nb and Ta-19at.%Nb. Irradiating wavelength 240 nm, solution: 0.5 M H₂SO₄ and potential scan rate 10 mV s⁻¹.

Figure 7. Photocurrent vs potential curve relating to 5 V anodic films grown on Nb. Irradiating wavelength 340 nm, solution: 0.5 M H₂SO₄ and potential scan rate 10 mV s⁻¹.

Table II. Parameters obtained by fitting according to power law, (I_{ph})ⁿ ∝ (U_E - V*) (see eq. 6) the experimental photocharacteristics recorded for anodic films grown to 5 V at 10 mV s⁻¹ on Ta and Ta-Nb alloys in 0.5 M H₂SO₄.

<table>
<thead>
<tr>
<th>Metallic substrate</th>
<th>Wavelength/nm</th>
<th>n</th>
<th>V* (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>240</td>
<td>0.975</td>
<td>−1.00</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.975</td>
<td>−1.02</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.975</td>
<td>−0.97</td>
</tr>
<tr>
<td>Ta-10at.%Nb</td>
<td>240</td>
<td>0.80</td>
<td>−0.52</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.65</td>
<td>−0.45</td>
</tr>
<tr>
<td>Ta-19at.%Nb</td>
<td>240</td>
<td>0.90</td>
<td>−0.39</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.65</td>
<td>−0.43</td>
</tr>
<tr>
<td>Ta-39at.%Nb</td>
<td>240</td>
<td>1.25</td>
<td>−0.30</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.78</td>
<td>−0.34</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.73</td>
<td>−0.32</td>
</tr>
<tr>
<td>Ta-66at.%Nb</td>
<td>240</td>
<td>1.15</td>
<td>−0.26</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>1.03</td>
<td>−0.24</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.85</td>
<td>−0.29</td>
</tr>
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</table>

Differential capacitance study.— In order to get information on the dielectric properties of the investigated oxides, we recorded differential capacitance curves as a function of the a.c. signal frequency as well as of the oxide composition in a wide electrode potential range (from 3 V to the flat band potential). In Fig. 8 we report the measured series capacitance, C_M, of the Ta/Ta₂O₅/electrolyte interface recorded in 0.5 M H₂SO₄ at three different frequencies. C_M depends on both the polarizing potential and a.c. frequency, as typical of amorphous semiconductors. However, the measured capacitance becomes almost independent on U_E when f_a.c. = 5 kHz. By increasing the Nb content the mixed oxides become more polarisable, as suggested by the differential capacitance recorded at 5 kHz and 100 Hz for all the investigated
films, reported in Fig. 9. In order to explain the dependence of C on the polarizing voltage as well as on the a.c., frequency, we have to recall briefly of amorphous semiconductor Schottky barrier,18, 19 which takes into account the influence on the electronic properties of the short range order of amorphous material. In fact, the main difference between crystalline and amorphous semiconductors is that the space charge region width, $x_{SC}$, depends on both the ionized impurities and the localized states within the mobility gap. These electronic states lying into the gap do not follow instantaneously the imposed ac signal. Thus, we expect that the higher is the measured capacitance the lower is $\omega$ (compare Figs. 9a and 9b), and that C rapidly increases when the polarizing voltage approaches the oxide flat band potential.

It is evident that even the anodic film grown on Ta-10at.%Nb shows a behavior different from that shown by Ta$_2$O$_5$. In spite of the very close band gap value, the anodic film with the lowest Nb content shows a flat band potential more anodic than that of tantalum oxide, very close band gap value, the anodic film with the lowest Nb content shows a flat band potential more anodic than that of tantalum oxide, in agreement with the photoelectrochemical results. The shift toward the anodic direction of the flat band potential of all the mixed oxide results, is confirmed by the differential capacitance curves of Fig. 9.

In the high band bending region, i.e. for $\omega \psi S > (E_g/2 - \Delta E_g)$, when a deep depletion region at the surface of a-SC/EI junctions takes into account the influence on the electronic properties of the short range order of amorphous material. In fact, the main difference between crystalline and amorphous semiconductors is that the space charge region width, $x_{SC}$, depends on both the ionized impurities and the localized states within the mobility gap. These electronic states lying into the gap do not follow instantaneously the imposed ac signal. Thus, we expect that the higher is the measured capacitance the lower is $\omega$ (compare Figs. 9a and 9b), and that C rapidly increases when the polarizing voltage approaches the oxide flat band potential.

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In the high band bending region, i.e. for $\omega \psi S > (E_g/2 - \Delta E_g)$, when a deep depletion region at the surface of a-SC/EI junctions.

$\tau$ increases sharply so that deep states (for which $\omega \tau \gg 1$) do not respond to the ac signal.

By assuming a full response for states satisfying the condition $\omega \tau \ll 1$ and a null response for states having $\omega \tau \gg 1$, a sharp cutoff energy level, $E_{c0}$ separating states responding from those not responding to the signal, can be defined from the condition: $\omega \tau = 1$, as:

$$E_C - E_{c0} = -k_B T \ln(\omega \tau_0)$$  \[8\]

The intersection of $E_{c0}$ with the Fermi level of material determines a characteristic point in the barrier, $x_C$, at which corresponds a band bending $\psi_S$ given by:

$$|e| \psi_S = |e| \psi(x_C) = -k_B T \ln(\omega \tau_0) - \Delta E_F$$  \[9\]

where $\Delta E_F = (E_C - E_{F0})_{bulk}$. $x_C$ is a distance in the barrier which changes with changing frequency, $\omega$, and band bending, $\psi_S$. From the theory it comes out that the total capacitance is sum of two series contribution coming from the $x < x_C$ and $x > x_C$ regions of the a-SC. In the hypothesis of a constant DOS the total capacitance is given by the sum of the two contributions:

$$\frac{1}{C(\psi_S, \omega)} = \frac{1}{C(\psi_S, 0)} + \frac{x_C}{\varepsilon \varepsilon_0}$$  \[10\]

where $C(\psi_S, 0) = \varepsilon \varepsilon_0 N$ and $x_C = \sqrt{\frac{N \omega}{k_B T}}$. $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the relative dielectric constant of the oxide and N is the density of states. The contribution to the measured capacitance deriving from the second term in eq. 10 becomes more significant with decreasing the a.c. signal frequency and by decreasing the band bending. Thus, we expect that the higher is the measured capacitance the lower is $\omega$ (compare Figs. 9a and 9b), and that C rapidly increases when the polarizing voltage approaches the oxide flat band potential.
appears\textsuperscript{19} the total capacitance of barrier can be modelled as a two series capacitance:

\[
\frac{1}{C(\psi_S, \omega)} = \frac{1}{C(\psi_E, \omega)} + \frac{X_g}{\varepsilon\varepsilon_0} \quad [11]
\]

where the first term of eq. 11 represents the low band bending contribution calculated at the electrode potential where the Fermi level crosses the mid gap energy and coincides with eq. 10 after notation substitution. The second term represents the capacitance of the deep depletion region going from the surface to the point \(x_g\) of the junction, where a parabolic potential distribution exists, and is frequency independent.

Under high band bending (\(\psi_0 > E_g/2 - \Delta E_g\)) and high frequency (\(\psi_0 \rightarrow 0\)), \(C(\psi_S, \omega) \approx C(\psi_E, 0)\) and, thus, we can assume that the space charge region width coincides with the whole oxide thickness. This allows to estimate the oxides’ dielectric constant according to the following eq.:

\[
C = \frac{\varepsilon\varepsilon_0}{d} \quad [12]
\]

By subtracting to the measured capacitance the Helmholtz double layer contribution, assumed \(\sim 20 \, \mu\text{F cm}^{-2}\) in concentrated aqueous solution (as 0.5 M H\textsubscript{2}SO\textsubscript{4} is\textsuperscript{20} we can have the idea on how the \(\varepsilon/d\) ratio changes by changing the oxide composition. We know from the anodizing curves (see previous sections) as well as from the transmission microscopy images of ultramicrotomed sections\textsuperscript{8} that the film thickness increases with increasing Nb content into the mixed oxide. The knowledge of d allows to estimate the oxide dielectric constant from the capacitance values measured at 5 kHz at the highest band bending (\(U_g = 3\, \text{V}\)) reported in Fig. 10 as a function of the film composition. \(\varepsilon\) monotonically increases with increasing Nb content, as found for thicker films grown on the same investigated alloys.\textsuperscript{8} Such dependence also agrees with the dielectric constant calculated by computation method for NbTaO\textsubscript{5}, reported in ref. 16.

Finally, we want to stress that eq. 9 allows to estimate \(\Delta E_g\), provided that it is possible to estimate a frequency of the a.c. signal high enough to make the capacitance almost independent on the applied potential. The simultaneous knowledge of this energy distance and of the band gap value of the oxide allows to get the energetics of the metal/oxide/electrolyte interface, as reported in Fig. 11 for anodic films grown on Ta, Ta-10at.%Nb and Ta-19at.%Nb. A work function of 4.25 eV has been assumed for tantalum and for the alloys,\textsuperscript{21} due to their low Nb content and by taking into account that a very close work function is reported for Nb (4.30 eV according to ref. 21). These sketches provide an idea of the band offset for the investigated metal/oxide systems. With a Nb content of 19%, we get a mixed oxide with a dielectric constant 10% higher than that of Ta\textsubscript{2}O\textsubscript{5} with a reduction of less than 3% of the band gap. However, to have a complete set of information it is very important to have a look to the energetics of the metal/oxide interface, that shows a reduction of the band offset (see Fig. 11). If we consider that the metal or alloys to be anodized can be easily sputtered on a metal with a properly selected work function, we can hypothesize to control the band offset by properly selecting the materials involved in the fabrication of the metal/oxide interface.

**Conclusions**

Ta\textsubscript{2}O\textsubscript{5}, Nb\textsubscript{2}O\textsubscript{5} and Ta-Nb containing oxides grown by anodizing sputter-deposited Ta, Nb and Ta-Nb alloys of different composition were characterized by Photocurrent Spectroscopy and by impedance measurements.

Band gap values of 4.1 eV and 3.4 eV were estimated for anodic Ta\textsubscript{2}O\textsubscript{5} and Nb\textsubscript{2}O\textsubscript{5}, respectively, while intermediate values were estimated for mixed oxides monotonically increasing by increasing the Ta content.

The estimated band gap values are in agreement with the proposed linear dependence of \(E_g\) on the squared difference of electronegativity of the oxide constituents. This finding shows the potential of this correlation to predict the band gap value of an oxide knowing its composition.

Differential capacitance curves, recorded for all the investigated oxides in a wide range of electrode potential and for several frequencies of the alternative signal, were interpreted on the basis of amorphous semiconductor Schottky barrier, and allowed to determine the dielectric constant of the investigated oxides. According to the

**Figure 11.** Sketch of the energetic levels of metal/oxide/electrolyte interface for anodic films grown on a) Ta, b) Ta-10at.%Nb, c) Ta-19at.%Nb.
estimated values, $\varepsilon$ depends almost linearly on the atomic fraction of one of the partner cations into the mixed oxide.

The experimental results reported in this work suggest that by properly selecting the alloy composition it is possible tailoring both the oxides band gap and dielectric constant, which are key parameters in determining the performance of high-k materials.

**Acknowledgment**

MS and FDQ gratefully thank USAITC-A for providing the grant no. W911NF-09-10461.

**References**