POLITECNICO
MILANO 1863

Milano, 30 Novembre 2018 - Politecnico di Milano

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Giornata di studio "Pietro Pedeferri"
Dalla ricerca all'industria: le nuove frontiere dell'ingegneria della corrosione

Caratterizzazione mediante Spettroscopia a Fotocorrente (PCS) di ossidi anodici accresciuti su leghe Ta - Nb in differenti soluzioni elettrolitiche

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Outline

- **Introduction and Aims**

- **Photocurrent Spectroscopy (PCS)** as in situ technique for semi-quantitative analysis of passive films and corrosion layers.

- **PCS** data analysis of passive films grown on Ta-Nb alloys in different solutions and their interpretation.

- **Conclusions and Critical issues** in the comparison of Eg values derived by different techniques .

Introduction

Anodic oxide films on tantalum and niobium have been studied for very long time for their possible application in electrolytic capacitors industry owing to their large values of dielectric permittivity (ε_{Nb2O5} = 50-57 and ε_{Ta2O5} = 27-31).

Recently anodic Ta_2O_5 have been proposed as possible candidates to be used in ReRAM applications (1) whilst in the past mixed tantalum oxides (containing d-metal cation, for instance Ti or Nb) have been suggested as gate dielectric in integrated circuits (2-3) as well as dielectrics for electrolytic capacitors (4).

Moreover the tailoring of band gap of mixed oxides by adding a variable amount of different oxides is attractive for the possible applications in several fields (photovoltaics, photocatalysis, high K materials etc..)

1) A. Zaffora et al., Adv. Mater., 29 (2017) 1703357 1-6
2) R.J. Cava et al., Nature 377, 215(1995); Mat. Res. Bull., 31, 295(1996).
3) S. Clima et al., J. Electrochem. Soc., 157, G20 (2010).
4) F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.
S. Komiyama et al., Journal of Solid State Electrochemistry, 16 (2012) 1595-1604.

Aims

In this work some results of an extensive PCS characterization of anodic films grown on magnetron sputtered Ta, Nb, and Ta-Nb alloys, spanning a large range of composition, will be presented in order to:

a) investigate the role of different process parameter (solution composition and film thickness) on the electronic and solid state properties ($E_{g,opt}$) of mixed oxide films.

b) discuss the origin of some discrepancies, reported in the literature, in the $E_{g,opt}$ values of anodic films grown on identical substrates but in different electrolytic solutions (1,2).

c) test the extent of validity of a previously proposed correlation between the optical band gap of crystalline and amorphous mixed oxide as a function of their composition.

d) carry out a comparison of different experimental data for evidencing the possible sources of differences in the band gap values derived by different techniques.

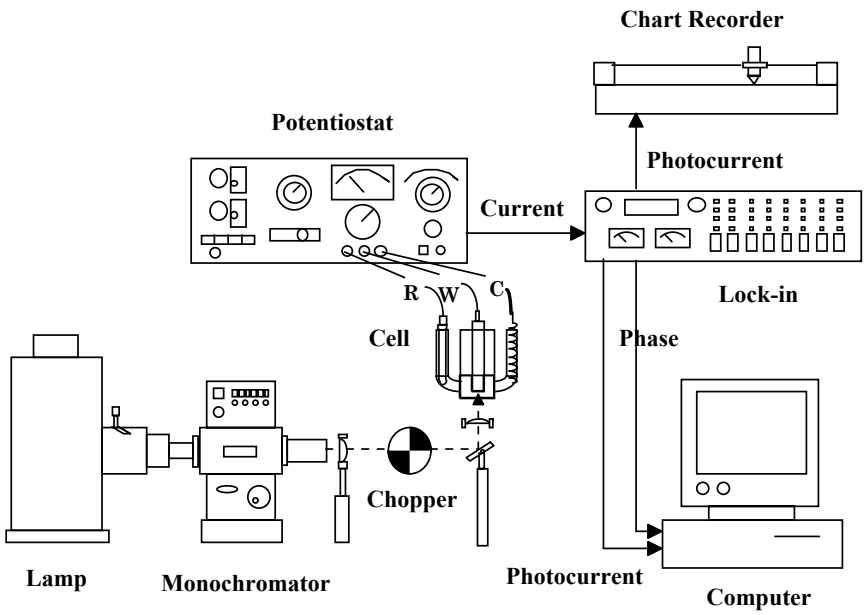
1) F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.

2) W. Limberger et al., RSC Advances, 2016, 6, 79934–79942

Introduction

Photocurrent Spectroscopy (PCS) is an *in-situ* electrochemical technique for the characterization of very thin (1-2 nm) and thick semiconductors (SC) and insulating materials.

- **Electronic structure** (n, p-type SC, Insulators, E_g value) of passive films *in situ* and under controlled potential in long lasting experiments;
- **Energetics at the metal/passive film/electrolyte interfaces** (U_{fb} determination, CB and VB edges location);
- **Mechanisms of generation** (geminate recombination effects) **and transport** of photocarriers (trap limited mobility) in amorphous and crystalline materials;
- **Kinetics of growth under illumination** of photoconducting films and interference effects in absorbing materials at constant growth rate.

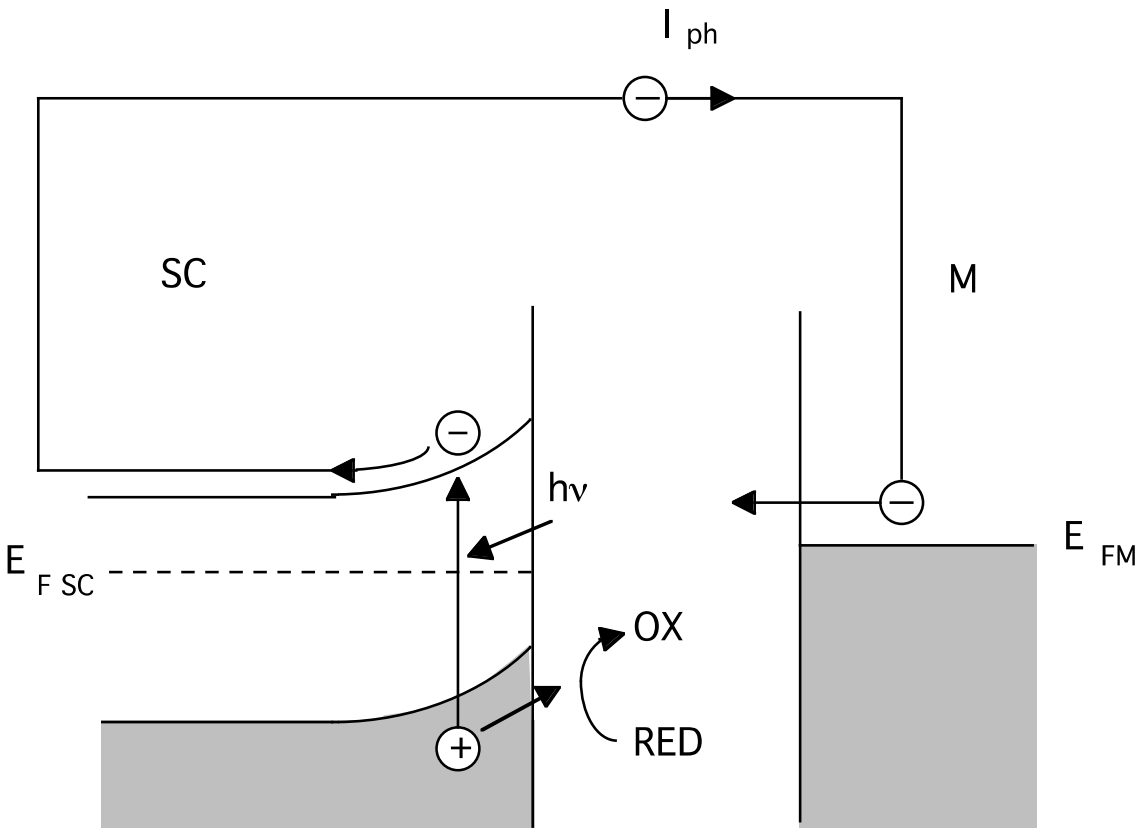


F. Di Quarto et al., in Modern Aspects of Electrochemistry, No. 46, 231-316, 2009.

F. Di Quarto et al., Journal of The Electrochemical Society, 164 (12) C671-C681 (2017).

Band gap determination in c-SC

Anodic Photocurrent



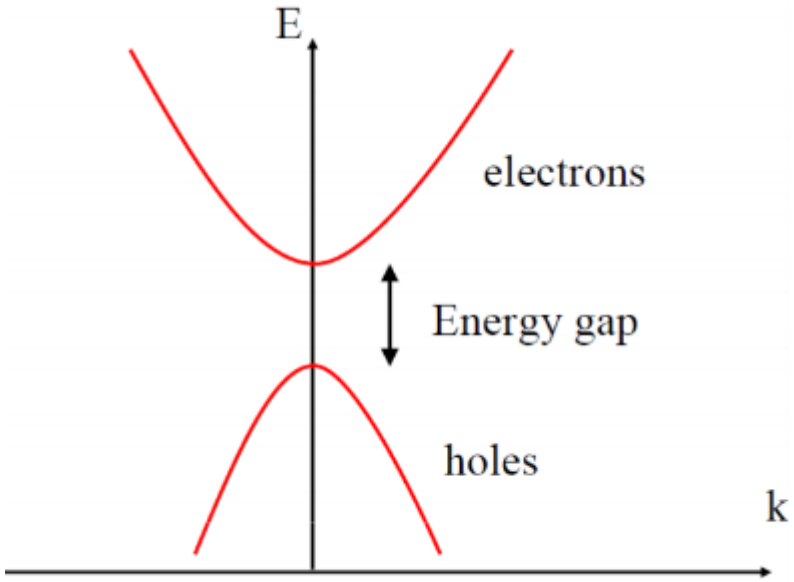
Band gap determination in c-SC

$$i_{ph} = e\Phi_0 \alpha x_{SC}^0 \left(U_E - U_{fb} - \frac{k_B T}{e} \right)^{1/2}$$

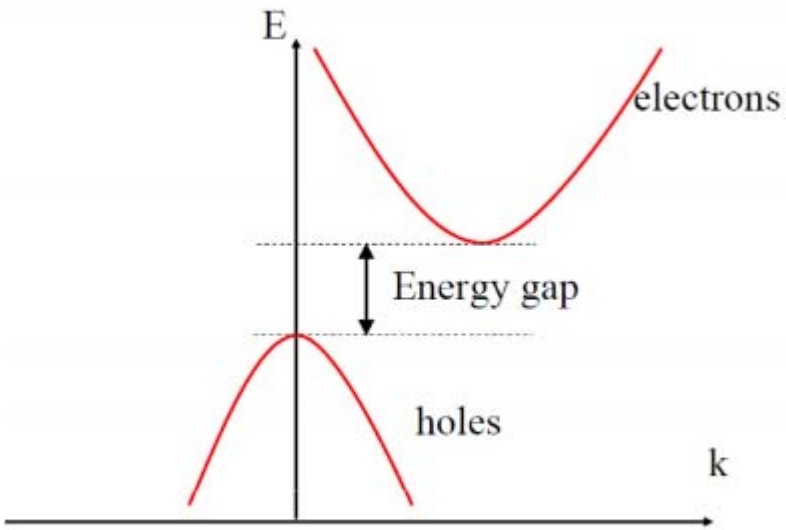
At U_E = const. → $Q = \frac{I_{ph}}{e\,\Phi_0} \propto \alpha$

$$\alpha = A \frac{(h\nu - E_g)^{n/2}}{h\nu} \rightarrow (Qh\nu)^{2/n} = A\,(h\nu - E_g)$$

Band gap determination in c-SC



Direct bandgap semiconductors



Indirect bandgap semiconductors

$$\alpha = A \frac{(h\nu - E_g^{opt})^{n/2}}{h\nu}$$

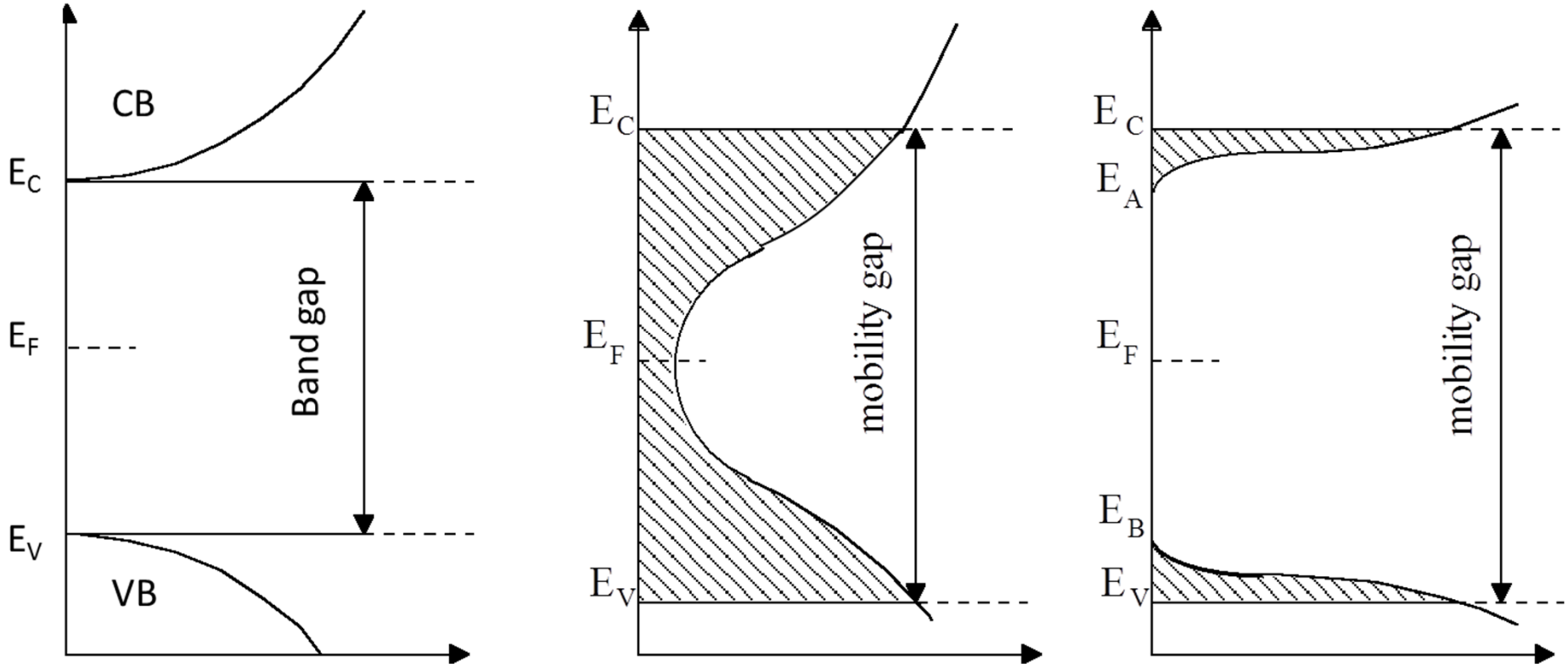
Direct

- Allowed: n = 1
- Forbidden: n = 3

Indirect

n = 4

Density of electronic states as function of the energy



Cohen-Fritzsche-Ovshinsky model

Mott-Davis model

Crystalline SC

Amorphous SC

Amorphous SC

Experimental

Materials

Ta, Nb and Ta-Nb alloys dc Magnetron Sputtered on Glass Substrates

Targets: Nb disk (99.9%) and Ta disk (99.9%)

Nb (at.%)	100	85	66	61	19	0
Ta (at.%)	0	15	34	44	81	100

Anodizing :10 mV s-1 (Potentiodynamic growth)

Electrolyte: 0.1 M NaOH, pH = 13

Formation Voltage: 5, 10 V vs. Ag/AgCl; Counter electrode: Pt

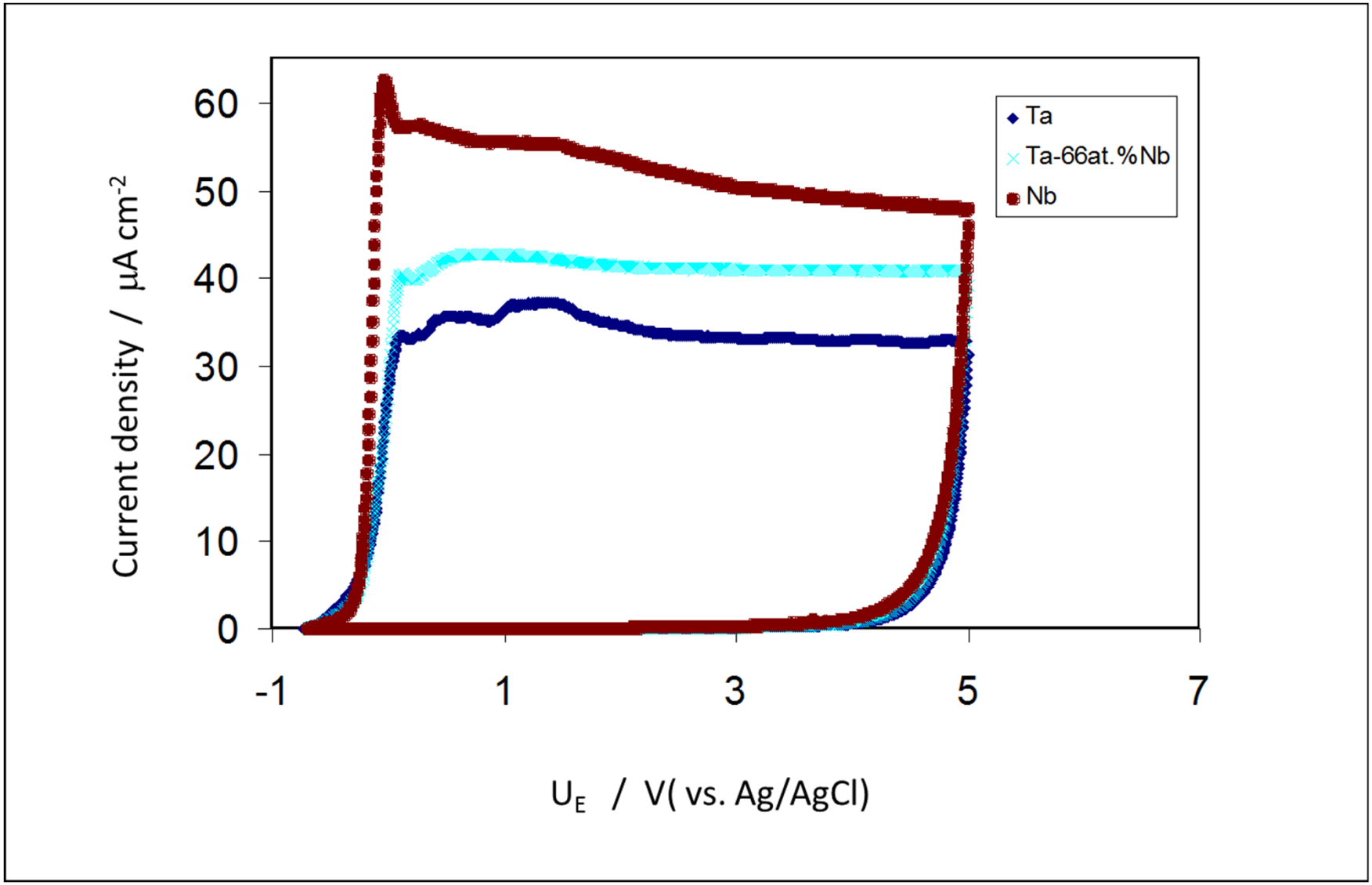
PCS Characterization:

Electrolyte: 0.5 M H2SO4; and/or 0.1 M Ammonium Biborate (ABE)

Ex situ: GDOES, RBS, XRD, TEM

$(Ta_xNb_{(1-x)})_2O_5$ Film Potentiodynamic Growth

Sol: 0.1 M NaOH dV/dt = 10 mV s^{-1}



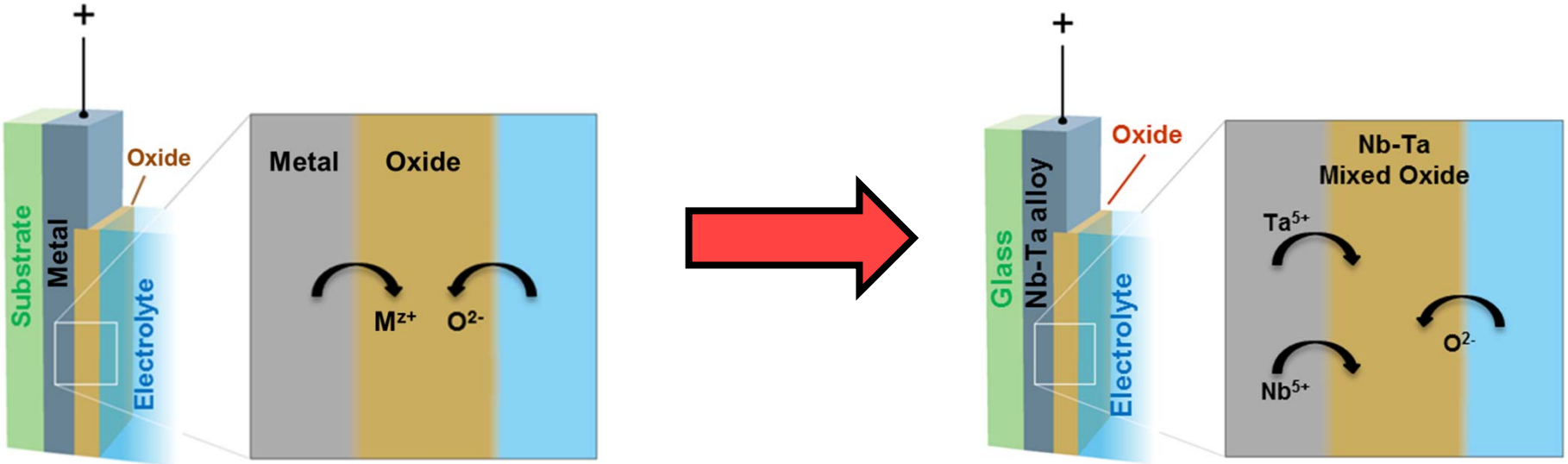
F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.

Anodizing

Mechanism of growth: fundamental equation for high-field ionic conductivity

$$i = i_0 \exp(\beta E) = N\nu q \exp\left(-\frac{W - aqE}{k_B T}\right)$$

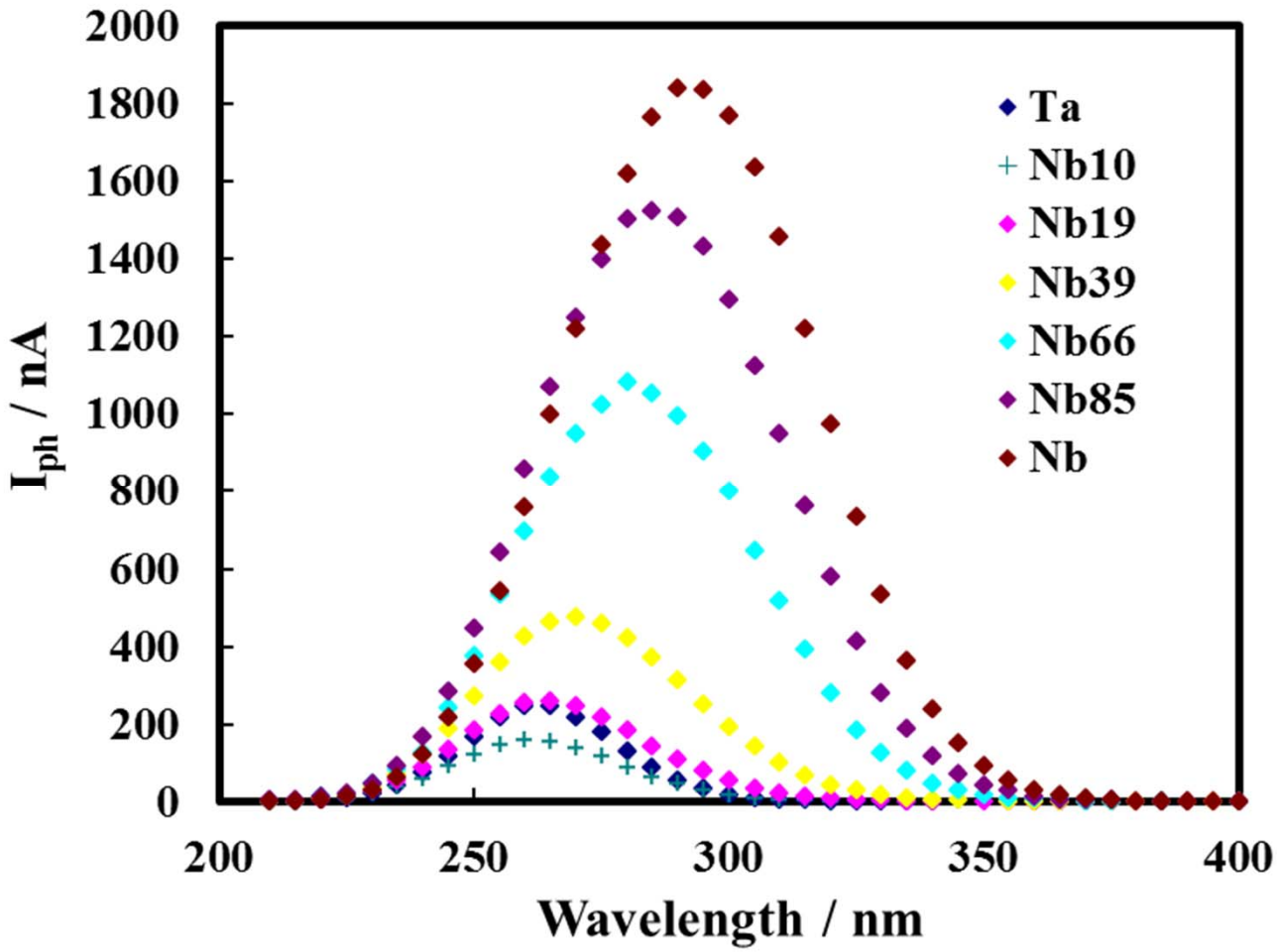
$$x\,M + y\,H_2O \longrightarrow M_xO_y + 2y\,H^+ + 2y\,e^-$$



F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.

Oxides characterization by PCS

Anodic film grown on **Ta-Nb** Alloys in 0.1 M NaOH, U_F = **5 V** vs. Ag/AgCl
Characterization electrolyte: 0.5 M H_2SO_4



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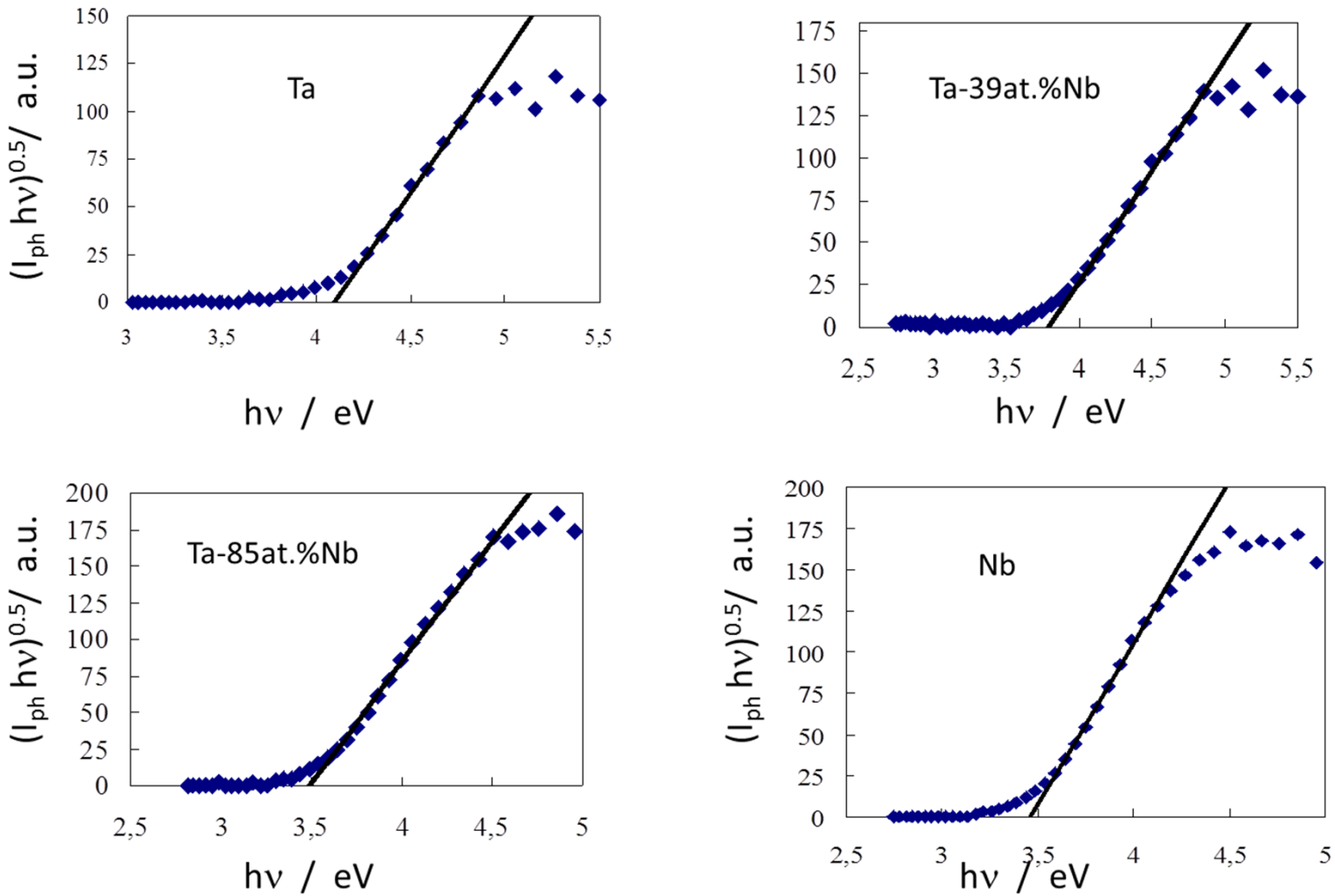
Oxides characterization by PCS: band gap values

Anodic film grown on **Ta-Nb** Alloys in 0.1 M NaOH, U_F = **5 V** vs. Ag/AgCl
Characterization electrolyte: 0.5 M H_2SO_4



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Oxides characterization by PCS: band gap values

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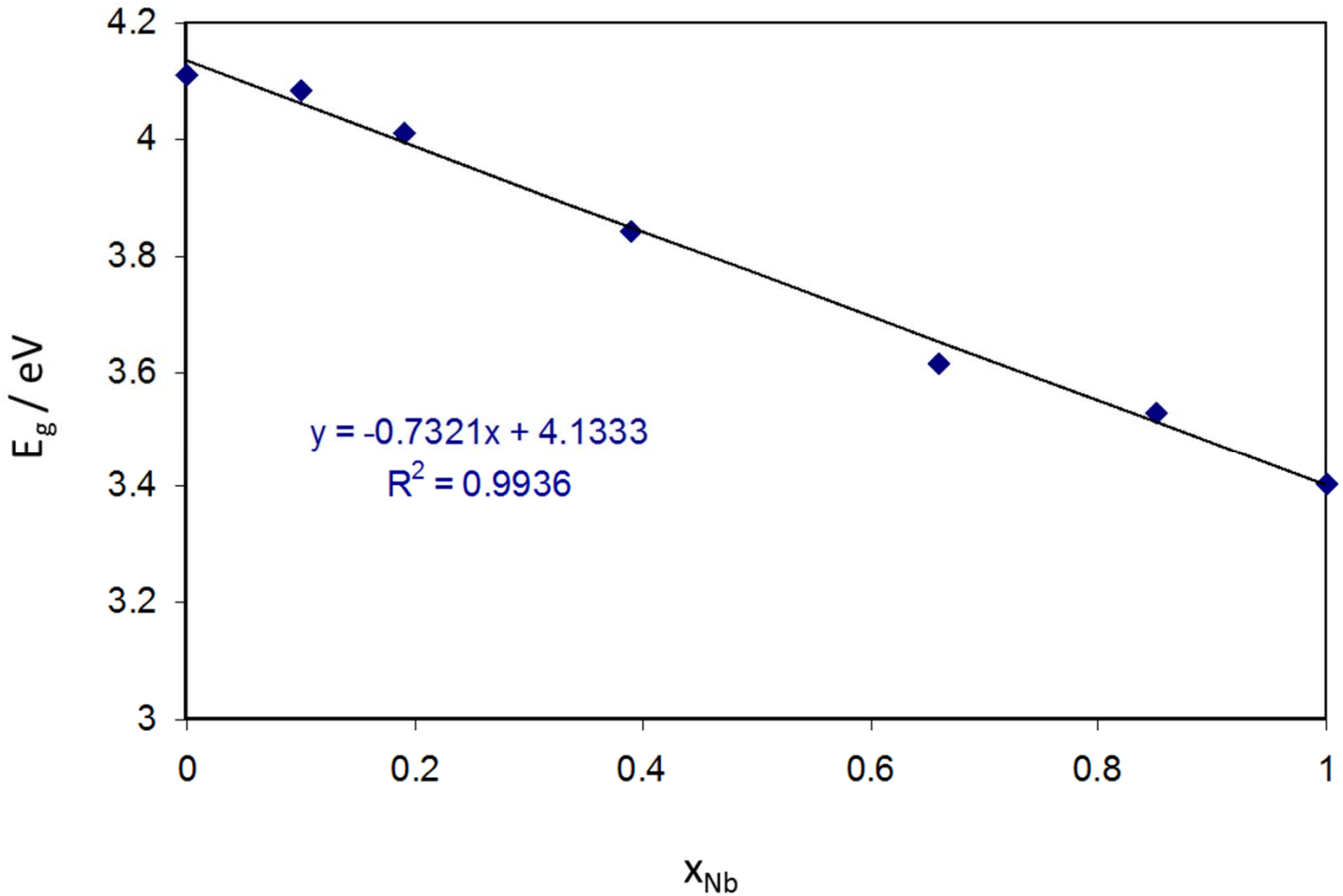


F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.

Experimental

- ***Magnetron Sputtered Nb, Ta, Nb-Ta alloys***

- ***Anodizing (Potentiodynamic growth):***
  Potential sweep rate: 10 mV s^{-1}
  Formation Voltage: 5, 10 V vs. Ag/AgCl
  Counter electrode: Pt

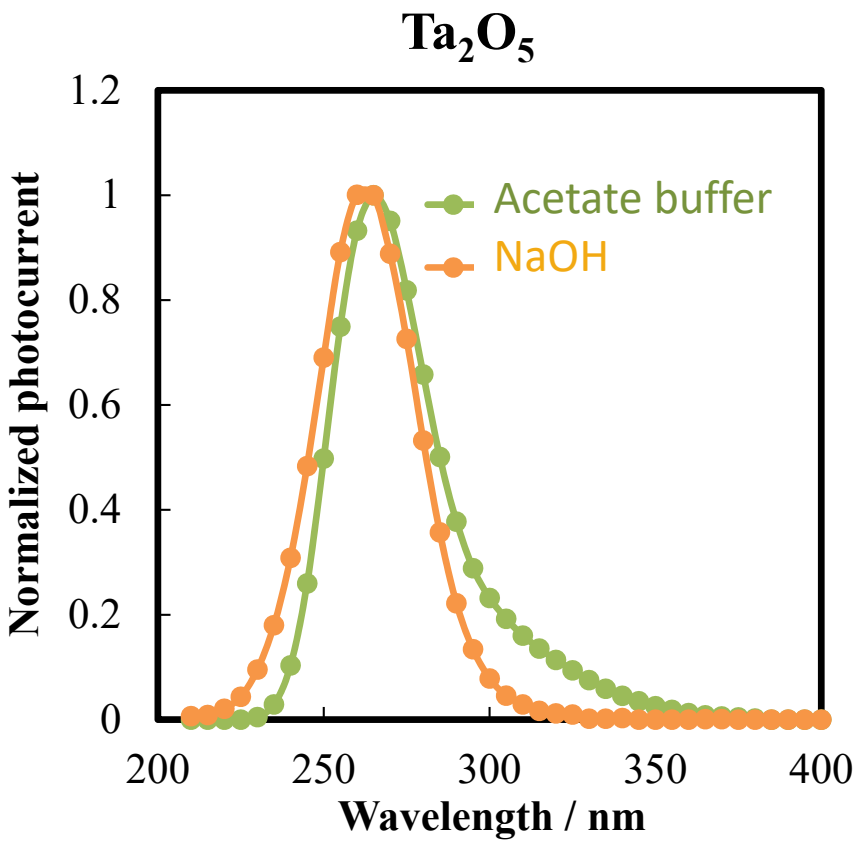
- *Electrolyte: Acetate buffer (CH_3COOH/CH_3COONa), pH = 6*

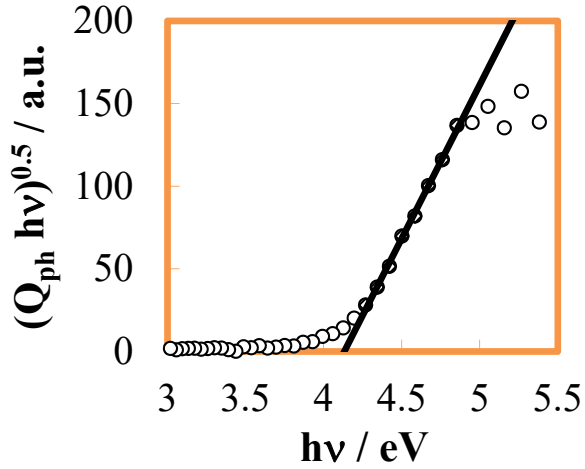
- ***Photocurrent Spectroscopy (PCS)***
  Characterization electrolyte: 0.1 M Ammonium Biborate (ABE)

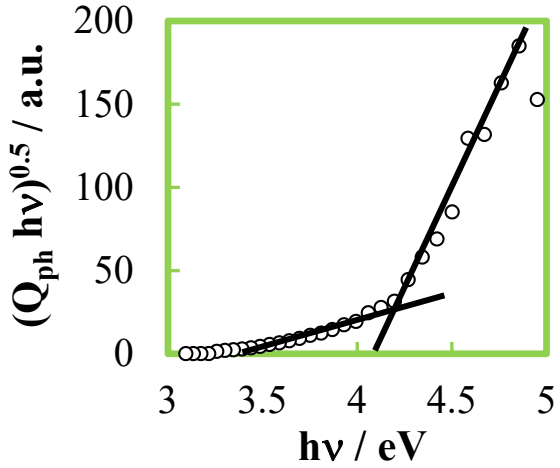
W. Limberger et al., RSC Advances, 2016, 6, 79934–79942

Oxides characterization by PCS

*Anodic film grown on **Ta**, U_F = **5 V** vs. Ag/AgCl*
Characterization electrolyte: 0.5 M H_2SO_4, 0.1 M ABE,
U_E = 2 V vs. Ag/AgCl

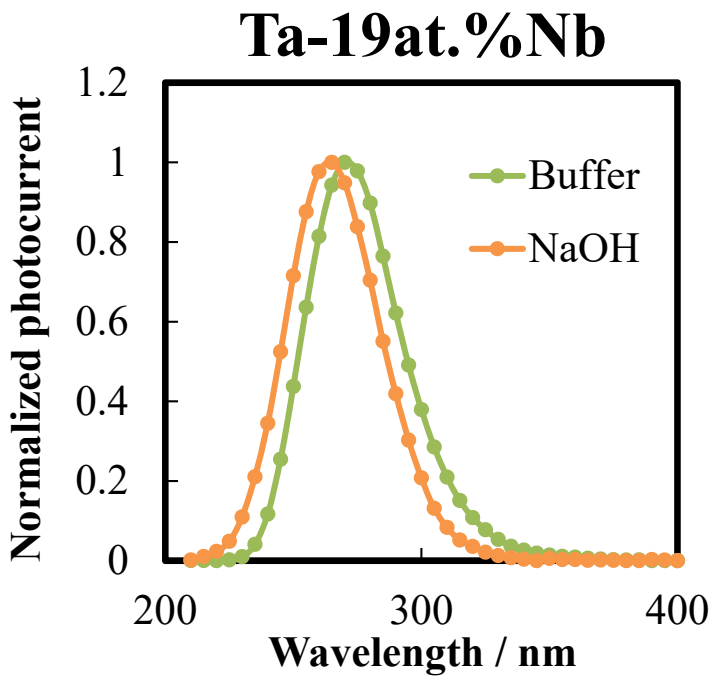


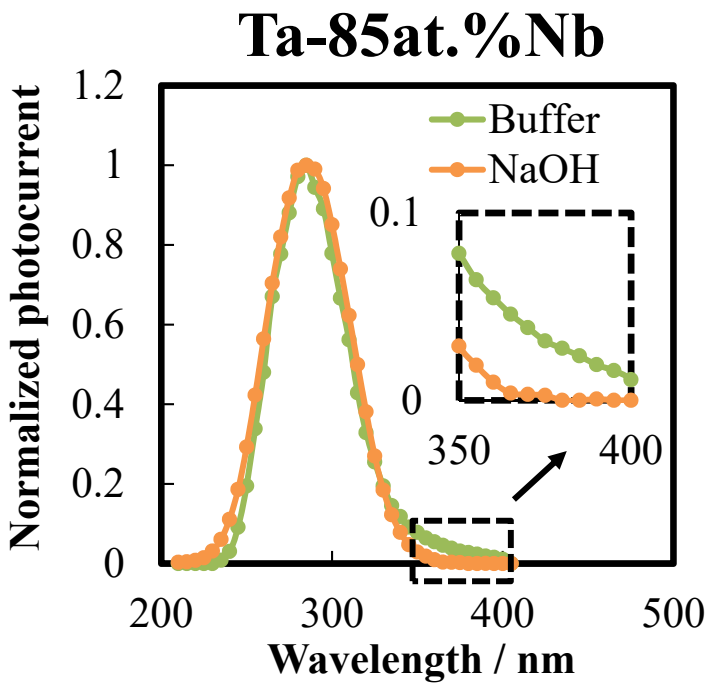




Oxides characterization by PCS

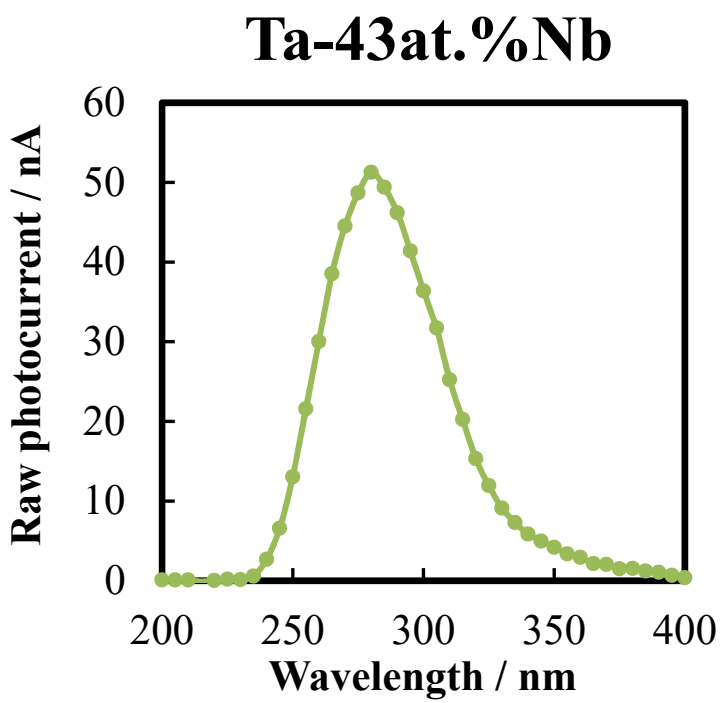
Anodic film grown on **Ta-Nb** Alloys, U_F = **5 V** vs. Ag/AgCl
Characterization electrolyte: 0.5 M H_2SO_4, 0.1 M ABE,
U_E = 2 V vs. Ag/AgCl

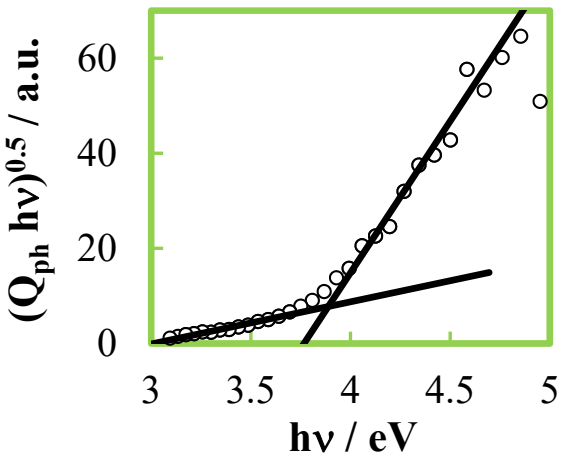




Oxides characterization by PCS

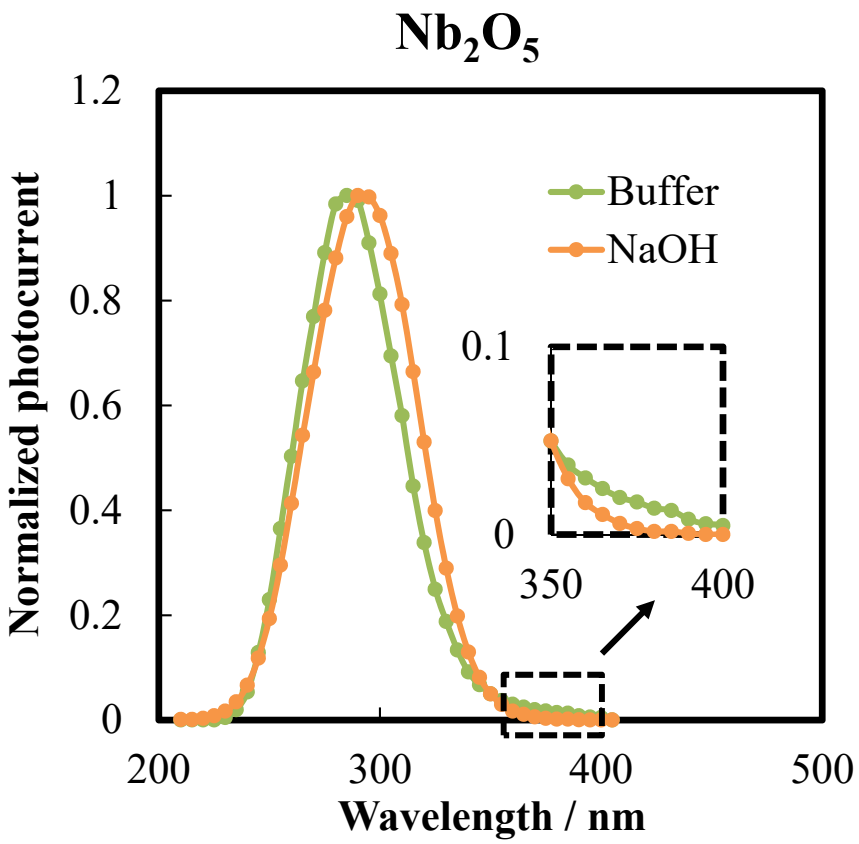
Anodic film grown on **Ta-Nb** Alloys, U_F = **5 V** vs. Ag/AgCl
Characterization electrolyte: 0.5 M H_2SO_4, 0.1 M ABE, U_E = 2 V vs. Ag/AgCl

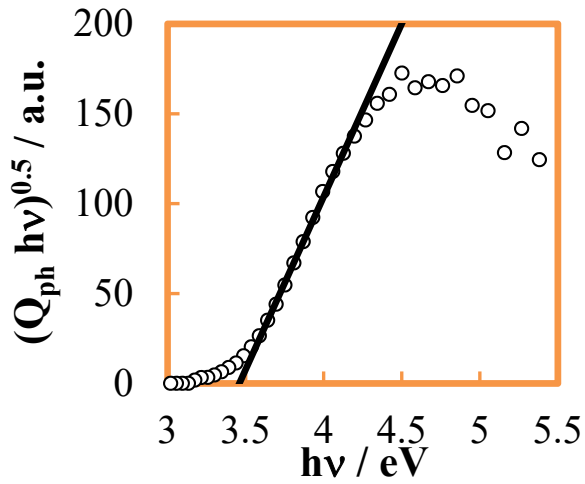


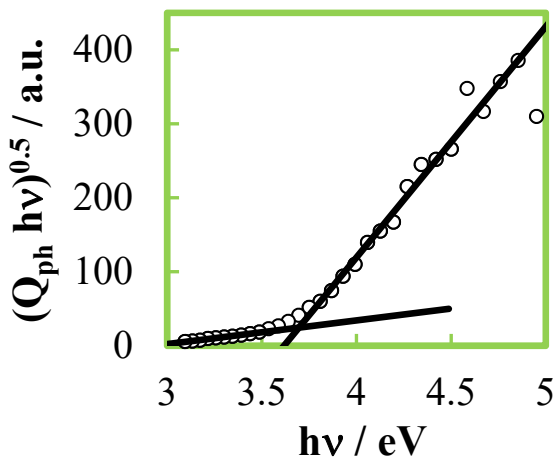


Oxides characterization by PCS

Anodic film grown on **Nb**, U_F = **5 V** vs. Ag/AgCl
Characterization electrolyte: 0.5 M H_2SO_4, 0.1 M ABE,
U_E = 2 V vs. Ag/AgCl

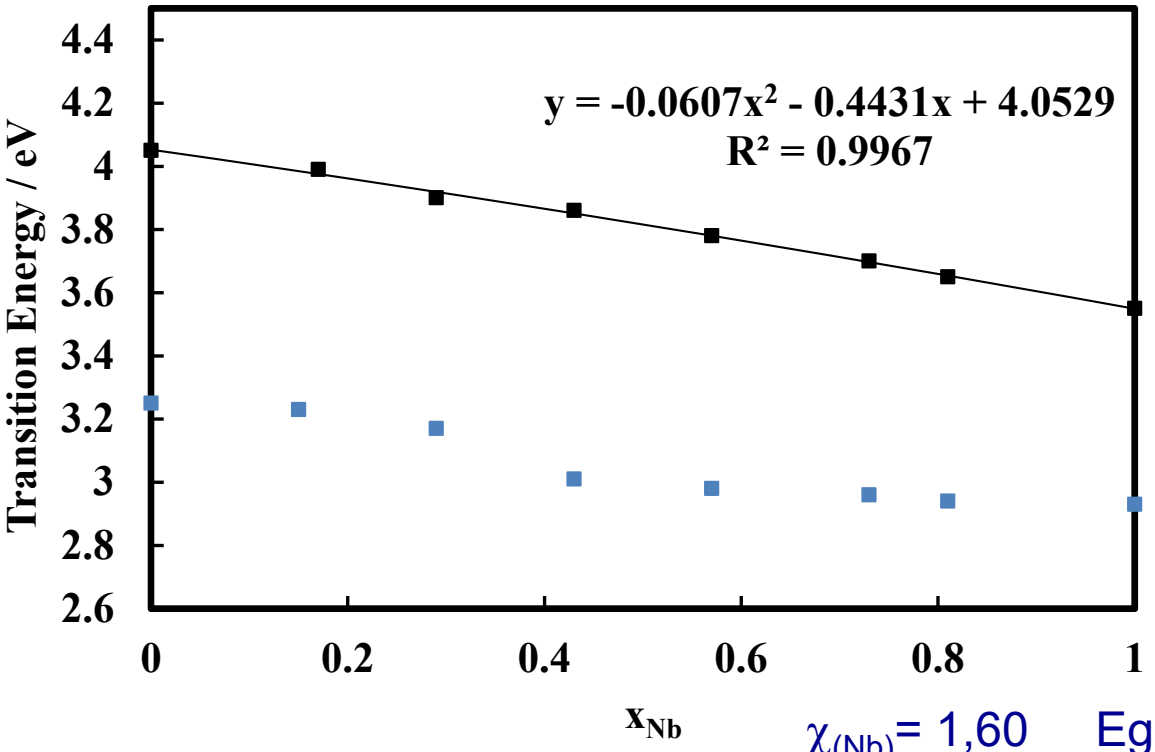






Quantitative use of PCS: Ternary (regular) Mixed Oxides

U_F = 5 V vs. Ag/AgCl



$\chi_{(Nb)}$= 1,60 eV $Eg(Nb_2O_5)$ = 3.37

$\chi_{(Ta)}$ = 1,51 eV $Eg(Ta_2O_5)$ = 3.85

$S_{l,th}$= 0,486; b = $S_{q,th}$ = 0,01;

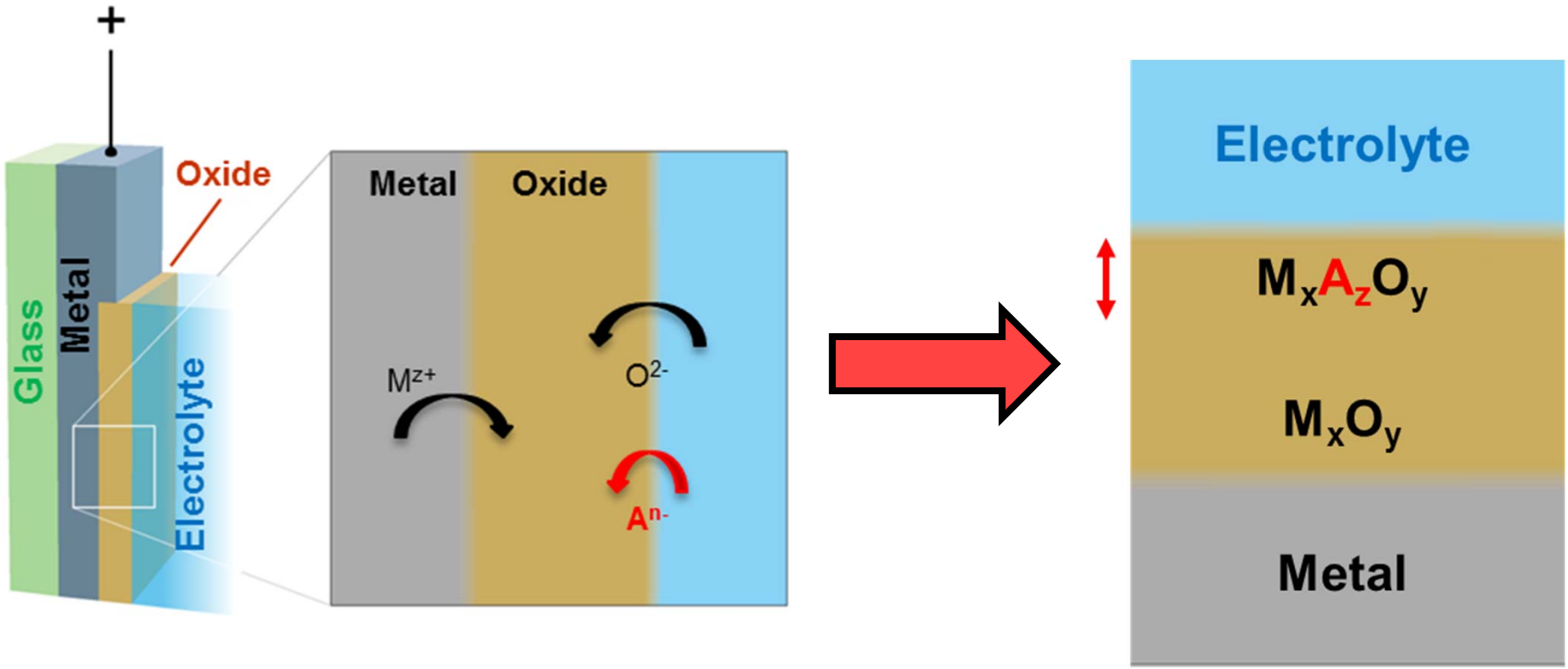
Oxide band gap

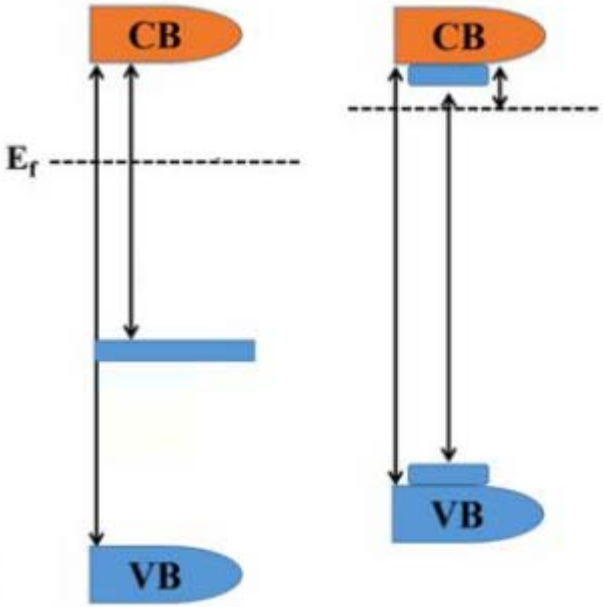
Threshold energy due to localized states generated by incorporation of electrolyte species

Influence of anodizing bath composition

Effect of Electrolyte Composition

Anion incorporation

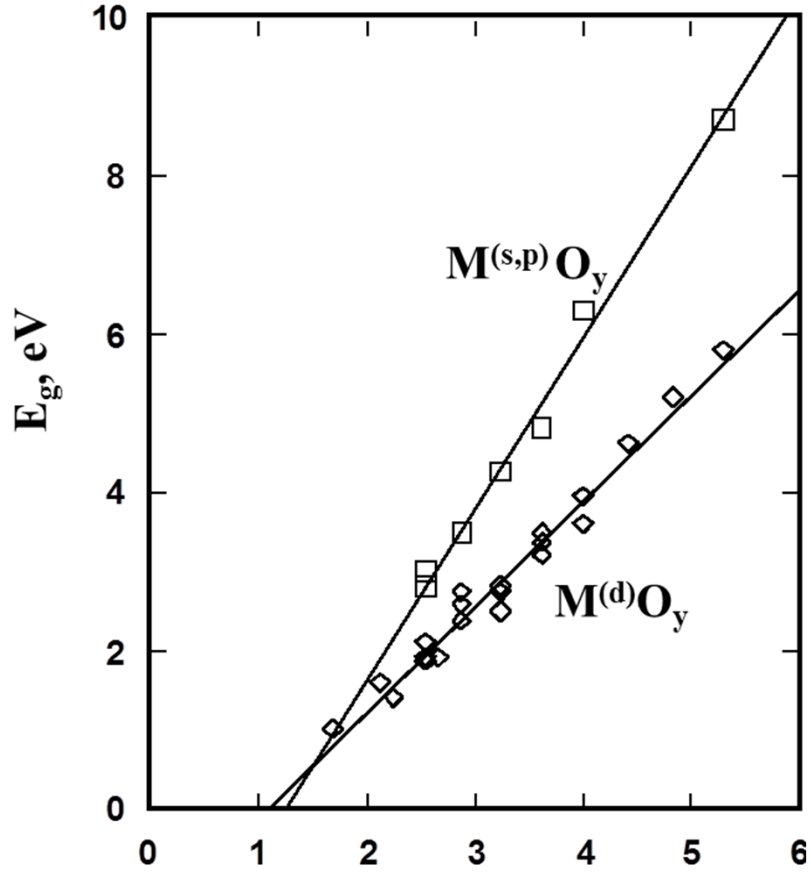



CB
E_f
VB
CB
VB

Quantitative use of PCS: Binary Oxides

Starting point…

Oxide	E_g, eV	Oxide	E_g, eV
MgO	8.70	Ta_2O_5	3.95
Al_2O_3	6.30	MnO	3.60
Ga_2O_3	4.80	Cr_2O_3	3.50
SnO	4.22	NiO	3.50
SnO_2	3.50	Nb_2O_5	3.35
Sb_2O_3	3.00	TiO_2	3.20
In_2O_3	2.80	ZnO	3.20
Bi_2O_3	2.80	WO_3	2.75
PbO ort	2.75	CoO	2.60
PbO tetr	1.90	CdO	2.50
Tl_2O_3	1.60	FeO	2.40
Y_2O_3	5.80	Fe_2O_3	1.90
MoO_3	2.90	HgO	1.90
V_2O_5	2.30	Cu_2O	1.86
HfO_2	5.20	CuO	1.40
ZrO_2	4.60	PdO	1.00



$(\chi_M - \chi_O)^2$

$M^{(s,p)}O_y$ $\quad E_g(eV) = 2.17\,(\chi_M-\chi_O)^2 - 2.71$

$M^{(d)}O_y$ $\quad E_g(eV) = 1.35\,(\chi_M-\chi_O)^2 - 1.49$

F. Di Quarto et al., *Semiempirical Correlation between Optical Band Gap Values of Oxides and the Difference of Electronegativity of the Elements. Its Importance for a Quantitative Use of Photocurrent Spectroscopy in Corrosion Studies*, J. Phys. Chem. B 101 (1997) 2519.

Ternary regular (d-d) Mixed Oxides

Journal of The Electrochemical Society, **164** (12) C671-C681 (2017) C671

Review—Photocurrent Spectroscopy in Corrosion and Passivity Studies: A Critical Assessment of the Use of Band Gap Value to Estimate the Oxide Film Composition

Francesco Di Quarto,[*,z] Andrea Zaffora, Francesco Di Franco,[*] and Monica Santamaria[*]

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$$E_g(M_mN_nO_o) = A(\chi_{av} - \chi_O)^2 + B$$

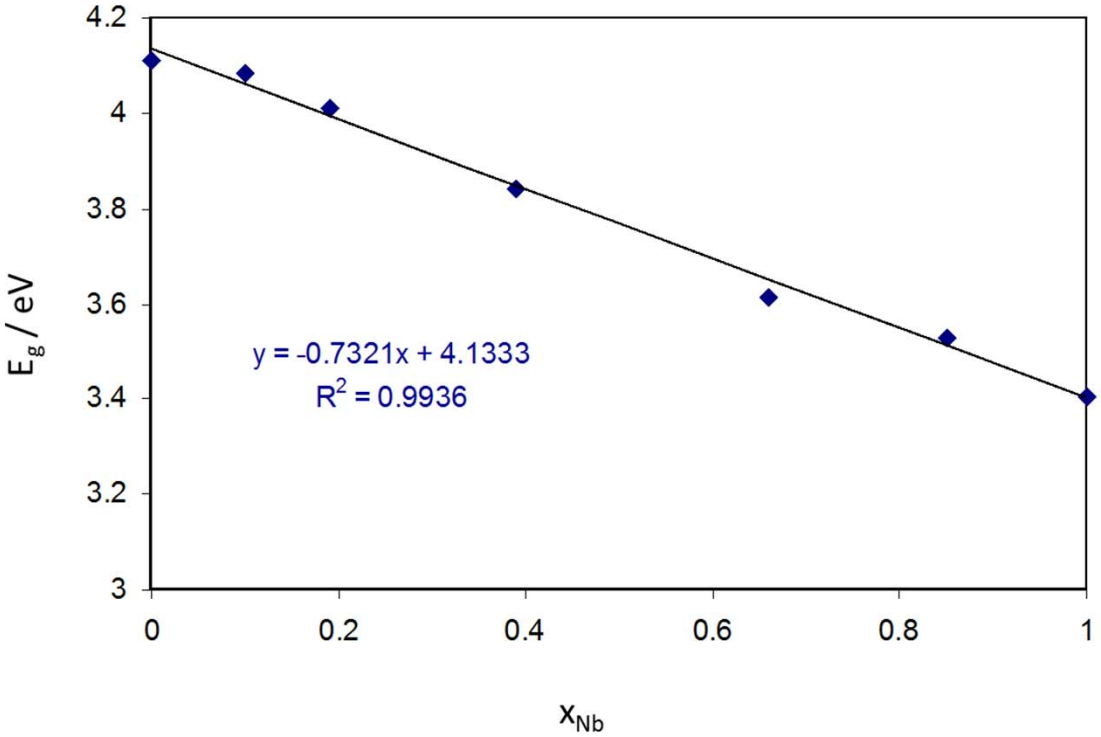
$$\chi_{av} = \frac{m\chi_M + n\chi_N}{m+n} = x_M\chi_M + x_N\chi_N \qquad x_M = \frac{m}{m+n} \qquad x_N = 1 - x_M$$

$$\boxed{E_g(x_N) = E_{g,M} + S_l x_N + S_q x_N^2}$$

$$S_l = 2A(\chi_M - \chi_N)(\chi_{an} - \chi_M) \qquad b = S_q = A(\chi_N - \chi_M)^2$$

Oxides characterization by PCS: band gap values

*Anodic film grown on **Ta-Nb** Alloys in 0.1 M NaOH, U_F = **5 V** vs. Ag/AgCl*
Characterization electrolyte: 0.5 M H_2SO_4



	E_g	
	DFT	Exp.
β		
Ta_2O_5	2.07	3.9-4.5 [4]
Nb_2O_5	1.60	3.4 [25]
$NbTaO_5$	1.82	-

S. Clima et al., ECS Transactions, 19 (2) (2009) 729-737.

$\chi_{(Nb)}$= 1,585; Eg(Nb_2O_5) = 3.35 eV

$\chi_{(Ta)}$ = 1,475; Eg(Ta_2O_5) = 4,04 eV

$S_{l,th}$= 0,67; b = $S_{q,th}$ = 0,012; $\Delta E_{g(am)} \leq$ 0,10 eV

F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.

Conclusions and Problems

a) The reported variability in the experimental Eg values of SC, not always accounted for in the comparison, can originate from different sources pertaining to the different experimental techniques (Electron Energy Loss Spectroscopy (EELS), Variable Angle Spectroscopy Ellipsometry (VASE), Diffuse Reflectance Spectroscopy (DRS), Electric Field Modulated Reflectance (ER), Photocurrent Spectroscopy (PCS), etc..) as well as in the data treatment employed in deriving the band gap values.

b) The extension to ternary oxides of the initial correlation between optical band values of pure oxides and difference of electronegativity between oxygen and metallic cation, carried out by using the concept of "average cationic electronegativity", is confirmed to be able to account, quantitatively, for the composition dependence of Eg,opt of mixed oxides grown on Ta-Nb alloys.

a) The anodizing process and the incorporation of species from electrolytic solution can affect the "true band gap" of pure and mixed oxides. Such evenience must be taken into account in the data processing. Whenever possible, a comparison with the Eg values of pure crystalline phases should be carried out to exclude such a source of error.

Acknowledgements

The authors would like to thank:

- Prof. Andrei I. Mardaren from Johannes Kepler University-Linz (Austria)
- Prof. H. Habazaki from Hokkaido University, Sapporo (Japan)

for providing the Ta-Nb alloys investigated in this work.

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Milano, 30 Novembre 2018 - Politecnico di Milano

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Giornata di studio "Pietro Pedeferri"
Dalla ricerca all'industria: le nuove frontiere dell'ingegneria della corrosione

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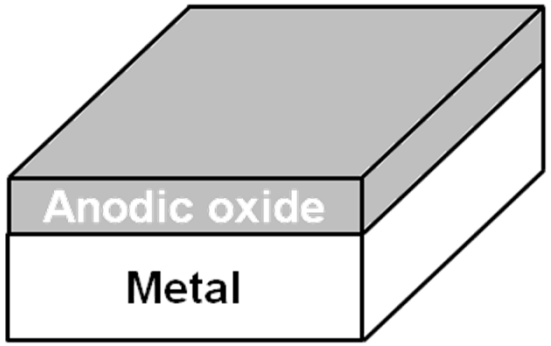
Band gap estimate by Spectroscopic Ellipsometry:

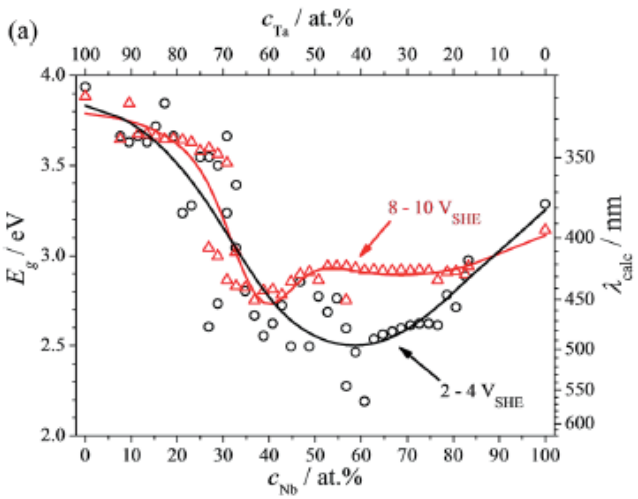
Two-layer model



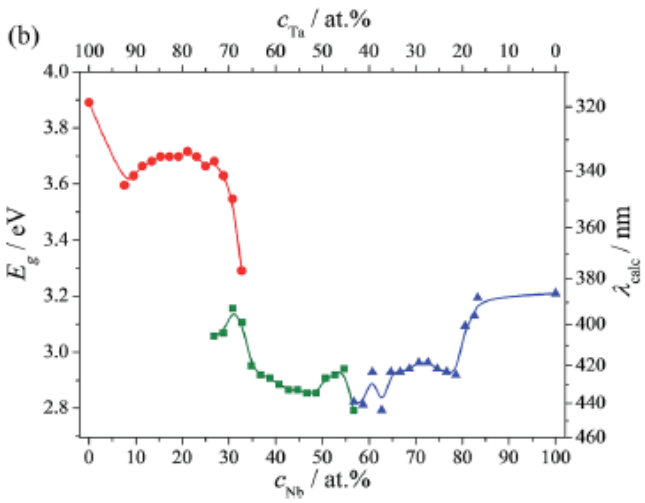
Oxide film described by a single Tauc-Lorentz (TL) oscillator:

$$E \geq E_g:\ \varepsilon_2(E) = \frac{A E_0 B (E - E_g)^2}{E\left((E^2 - E_0^2)^2 + (BE)^2\right)}$$

$$E < E_g:\ \varepsilon_2(E) = 0$$



Nb-Ta anodic oxides optical bandgap for thin and thick films

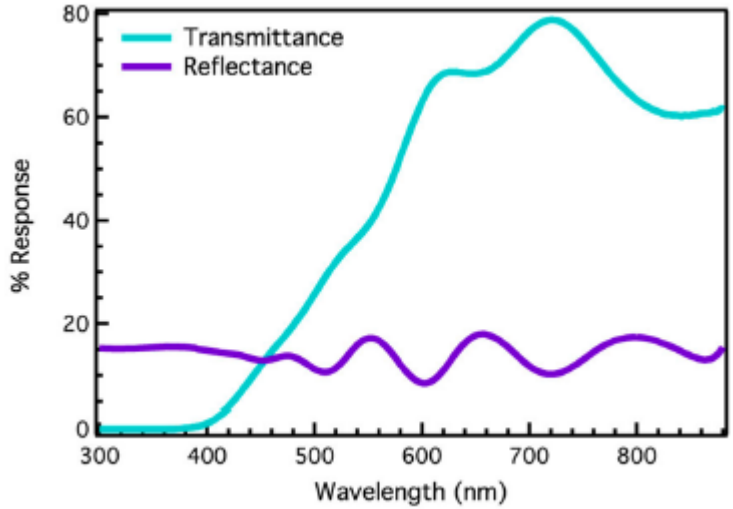


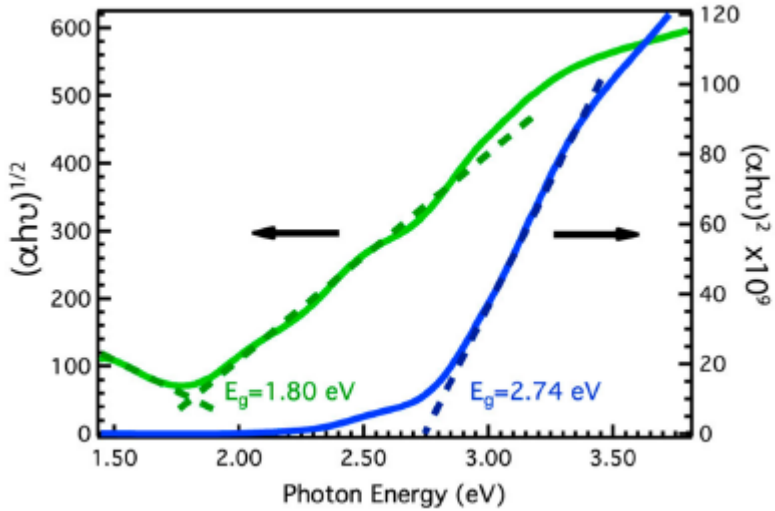
Nb-Ta anodic oxides optical bandgap obtained by fitting the optical dataset

W. Limberger et al., RSC Advances, 2016, 6, 79934–79942

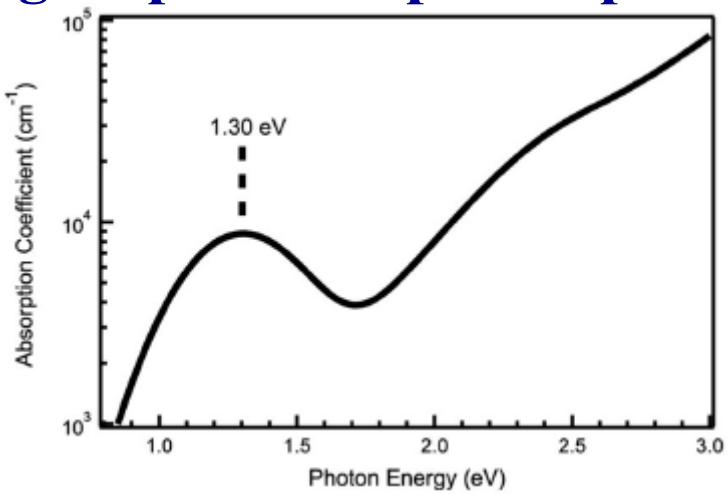
Band gap determination

γ-$Cu_3V_2O_8$





Variable Angle Spectroscopic Ellipsometry (VASE)



C.-M. Jiang et al., Chemistry of Materials, 29 (2017) 3334-3345.

The Schuster-Kubelka-Munk Theory

Assumptions

- incident light diffuse
- isotropic distribution (Lambert cosine law valid) , i.e. no regular reflection
- particles randomly distributed
- particles much smaller than thickness of layer

2 constants are needed to describe the reflectance:
absorption coefficient k
scattering coefficient s

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{k}{s}$$

Kubelka-Munk function
remission function

Kubelka-Munk Function

- mostly we measure R'_∞, i.e. not the absolute reflectance R_∞ but the reflectance relative to a standard
- depends on wavelength $F(R'_\infty)_\lambda$
- corresponds to extinction in transmission spectroscopy
- in case of a dilute species is proportional to the concentration of the species (similar to the Lambert-Beer law):

$$F(R'_\infty) \propto \frac{\varepsilon\, c}{s}$$

Deviations from & Limitations of the Kubelka-Munk Theory

incident radiation

- should be diffuse and not directed, however, it is assumed that after a few scattering events the distribution is isotropic
- directed incident radiation can be a problem on very rough surfaces: shadowing effects

any regular reflection

- will cause deviation

low reflectance values

- applicability of Kubelka-Munk theory questionable
- smallest error between $0.2 < R_\infty < 0.6$

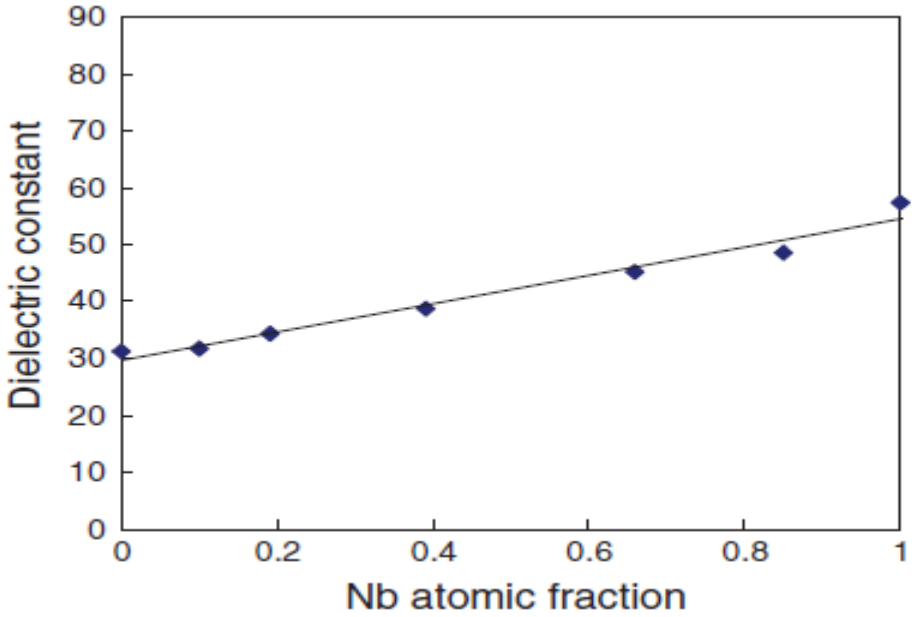
Anodic oxides grown on Nb-Ta alloys

Table 1 Results of RBS analyses for anodic oxide films formed on the magnetron-sputtered Ta–Nb alloys to 80 V at 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 293 K

Alloy composition	Anodic oxide film		
	Thickness (nm), outer layer/inner layer	Composition, outer layer/Inner layer	Density (Mg m^{-3}), outer layer/inner layer
Ta	125	Ta_2O_5	7.3
Ta–12 at.% Nb	2.5/128	$Nb_2O_5/(Ta_{0.89}Nb_{0.11})_2O_5$	4.2/6.6
Ta–22 at.% Nb	3/132	$Nb_2O_5/(Ta_{0.80}Nb_{0.20})_2O_5$	4.2/6.4
Ta–43 at.% Nb	4/144	$Nb_2O_5/(Ta_{0.59}Nb_{0.41})_2O_5$	4.2/5.8
Ta–70 at.% Nb	8/155	$Nb_2O_5/(Ta_{0.31}Nb_{0.69})_2O_5$	4.2/5.0
Ta–87 at.% Nb	12/168	$Nb_2O_5/(Ta_{0.14}Nb_{0.86})_2O_5$	4.2/4.5
Nb	186	Nb_2O_5	4.2

V_F = 80 V

S. Komiyama et al., Journal of Solid State Electrochemistry, 16 (2012) 1595-1604.



U_F = 5 V vs. Ag/AgCl

F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.

Experimental

Materials

Ta, Nb and Ta-Nb alloys dc Magnetron Sputtered on Glass Substrates

Targets: Nb disk (99.9%) and Ta disk (99.9%)

Nb (at.%)	100	85	66	61	19	0
Ta (at.%)	0	15	34	44	81	100

Anodizing:

a) Potentiodynamically at 10 mV s^{-1} in 0.1 M NaOH and ABE solution at different pH values; $U_f = 5V$ vs (Ag/AgCl)

b) Galvanostatically (50 A m^{-2}) in ABE solution; $U_f = 50V$

Characterization:

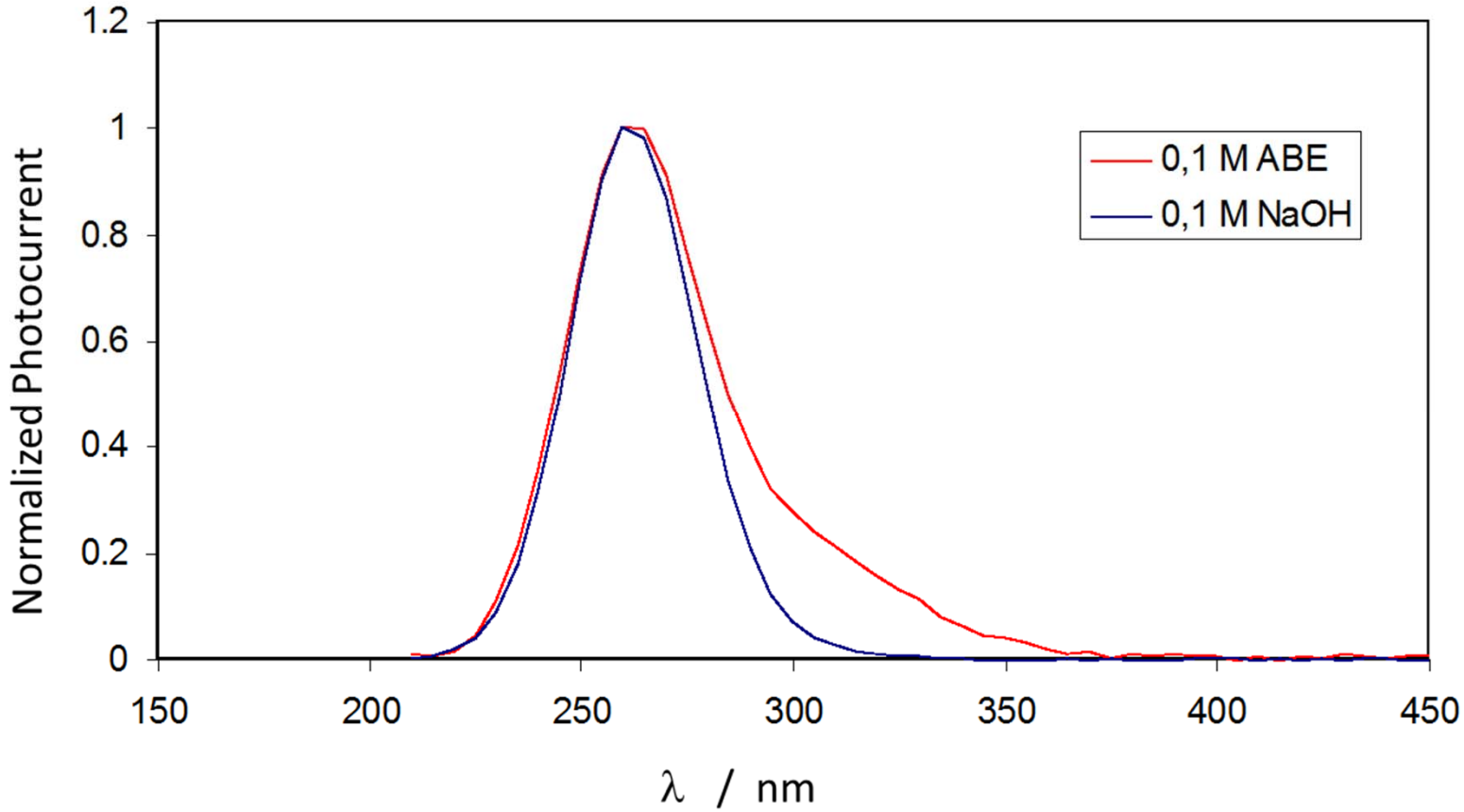
In situ PCS, EIS, DA in 0.5 M H_2SO_4 Solution

Ex situ GDOES, RBS, XRD, TEM

F. Di Franco et al., Electrochimica Acta 59 (2012) 382– 386.

Oxides characterization by PCS

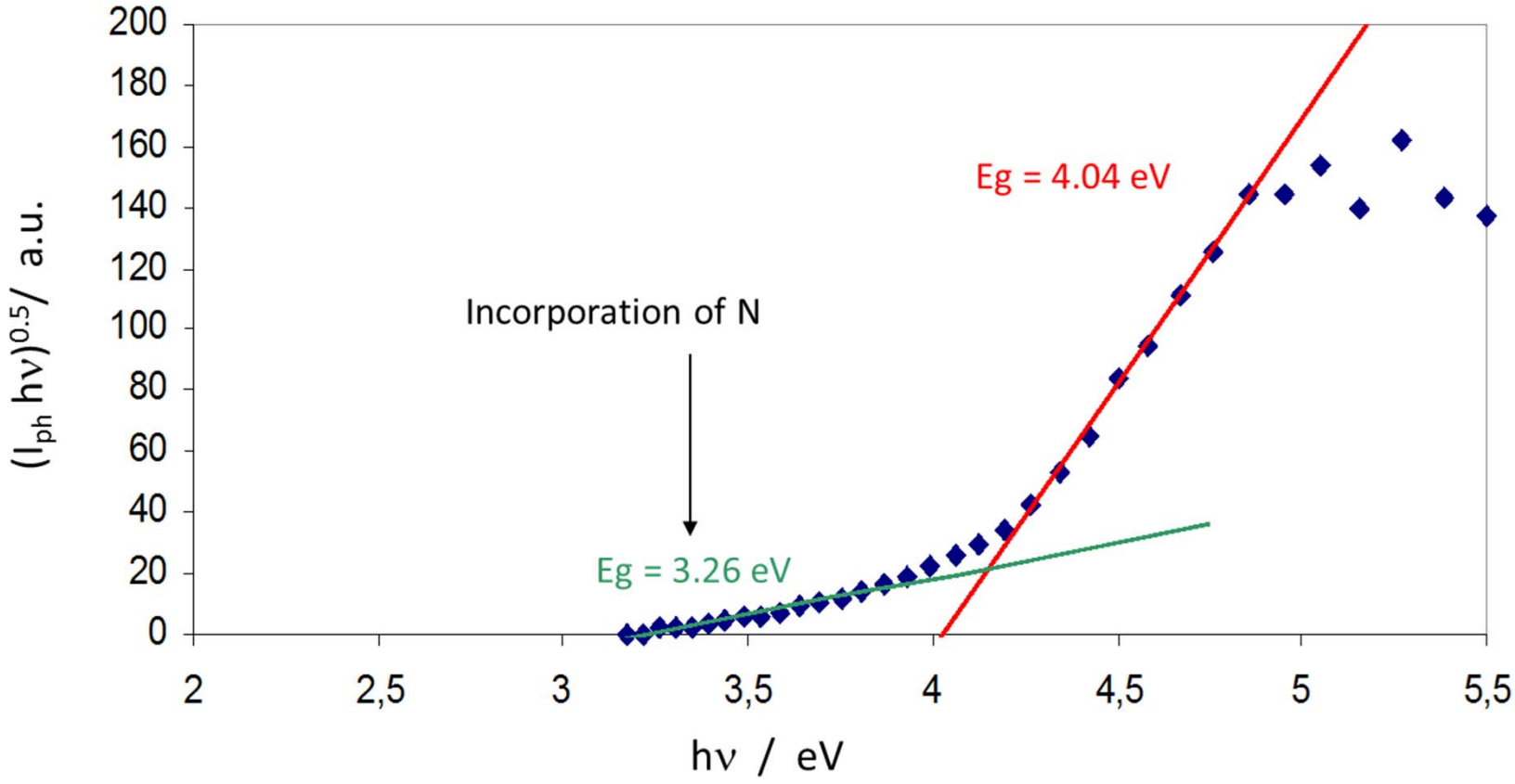
*Anodic film grown on **Ta** in 0.1 M ABE and 0.1 M NaOH, U_F = **5 V** vs. Ag/AgCl*
Characterization electrolyte: 0.5 M H_2SO_4, U_E = 1.5 V vs. Ag/AgCl



F. Di Franco et al., Electrochimica Acta 59 (2012) 382– 386.

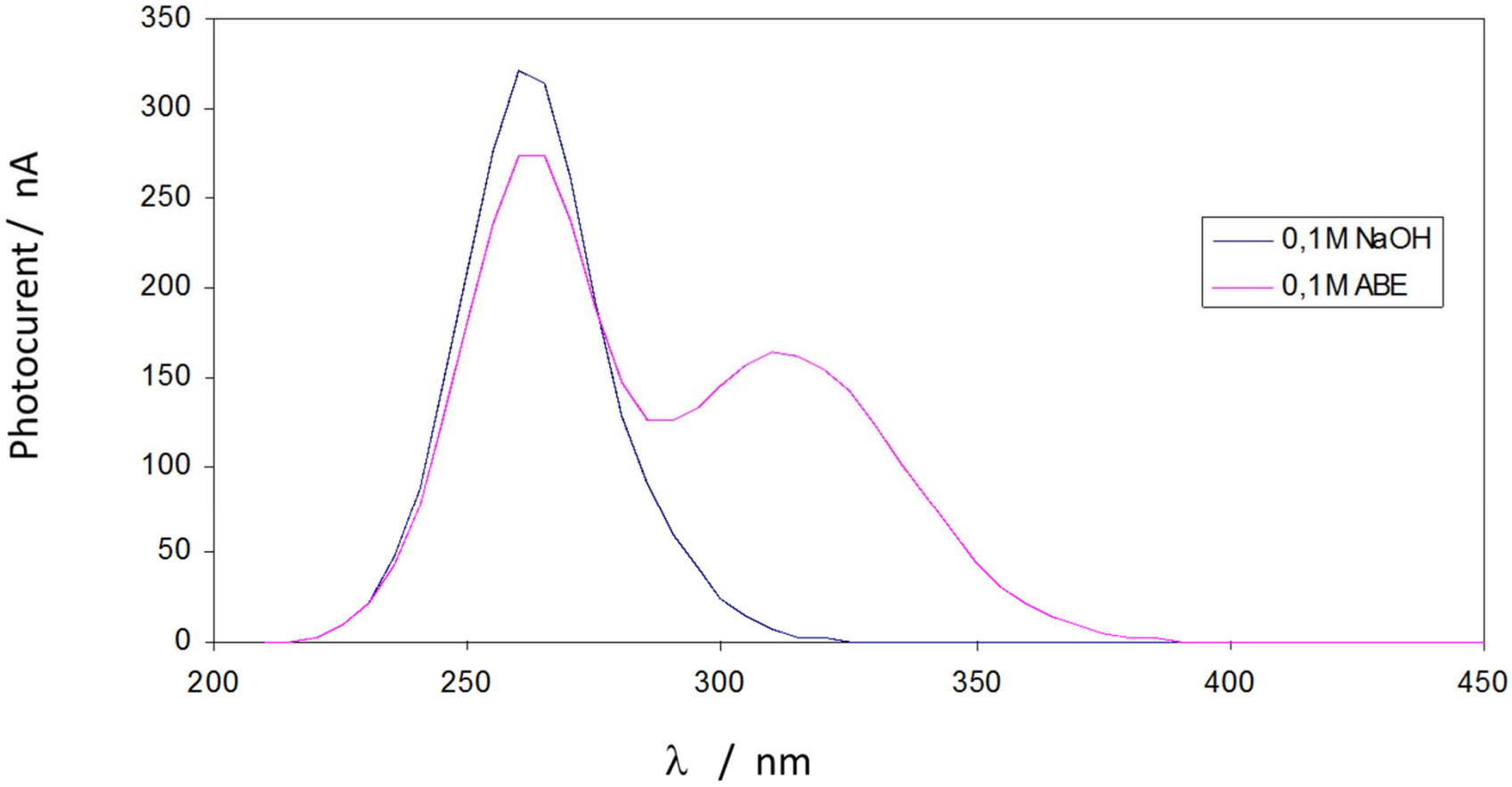
Oxides characterization by PCS

*Anodic film grown on **Ta** in 0.1 M ABE, U_F = **5 V** vs. Ag/AgCl*
Characterization electrolyte: 0.5 M H_2SO_4, U_E = 1.5 V vs. Ag/AgCl



Oxides characterization by PCS

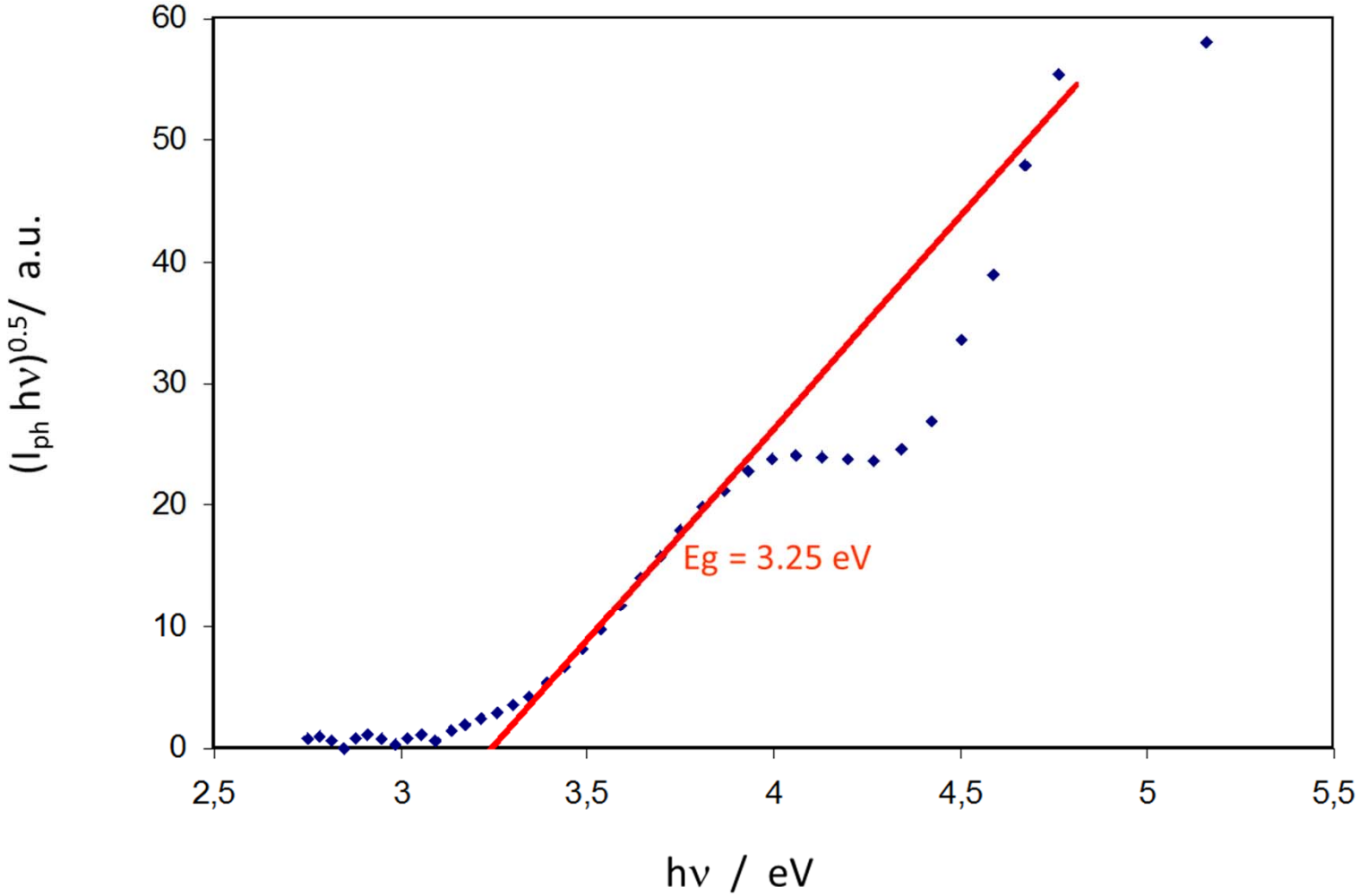
*Anodic film grown on **Ta** in 0.1 M ABE, U_F = **50 V** vs. cathode*
Characterization electrolyte: 0.5 M H_2SO_4, U_E = 3 V vs. Ag/AgCl



F. Di Franco et al., Electrochimica Acta 59 (2012) 382– 386.

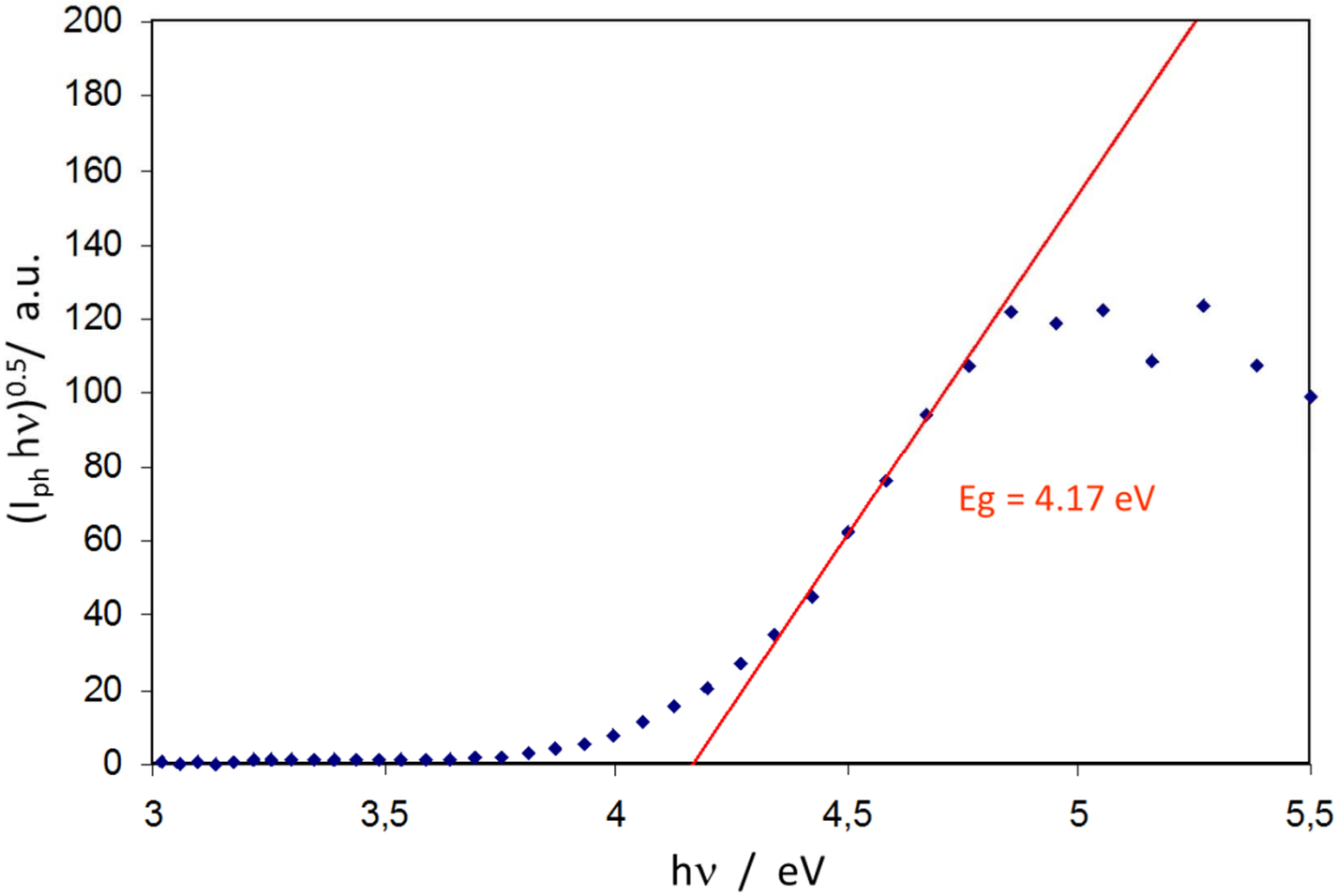
Oxides characterization by PCS

*Anodic film grown on **Ta** in 0.1 M ABE, U_F = **50 V** vs. cathode*
Characterization electrolyte: 0.5 M H_2SO_4, U_E = 3 V vs. Ag/AgCl



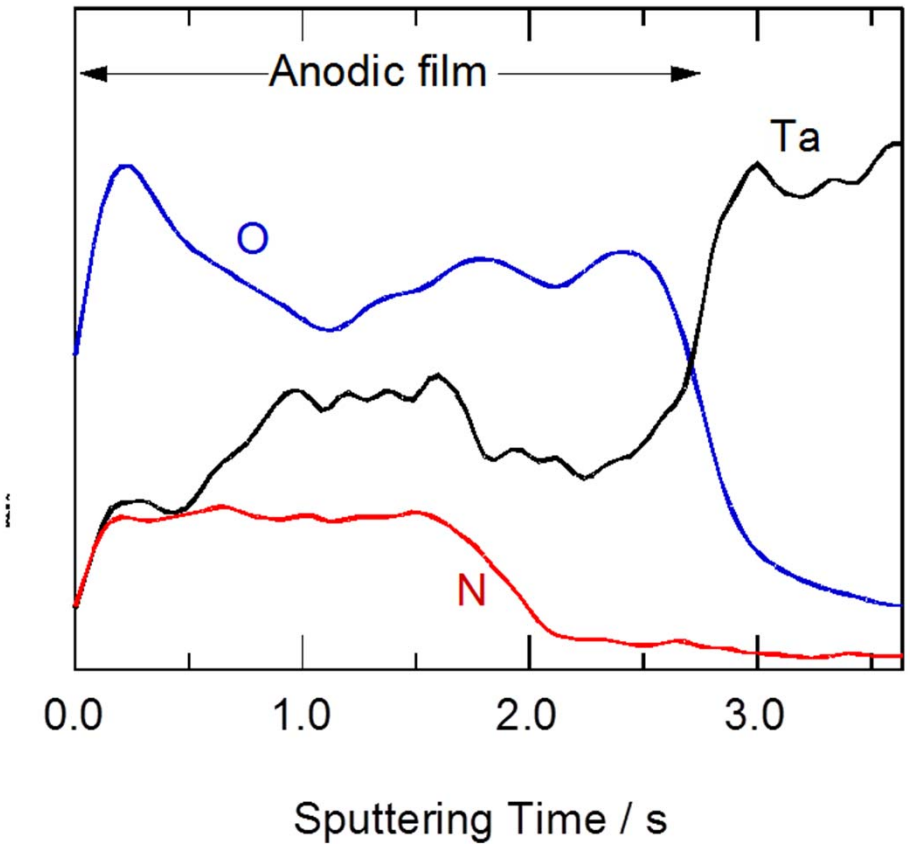
Oxides characterization by PCS

*Anodic film grown on **Ta** in 0.1 M NaOH, U_F = **50 V** vs. cathode*
Characterization electrolyte: 0.5 M H_2SO_4, U_E = 3 V vs. Ag/AgCl



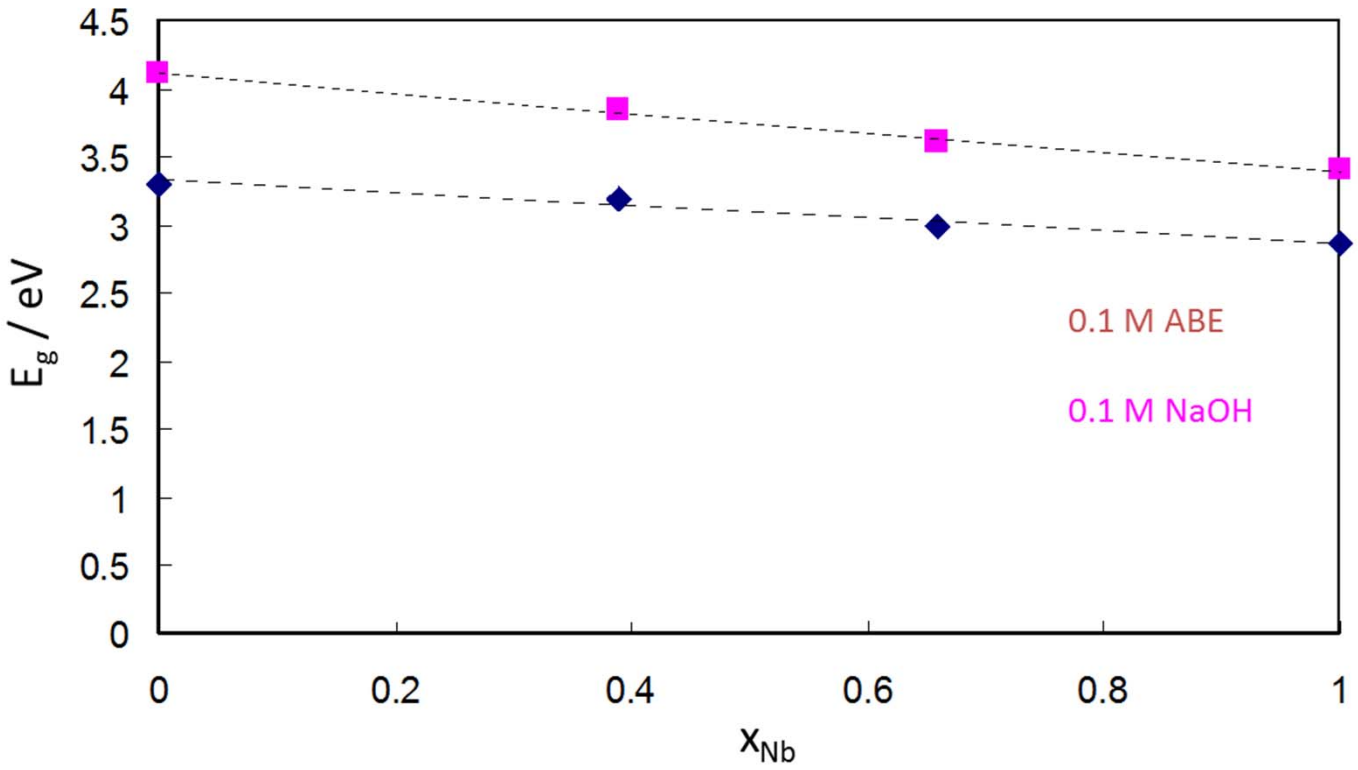
Oxides characterization by GDOES

Anodic film grown on **Ta** in 0.1 M ABE, U_F = **50 V** vs. cathode



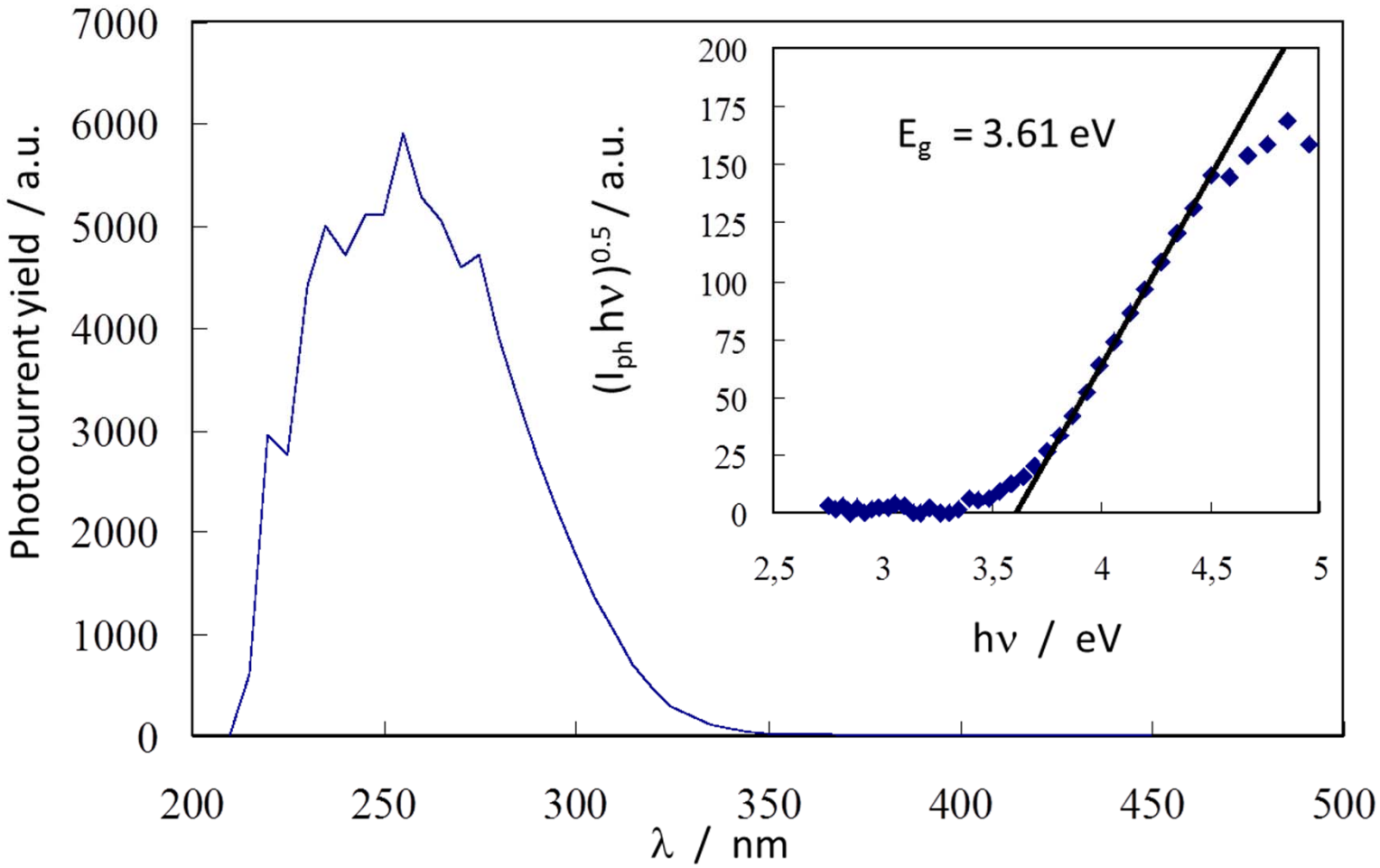
Band gap of mixed Ta-Nb oxides

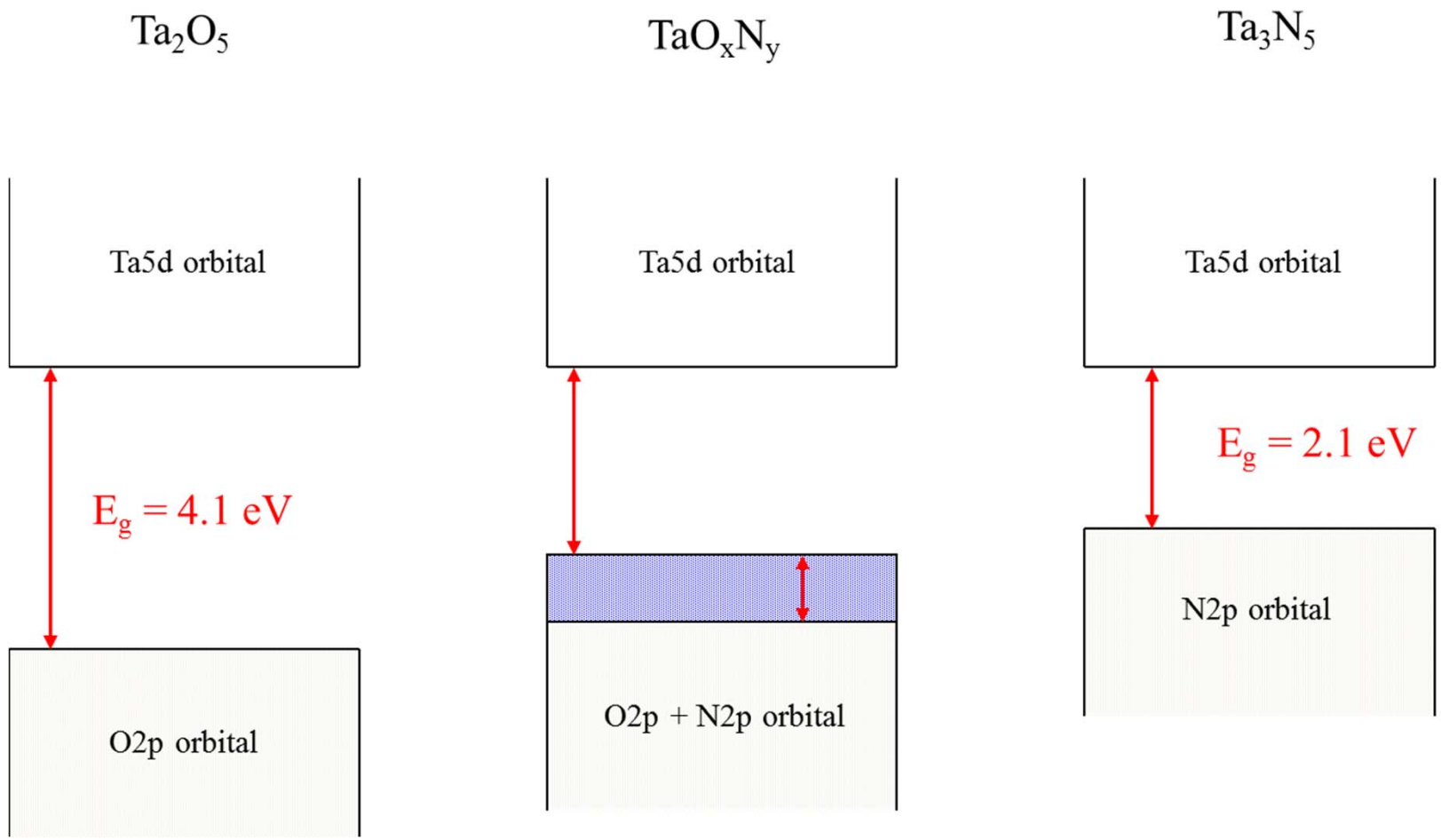
Effect of Electrolyte Composition



Oxides characterization by PCS

Anodic film grown on **Ta-66at%Nb** Alloys in 0.1 M NaOH, U_F = **5 V** vs. Ag/AgCl
Characterization electrolyte: 0.5 M H_2SO_4



F. Di Franco et al., Journal of The Electrochemical Society, 159 (2012) C33-C39.

Band structure of tantalum oxide, oxy-nitride and nitride