

# Electrochemical Formation of Semi-conducting Oxides for Solar Energy Conversion

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*Abstract:* - The formation of anodic oxide films on Nb electrodes in 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH, for potential region from 0 to 90 V SCE, have been investigated. The film thickness growth, refractive indices and dielectric constants of formed films, depending of applied potential and time of anodization, have been determined using ellipsometric method. By Raman spectroscopical measurements the amorphous structure of anodic oxide films, up to 10 V SCE and progressive evolution of crystallization from 10 to 90 V has been shown. The semi-conducting properties (n or p tip semi-conductor, energy gap and flat bend potentials) has been determined using photocurrent measurements.

*Key-Words:* - Nb oxides, semiconductors, ellipsometry, Raman spectroscopy, photo current measurements

## 1 Introduction

The semi-conducting electrodes can efficiently absorb sunlight and to produce an electrical current that leads to energy conversion. Niobium oxides is now starting to replace tantalum oxides as a dielectric material in specific capacitors for the electronic industry. They are also other potential application for opto-electronic screens and solar energy conversion cells, since the oxides show electrochromic and photo-electrochemical properties [1]. By anodic oxidation of Nb in aqueous media yields an oxide film of uniform thickness whose approximate composition is Nb<sub>2</sub>O<sub>5</sub>. Applying different electro-chemical perturbations can modify the semi-conducting properties of this film. Niobium is an easily passivated metal with high corrosion resistance in most common aqueous solutions [2]. It is a valve metal whose thin passive film may be easily thickened by anodization [3]. The anodic oxide growth occurs by high field ion migration in the film. During the electrochemical oxidation, the electronic conductivity in the film remains negligible compared to ionic conductivity and the electric field is uniform throughout the film. The rates of electron transfer reactions at oxide covered metal electrodes were observed to be much slower than of bare metal electrodes [4]. The semi-conducting properties of anodic oxides on Nb can changed in a wide range simply by varying the thickness of the oxide film. The anodic oxide layers always contain a deficit of oxygen which leads to the formation of oxide vacan-

cies. The stoichiometric defects act as electron donors and the kinetics of electron transfer reaction at the amorphous anodic oxide is also described by the theory which uses the concept of energy bands developed for well crystallized materials [5]

## 2 Problem Formulation

In spite of the work already done, there remain a number of questions concerning the influence of the forming electrolyte and applied potential on the dielectric behavior on Nb/Nb<sub>x</sub>O<sub>y</sub>/electrolyte system, which have yet to be addressed. Taking into account the potential application of semi-conducting niobium oxides in solar energy conversion cells, the aim of this work is to define some crucial electrochemical, optical and semi-conducting parameters during the anodic synthesis of niobium oxides on Nb electrodes in acid and hydroxide electrolytic solutions. Our investigations will be focused on the influence of: oxide film grown depending of applied potential and time of anodization, kinetic law of oxide film growth, amorphous and crystallographic structure, electrochemical conditions for transformation of amorphous structure etc. to the crystallographic form and evolution of crystallization with rising the anodic potential and variation of semi-conducting properties depending of film thickness. We strongly believe that the new obtained data will successfully serve in the future application of niobium oxides as cells in solar energy conversion.

### 3 Problem Solution

The electrochemical parameters for formation of thin oxide films on Nb surfaces can be most easily determined by potentiodynamic methods.

Fig. 1. shows potentiodynamic I/E profile of Nb electrode in 1 M KOH.

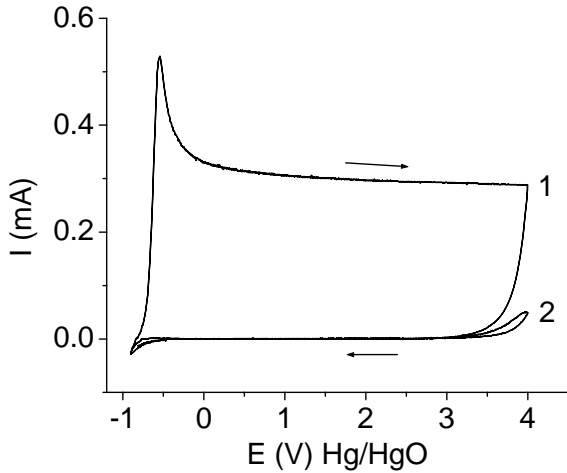
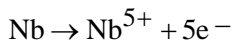


Fig.1. Potentiodynamic curves of electropolished Nb surface in 1 M KOH ( $v = 200 \text{ mV/s}$ ). 1 – 1-st cycle, 2 – 2-nd cycle

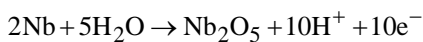
This profile consists active/passive transition that involves active metal dissolution followed by formation of poorly conducting passive film. The potential sweep was initiated at  $-0.9 \text{ V}$  where negligible cathodic current is observed and ended at  $4 \text{ V}$  where the passive film of about  $90 \text{ nm}$  is formed.

The higher initial value of the current in  $1 \text{ M KOH}$  solution with comparison with  $1 \text{ M H}_2\text{SO}_4$  is a consequence of the shift of the beginning of oxide growth to more negative potentials as pH increases. This assumption has been proved by our in-situ ellipsometric measurements and the anodic passive film was found to be thicker in  $1 \text{ M KOH}$  than in  $1 \text{ M H}_2\text{SO}_4$ .

As suggested in ref. [6-7] the electrode dissolution in the active region occurs via the reaction :



while in the passive region the film thickness grows according to the reaction:



The progress of each reaction depends on the electrolytic concentration, surface pre-treatment and initial electrochemical conditions.

In the first reverse cycle no cathodic peaks was observed, up to  $-0.9 \text{ V}$ . The passive film formed in the 1-th scan can not be cathodically reduced. In the second and the next subsequent cycles, large current plateaus, with values close to zero, were recorded for both forward and reverse scans.

During the anodic oxidation of Nb electrode in  $1 \text{ M H}_2\text{SO}_4$  and  $1 \text{ M KOH}$  for potential region from  $0$  to  $90 \text{ V}$  the film thickness growth. This growth and optical constants of the anodic oxide films were determined by in-situ ellipsometric measurements [8]

On fig.2 the the film thickness growth as a function of applied potential, obtained by in-situ ellipsometric parameters  $\Delta$  and  $\psi$ , is shown. As it can seen from fig.2. there exists two linear plots with two different slopes, indicating two different mechanisms of film thickness growth. From the slope of linear plots the coefficient of film thickness growth  $\alpha$  are calculated. For lower applied potentials, from  $0$  to approx.  $10 \text{ V}$  the coefficient  $\alpha_1 = 2.55 \text{ nm/V}$ , while for higher applied potentials, approx. from  $10$  to  $90 \text{ V}$  this coefficient  $\alpha_2 = 2.28$

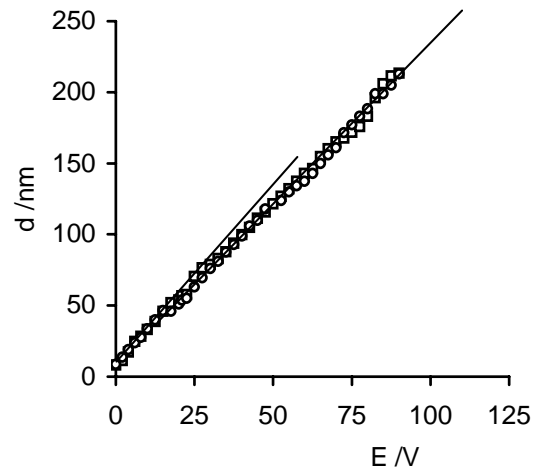


Fig.2. Film thickness growth as a function of applied potentials of Nb electrode in  $1 \text{ M KOH}$ .

In Table 1 the calculated values from ellipsometric measurements are listed.

Table 1. Coefficients  $\alpha$  and complex refractive indexes  $n$  of formed anodic oxide films

Electrolyte	$\alpha_1$	$\alpha_2$	$n$
$1 \text{ M H}_2\text{SO}_4$	2.52	2.25	$2.345(1-0.0005i)$
$1 \text{ M KOH}$	2.55	2.28	$2.347(1-0.0007i)$

From parameters in table 1 it can conclude that the anodic oxide films in KOH are a little bit thicker

than in 1 M  $\text{H}_2\text{SO}_4$  and that in the both electrolytes the formed film are nearly transparent. The refractive indices in 1 M KOH are also a little bit higher than in 1M  $\text{H}_2\text{SO}_4$  indicating that the anodic oxide film formed in 1 M KOH is more conductive than in 1 M  $\text{H}_2\text{SO}_4$ .

With ellipsometric measurements the kinetic law of film thickness growth with time for various fixed potentials have been also determined.

Fig.3. shows logarithmic film thickness growth at one fixed applied potential in both electrolytes.

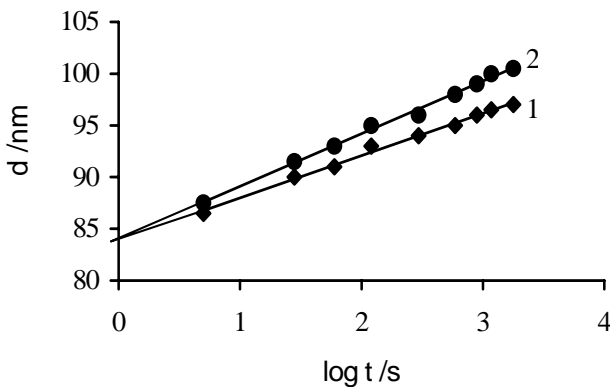


Fig.3. Film thickness growth of anodically formed films on Nb electrode at voltage of 40 V. 1 – 1M  $\text{H}_2\text{SO}_4$ , 2 – 1M KOH

From linear plots in fig. 3 it can be proved again that the anodic oxide films are thicker in 1 M KOH than in 1 M  $\text{H}_2\text{SO}_4$ . The logarithmic law begins to deviate from linear plots at fixed potentials of 80 and 90 V, as a result of significant film breakdown processes during its formation.

The structure of anodic oxide films has been investigated by Raman spectroscopical measurements using red laser at a power of 1 mW.

In fig.4. the Raman spectra obtained at lower anodic potentials, up to 20 V are shown. For thinner passive films formed in 1 M KOH and in 1 M  $\text{H}_2\text{SO}_4$ , no active Raman bands were monitored (spectrum 1), confirming the amorphous structure of the passive films. The appearances of first Raman bands at anodic potential of 10 V are due from initial crystallization of amorphous film. At this potential two broad and ill defined Raman bands located at 230 and 690  $\text{cm}^{-1}$  appear (spectrum 2). With increasing the anodic potential these two bands rise in intensity (spectrum 3) and become less broad. They can be attributed to  $\text{H-Nb}_2\text{O}_5$  and  $\text{NbO}_2$  respectively [9]. According to literature data, all Raman bands in 200-300  $\text{cm}^{-1}$  wave number region are assigned to the bending modes of the Nb-O-Nb [9]. The associated symmetric and anti-symmetric stretching

modes appear in the higher wave number region (400–800  $\text{cm}^{-1}$ ).

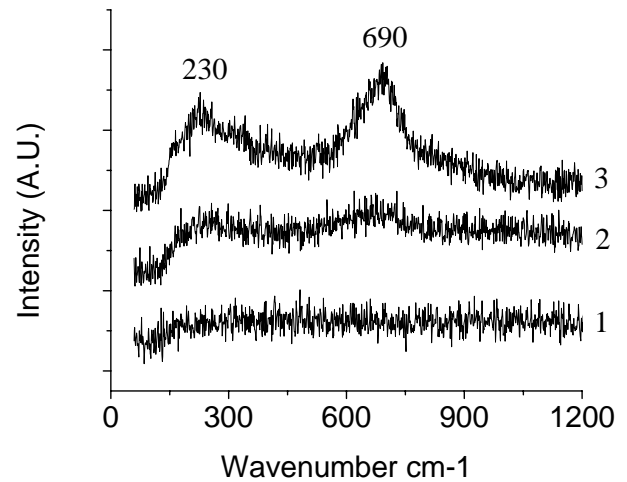


Fig.4. Raman spectra of 1 - passive films formed at 4 V, 2 - anodic oxide film formed at 10 V and 3 - anodic oxide film formed at 20 V in solutions of 1 M  $\text{H}_2\text{SO}_4$  and/or 1 M KOH

The wave number region from 800-1200  $\text{cm}^{-1}$  is characteristic for the symmetric and anti-symmetric stretching modes of Nb=O terminal double bond in the structure of  $\text{Nb}_2\text{O}_5$ .

With further increasing the anodic potential from 20 to 90 V, the bands rise in intensity and additional bands located at: 261, 305, and 995  $\text{cm}^{-1}$  appear. At 90 V, fig.5. the Raman band at 690  $\text{cm}^{-1}$ , characteristic for  $\text{NbO}_2$  is split into two new bands located at 628 and 680  $\text{cm}^{-1}$  assigned to the transformation of  $\text{NbO}_2$  to the  $\text{Nb}_2\text{O}_5$

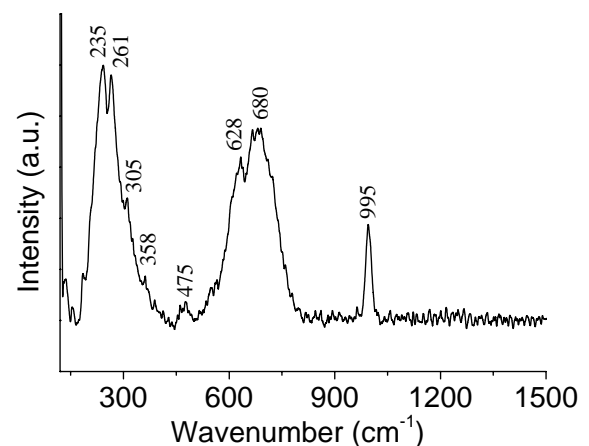


Fig.5. Raman spectrum of anodically oxidized Nb in 1 M  $\text{H}_2\text{SO}_4$  at potential of 90 V

The strong band at 995  $\text{cm}^{-1}$ , medium bands at 628 and 261  $\text{cm}^{-1}$  can be attributed to  $\text{Nb}_2\text{O}_5$ .

It is evident at higher anodic potentials the oxide films consist only  $\text{Nb}_2\text{O}_5$ .

For determining the semi-conducting properties of anodic oxide films in 1 M  $\text{H}_2\text{SO}_4$  and 1 M KOH the photocurrent measurements on Nb electrode with various thickness of oxide films were performed.

Illumination of the oxide films with light of energy greater than, or equal to the band gap energy  $E_g$ , can excite electrons from the valence band to the conduction band.

It is well known that the majority of solar irradiation is centered in the region between 1 and 3 eV. The use of semiconductor with smaller band gap energy than 3 eV would be advantages to absorb of most of the solar spectrum. The semiconductors with band gaps energy between 1.1 and 1.7 eV are the best absorbers for solar energy conversion devices.

The photocurrent spectra on fig.6. show that the photocurrent maximum shifts to higher values of wavelength if the oxide films are formed at the higher anodic potentials. This shift is a result of stepwise increase the film breakdown. The intensity of film breakdown influenced to the intensity of photocurrent maximum.

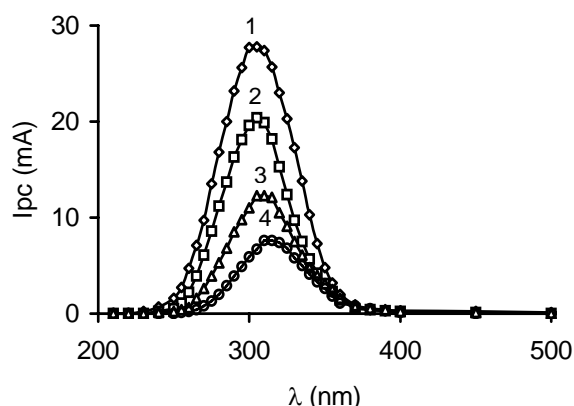


Fig.6. Photocurrent spectra of anodically polarized Nb in 1 M  $\text{H}_2\text{SO}_4$  at: 1 – 10 V; 2 – 50 V; 3 – 70 V; 4 – 90 V.

From photocurrent spectra on fig.6. the band gap energies were determined, Table 1. As it can be seen from Table 1, the band gap energies in both electrolyte is very similar for each applied potential, confirming that there is no significant difference in conductivity of both films. But the thicker films have smaller band gap energy and are more suitable for solar energy conversion. Large band gap materials, such as  $\text{Nb}_2\text{O}_5$ , will therefore only absorb at short wavelengths and will not absorb as many photons from sunlight as small band gap semiconductors such as Si.

On Table 1 are also listed the values of flat band potentials  $E_{fb}$ , (potential of zero electrical field, i.e. when the sign change of the current occurs).

Table 1. Photocurrent parameters of anodic oxide films

Pot (V)	1 M $\text{H}_2\text{SO}_4$		1 M KOH	
	$E_g$ (eV)	$E_{fb}$ (V)	$E_g$ (eV)	$E_{fb}$ (V)
10	3.14	-0.450	3.10	-0.98
20	3.13	-0.455	3.09	-1.10
30	3.13	-0.460	3.08	-1.20
40	3.12	-0.470	3.07	-1.30
50	3.12	-0.485	3.07	-1.35
60	3.10	-0.500	3.06	-1.40
70	3.08	-0.520	3.04	-1.44
80	3.04	-0.575	3.02	-1.47
90	3.00	-0.620	2.98	-1.49

Taking into account that the flat band potential depends of pH, film thickness, structural defects in the film, etc. it is expected that its values will shift in cathodic direction with film thickness grows and that this shift will be more pronounced in 1 M KOH than in 1 M  $\text{H}_2\text{SO}_4$ .

To optimally create charge and effectively produce a photocurrent, the semi-conductors need to be thick enough to absorb essentially all the photons. In the thicker films increase the concentration of the ionized donors which influenced on the stoichiometric participation of oxygen and niobium in the formed films. With increasing the film thickness increase the carriers concentration gradient on the interface oxide film/electrolyte. As a result of redistribution of carriers in the thicker films the bending of valence and conducting bands are greater, so that the flat band potential shift in cathodic direction.

## 4 Conclusion

The thickness of the anodic oxide films on Nb electrode in 1 M  $\text{H}_2\text{SO}_4$  and 1 M KOH increase linearly with applied potential and in the potential region between 0 and 90 V two linear plots with two different slopes can be distinguished.

Raman spectra confirmed that these two different plots are in close relation with amorphous and crystalline structure of the film. The chemical composition of anodic oxide films on Nb electrode for amorphous structure of the film is a mixture of  $\text{NbO}_2$  and  $\text{Nb}_2\text{O}_5$ . For crystalline structure of the film the  $\text{NbO}_2$  transforms into  $\text{Nb}_2\text{O}_5$ .

From photocurrent spectra the determined band gap energies fall in the region from 3.14 eV for potential

of 10 V to 3.00 eV for potential of 90 V in 1 M H<sub>2</sub>SO<sub>4</sub> and in the region from 3.1 eV for potential of 10 V to 2.98 eV for potential of 90 V in 1 M KOH. The anodic oxide films formed in 1 M KOH and at higher anodic potentials are more conductive than the films formed in 1 M H<sub>2</sub>SO<sub>4</sub> and at lower anodic potentials.

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