

## Electrode Processes in Electrochromic Anodic Oxide Films on Niobium

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### ABSTRACT

We review the following issues: peculiarities of polycrystalline AOP development at niobium in nitrate salt melt at temperatures of Nb<sub>2</sub>O<sub>5</sub> recrystallization, the mechanisms of change in structure and properties of niobium pentoxide in the result of electrode processes under cathodic polarization (at the model structure of polycrystalline film), as well as the methods of amorphous electrochromic AOP development and ways of electrochromic processes optimization at such films.

### Keywords

Anodic film, niobium, electrochromism

### INTRODUCTION

Anodic oxide films (AOF) of niobium Nb<sub>2</sub>O<sub>5</sub> are widely used for generation of solid-electrolyte capacitors (SEC), which implement electric capacitance in «Nb – AOF Nb<sub>2</sub>O<sub>5</sub> – electrolyte» system (MOE – system), and electrochromic indicating devices (EID), operating due to electrochromic effect (ECE) – reversible change of optical and electrophysical properties of Nb<sub>2</sub>O<sub>5</sub> films at alternate electrochemical polarization in MOE-systems.

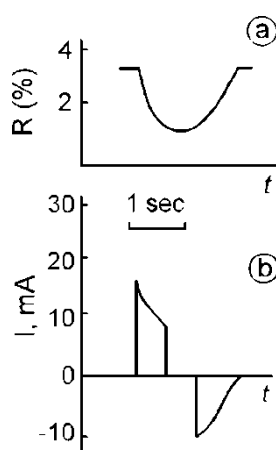
### 2. Experimental

In the present survey for the purpose of experimental verification of possibility of ECP activation in amorphous niobium pentoxide by changing of the morphology of oxide surface it has been developed a method of producing of amorphous Nb<sub>2</sub>O<sub>5</sub> films possessing developed surface. It is known [1] that the anodic oxide film (AOF) on aluminum can be produced with a porous surface in electrolytes which etch oxides. Thus, oxide layers produced in an electrolyte containing etching ingredient - hydrofluoric acid (HF) is considered as the key object of study in this work. Niobium in the form of foil, annealed at the temperature of 2300K in vacuum, not less than 10<sup>-5</sup> Torr, has been oxidised in electrolyte containing 25 ml of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and 25 ml of HF per liter of water alternating asymmetric current with cathode half-cycle to anodic amplitude ratio in the amount of 5:1 in two stages: first at a fixed current density  $j = 5 \text{ mA/cm}^2$  (galvanostatic mode) up to a voltage of 40-50 V, and then at a fixed voltage  $U = 10\text{V}$  (voltstatic mode) for 20-30 minutes.

The resulting films had a light gray uniform color. The oxide layer thickness was dependent on the oxidation mode, and ranged from 0.2 - 0.3 mm with a shutter speed within 1 hour at a voltage of 50 V. The films are amorphous, as evidenced by the halo electron diffraction obtained from them.

### Results and Discussion

Figure 1 shows time dependencies between the intensity of the reflected light and current received for Nb<sub>2</sub>O<sub>5</sub> AOP (coloring voltage was 1 V, area of the sample  $S = 0,5 \text{ cm}^2$ ).



**Fig:1 The time dependence of the intensity of the reflected light (a) and the current (b).**

Thus, the applied method of niobium oxidation allows obtaining of amorphous films of Nb<sub>2</sub>O<sub>5</sub> with apparent ECE, as a result of oxide surface development. The resulting oxide layers can withstand not less than 10<sup>6</sup> cycles of staining - bleaching, as well as long-term storage without any signs of degradation.

Given results support the decisive role in the ECE oxide surface. Detection of correlations between surface morphology and ECE efficiency contributes to optimization of Nb<sub>2</sub>O<sub>5</sub> electrochromic amorphous films producing technique, by means



of both anodic oxidation and vacuum condensation, which reveals prospects of niobium pentoxide application in electrochromic display devices.

An alternative was found to electrochrome process (ECP), and it is the process of recombination of hydrogen atoms emitted on the surface anode oxide film (AOF) and their subsequent evacuation as gas bubbles, which considerably limits the ECP rate. We have found that when Nb<sub>2</sub>O<sub>5</sub> AOF is polarized by the packages of microsecond pulses, starting potential of gas emission can be enhanced three- to fivefold, which promotes significant increase in current density on film electrode, and, thus, raises the ECP rate.

A number of papers discuss the emergence of states differing in their life times and emergence nature on AOF surfaces. Thus, slow surface states (SSS) generated by the electrolyte chemisorbed ions participate in adsorption and even initiate it [2].

It is found that ECP can take place similarly to the catalytic mechanism of dissociated chemisorption. Kinetic factors of such mechanism can be taken into account upon the examination of diffusion equation and Frumkin's isotherm [3]. The equation first term contains Q parameter, characterizing the extent of surface filling during adsorption. It is possible that Q parameter, constant for normal conditions, can grow by the superposition of packages of microsecond-duration pulses, i.e. electroadsorption effect is realized. The Q growth accelerates ionization of hydrogen atoms and their subsequent diffusion to the AOF solid phase, and prevents the development of rivaling recombination and gas emission processes.

At analysis of the field effect on Ge, the authors [21] have determined that attachment of transverse electric field pulses to the sample causes positive charge accumulation in the surface states (related to water adsorption). Such accumulation is observed due to the fact that a positive charge is not capable to discharge within the time between pulses.

It has been shown that the pulses of transverse electric field, applied to the sample, result in the accumulation of positive charge in SSS associated with water adsorption, which has no time to resolve in the interpulse period. The "accumulation effect" was explained by electroadsorption. In our case, it is also evident that polarization of pulses with period-to-pulse duration ratio smaller than the SSS life times result in the increase of surface concentration of OH<sub>3</sub><sup>+</sup> - groups, caused by the accumulation effect, and in subsequent discharge of hydrogen atoms.

In other words, the application of pulse electrochemical polarization by the packages of microsecond pulses with low period-to-pulse duration ratio promotes significant increase of ECP rate in niobium pentoxide at the expense of added filling of AOF surface by hydrogen ions.

## References

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