

УДК 621.357.12.

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POTENTIAL MODIFICATION OF ELECTROCHEMICAL PROPERTIES IN ANODE NIOBIUM PENTOXIDE

У роботі запропонована методика формування анодних оксидних плівок Nb_2O_5 , що володіють електрохромним ефектом (ЕХЕ). Встановлено, що поляризація оксидів пакетами мікросекундних імпульсів підвищує в 3-5 разів потенціал почала газовиділення і, таким чином, підвищує густину струму на електроді, інтенсифікуючи ЕХЕ.

In the present work the technique for generation of electrochrome effect (ECE) in Nb_2O_5 amorphous anodic oxide films (AOF) is proposed. We have also found that when AOF is polarized by the packages of microsecond pulses, initial potential of gas emission can be increased three- to fivefold, which promotes significant increase in current density on film electrode, and, thus, raises the ECE.

Introduction. Until the present time electrochromism has been observed and studied in Nb_2O_5 polycrystalline anode layers which, unlike amorphous ones, demonstrate pronounced electrochrome properties [1].

These differing (from the electrochrome effect viewpoint) properties of Nb_2O_5 amorphous and polycrystalline anode films make us turn our attention to the surface morphology of oxide layers, since the volumetric properties of amorphous Nb_2O_5 are known to be favorable for electrochromism. The comparison of Nb_2O_5 amorphous and polycrystalline layers reveal multipores surface in polycrystalline oxides, and highly unbroken surface in amorphous ones.

Experimental Details. The technique for generation of anode layers with highly developed surface has been devised to examine the realization of potential electrochromism in Nb_2O_5 amorphous anodic films by surface development in these films. It is known [2] that in aluminium, AOF can be obtained with porous surface in oxide-etching electrolytes. Hence, oxide layers, obtained in etching component-containing-hydrofluoric acid (HF) – electrolyte were our object of study. Niobium as a foil annealed under 2200 K in a vacuum not less than 10^{-5} Torr was oxidized in electrolyte, containing 25 ml of orthophosphoric acid (H_3PO_4) 25 ml of pure HF per 1 liter of water, by alternate asymmetrical current with 5 : 1 ratio of cathode half-period amplitude to anode one, by two stages: first, under

fixed current density $j = 5 - 7 \text{ mA/cm}^2$ up to the voltage of 40 – 50 V, and then under fixed voltage $U = 10 \text{ V}$ (voltstatic mode) for 20 to 30 min. The films obtained had uniform light gray color. Oxide layer thickness was dependable on the oxidizing conditions, and varied from 0.2 – 0.3 nm under above specified conditions, to 30 nm upon 1-hour exposure under 50 V voltage. The anode oxide thickness was determined by the weight technique of [2].

Discussion. The anodic films obtained by this technique are amorphous, which is evidenced by haloes on electron diffraction patterns. Also generated niobium pentoxide films possess typical electrochromic properties.

It should be emphasized that despite the fact that the metal-semiconductor phase transition with absorption jump-including ECE scenario, reported in [3], relates to polycrystalline Nb_2O_5 AOF, it is rather probable that in obtained amorphous AOF of niobium pentoxide, the ECE mechanism is also similar to above described model.

We would notice that, as was shown in [4], the absence of distant order in amorphous structure, generated during anodic oxide growth, does not result in the suppression of such phase transition as we have considered above, in AOF. An alternative was found to the ECE, and it is the process of recombination of hydrogens emitted on the surface of AOF and their subsequent evacuation as gas bubbles, which considerably limits the ECE rate. A number of papers discuss the emergence of states differing in their life times and 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 [5].

It is found that ECE can take place similarly to the catalytic mechanism of dissociated chemisorption [6]. Kinetic factors of such mechanism can be taken into account upon examination of diffusion equation [7]. The equation first term contains Θ parameter, characterizing the extent of surface filling during adsorption. It is possible that Θ parameter, constant for normal conditions, can grow by the superposition of packages of microsecond-duration pulses, i.e. electroadsorption effect is realized.

The Θ 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.

It has been shown earlier [8], 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 results in the increase of surface concentration of OH^+ – groups, caused by the accumulation effect, and in subsequent discharge of hydrogen atoms.

In other words, the application of pulse polarization by the packages of micro-second pulses with low period-to-pulse duration ratio promotes significant increase of ECE rate in Nb_2O_5 at the expense of added filling of AOF surface by hydrogen ions.

The electron Auger spectroscopy study of AOF phase structure upon layer-by-layer etching by argon ions showed that the generated films look like “sandwich” of Nb_2O_5 , NbO_2 and NbO phases (in the direction from oxide surface to the niobium). In this process, during anodization, oxygen actively dissolves in niobium substrate and penetrates into it by the thickness considerably exceeding the oxide thickness. This phenomenon is caused by high getter properties of niobium with regard to oxygen at 600 – 800 K [9] and can significantly affect the mechanical and electrophysical characteristics of generated structure because of structural modifications in metal/oxide surface. X-ray photography made in irradiation of chromium anode permitted identify the oxide film outer layer as low-temperature modification of niobium pentoxide with pseudo hexagonal lattice and elementary cell parameters such as $a = 0.3607\text{nm}$, $c = 0.3925\text{ nm}$.

The studies of possible inclusion of electrolyte components into the oxide led to the result, appearing contradictory at first glance: during its grown the oxide is saturated not only with anions (as might be expected in similarity with anodization in water electrolytes) but with cations as well. So, nitrogen concentration in the film is seen to be maximal in the niobium substrate- adjacent layer and diminishes towards the AOF outer surface, whereas potassium concentration profile is opposite. The result as well as the fact that potassium and nitrogen overall concentrations remain constant along the entire oxide thickness can be explained as follows. Maintenance of permanent electric fields strength in oxide up to 20V is a very condition necessary for the initial stages of AOF growth. In this process, oxide film, being still amorphous, incorporates anions, following the mechanism known for water electrolytes [10]. It can explain the predominant location of anions in the niobium-adjacent layers.

When thermal-field crystallization of oxide starts, the AOF active growth is observed which occurs actually without any increase in applied voltage. Dispersion

of oxide surface caused by AOF crystallization dramatically increases its reactivity according to [11] mechanism; the fact that along with considerable decrease in field strength makes possible the occurrence of a competing process – the AOF chemical final oxidation by the electrolyte components, the most active being cation peroxide peroxide compounds. It results in possible generation of solid solutions of cation oxygen compounds and niobium oxides – and thus the electrolyte-adjacent oxide film layers become potassium enriched. Potassium quantitative content in oxide was also studied by X-ray fluorescent analysis, from the intensity of lines of the specimen fluorescent radiation minus background. KCl crystal was used as potassium reference. Potassium concentration value, which amounted to about 9%, was calculated on the assumption of 50% potassium content in the reference and of radiation intensity linear dependence on the element concentration. These findings permit to assume the generation of potassium solid solutions in niobium oxide during AOF crystallization.

The results. The following results have been received during this work: Along with study of Nb₂O₅ polycrystalline films whose electrochromism has been established we were the first to obtain AMORPHOUS AOF of niobium pentoxide that show pronounced electrochrome effect, i.e. retain high contrast during numerous "coloring-discoloration" cycles. In practical terms, amorphous AOF are of particular interest as they are free from degradation typical for a crystalline structure.

We have stated the EChE mechanism both in polycrystalline and in amorphous AOF of Nb₂O₅ and then proved experimentally. Besides, we have developed the pulsed electrochemical polarization conditions for already known electrochrome structures (not only on niobium), which permit to raise coloring voltage, and consequently, electrochrome process rate, still preserving the predominance of hydrogen injection into oxide over gas discharge.

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Поступила в редколлегию 27.02.08