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Using Mott-Schottky equation for studing the influence of impurities in niobium on the properties of anodic niobium films

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ABSTRACT

The aim of this work – analysis of additive influence in niobium on formation of defects in anodic layers Nb_2O_5. It was shown that occurrence in niobium of minor amount of metal admixtures, which generate in electric field cations with a charge equal to the charge of oxygen vacancies, causes an increase in defect concentration in anodic niobium pentoxide (ANP). © 2014 Trade Science Inc. - INDIA

KEYWORDS

Niobium anodic oxide;
Mott-Schottky plot;
Impurities.

INTRODUCTION

Key role in formation of the properties of ANP is related to defects of their own or additive nature, while the main defects are oxygen vacancies[1]. It has reported[2] that oxygen vacancies in ANP act as donors whose concentration N_D can be determined via capacitance-voltage characteristic of the oxide using Mott–Schottky equation (1):

$$C^{-2} = 2(\varepsilon\varepsilon_0 A^2 e N_D)^{-1}(V - V_{FB} - k_B T / e) \qquad (1)$$

Here C and A are the interfacial capacitance and area, respectively, N_D the number of donors, V the applied voltage, k_B is Boltzmann's constant, T the absolute temperature, and e is the electronic charge. Therefore, a plot of C^{-2} against V (Mott – Schottky plot[3]) should yield a straight line from which V_{FB} can be determined from the intercept on the V axis. The value of N_D can also be conveniently found from the slope knowing ε and A.

RESULTS AND DISCUSSION

Ovchinnikov has reported[4] the following mechanism of defects generation at the metal-oxide boundary during formation of anodic oxide layer has been introduced: as a result of oxygen anion leap from oxide into metal, oxygen vacancies are generated in the oxide, while the oxygen anions displace a certain amount of metal atoms into the interstices. Interstitial metal atoms in an electric field become electrically charged and get attracted by the field in the oxide volume. In strong magnetic fields, occurred data anodic oxidation, defects transfer at the depends on the charge ratio of the latter: defects having a high

charge rate (in our case, Nb^{5+} cations), move in the oxide volume faster than oxygen vacancies. The issue of participation of wide spectrum of admixtures, contained in niobium, in the defects generation process appears to be significantly up-to-date.

The object of the study were layers of Nb_2O_5, formed by anodic oxidation of the sintered niobium pellets of two types (denoted as A and B), differ by the presence on the surface of A type samples of Mg additive, controlled by X-ray photoelectron spectroscopy (XFES). It shall be noted that XFES - initial analysis of the niobium powder applied at generation of samples of both types, has shown no differences in the composition of additives; presence of Mg has only been detected on the surface of the pellets formed by high-temperature vacuum powder sintering (T=1900K; p=10^{-5}Pa).. This fact affirms that additives located in the niobium powder as a result of sintering are concentrated on the pellet's surface probably according to the bulk diffusion mechanism described in[5].

Anodic oxidation of niobium was a similar on way proposed in[6] and carried out in two stages: in a galvanostatic mode, to a voltage of 130 V followed by the subsequent exposure at the specified voltage for 3 hours.

The Figure 1 shows the linearized in a Mott-Schottky coordinates picture after anodic oxidation in (a) galvanostatic and (b) two-staged modes.

The TABLE 1 shows defects concentration values determined from angular coefficients of Mott-Schottky plots.

As seen from the TABLE 1, as a result of anodic oxidation in a two-staged mode, concentration of defects at Nb_2O_5 outer layers higher in oxide layers formed on niobium of A type, where as at galvanostatic mode defects concentrations ratio of in the samples of A and B types are opposite.

In the scope of above-mentioned mechanism of defects generation, the received results can be considered as follows.

At the first (galvanostatic) stage of A type sample anodic oxidation, the atoms displaced from metal pellet into oxide are partly represented by the atoms of admixture metal A (Mg), which behaviour in the electric fields described by mechanisms typical for anionic defects. As a result, after galvanostatic stage into the volume and oxide / electrolyte boundary it will be displaced fewer defects than it is in case of B type sample. Further, at transition to potentiostatic mode of oxidation, along with the basic (anionic) defects, Mg^{2+} cations are moved to the outer bound-

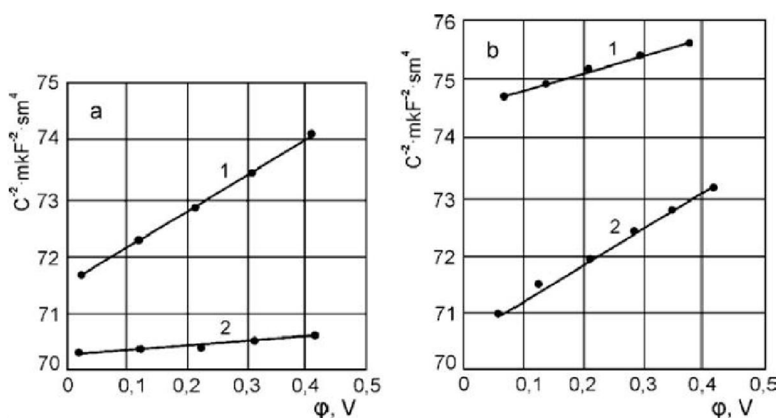

Figure 1 : Mott-Schottky plot for anodic oxide Nb_2O_5: a - oxidation in galvanostatic mode: b - oxidation in two-step mode; 1 – sample A; 2 – sample B

TABLE 1 : Concentration of defects in anodic oxide layers (N_D, cm^{-3})

Sample	N_D, cm^{-3}	
	Galvanostatic mode of Oxidation	**Two-step mode of Oxidation**
A	3.5×10^{19}	3.5×10^{20}
B	2.3×10^{20}	8.3×10^{19}

ary of the oxide layer up to increase of the charged defects concentration in Nb_2O_5 surface layer.

Its should been emphasized that despite of the defects concentration increase at the outer boundaries of the oxide layer observed in A type samples at the potentiostatic stage, application of this oxidation mode is a must as long as it results in improvement of dielectric properties of Nb_2O_5 by means of "healing" of defects in the oxide layer and alignment of oxide phase composition as to thickness.

Measurement of electrical conductivity has shown[7] that immediately after anodic oxidation values for the samples of both types are almost identical, however after heat treatment, related with application of manganese dioxide, the leakage currents for the structures obtained on the basis of samples of A type samples, are three times higher than current value for A type samples. Such a result indicates a significant impact of niobium admixtures on Nb_2O_5 properties associated with concentration of defects in the oxide.

Indeed, as stated in[8], at thermal load of Nb-Nb_2O_5–MnO_2 structure electrical conductivity increases with the increase of defects concentration in anodic oxide layer; it is defined redox processes at the boundaries of oxide layer with metal and with manganese dioxide. At the same time even small amount to admixtures in the niobium pentoxide affects redox properties of the latter in a way of increase of defects concentration.

Thus, oxide defects concentration increase, indicated by capacitance-voltage measurements, is observed even for a small amount of admixtures in niobium, not affecting properties of the oxide layer immediately after anodizing, but significantly affecting electrical characteristics of observed structure.

CONCLUSIONS

It is shown that occurrence in niobium of minor amount of metal admixtures, which generate in electric field cations with a charge equal to the charge of oxygen vacancies, causes an increase in defect concentration in Nb_2O_5 anodic oxide layer.

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