

The Influence of Donor Density on the Critical Breakdown Potential of Niobium Oxide Films in Bromide-Containing Solutions [†]

Eirini Lappa ^{1,*}, Dimitra Sazou ¹

¹ Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; lappaeirini@chem.auth.gr (E.L.); sazou@chem.auth.gr (D.S.);

* Correspondence: lappaeirini@chem.auth.gr (E.L.);

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Abstract: Niobium oxide has n-type semiconductive properties with an excess of donors, which are linked with the excess of oxygen vacancies though the presence of niobium interstitials cannot be excluded. The donor density, N_D , seems to play a significant role in the growth and hence on the stability of the oxide, which seems to be exceptionally susceptible to a bromide-induced breakdown. The goal of the present study is to investigate the influence of N_D on the critical breakdown potential, E_b , of the niobium passive state (Nb_2O_5). Initially, the growth of oxides of constant thickness, L , and different N_D was carried out galvanostatically in 0.5M H_2SO_4 (Fig. 1). The different values of N_D were achieved by applying different anodic current densities, while the constant oxide thickness ($L \sim 5$ nm) was determined by the final formation potential, $E_f = 1.5$ V, implemented for the galvanostatic oxide growth. The N_D was estimated using the Mott-Schottky analysis. The E_b of the oxides of different N_D was estimated in 0.5 M KBr using potentiodynamic curves in 0.5 M KBr. Metastable pitting associated with current instabilities was observed close to E_b , before the sudden increase of the current assigned to the stable pitting corrosion of the passivity on Nb. Analysis of these measurements indicates that the E_b decreases upon increasing N_D (Fig. 2), indicating that oxygen vacancies may be involved in the mechanism underlying the bromide-induced pitting corrosion of the passive Nb.

Keywords: galvanostatically grown Nb_2O_5 ; bromide effect; localized breakdown of passivity on niobium.

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Conflicts of Interest

The authors declare no conflict of interest.

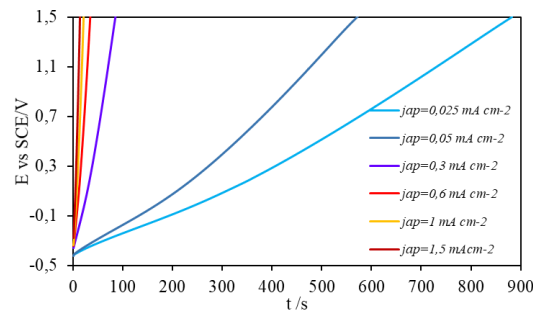


Figure 1. Galvanostatic curves traced during the Nb anodization in 0.5 M H₂SO₄ at various applied current densities, j_{ap} indicating the time evolution of the potential for the formation of niobium oxides with constant thickness and different donor density as the potential limit was kept constant at 1.5 V_{SCE}.

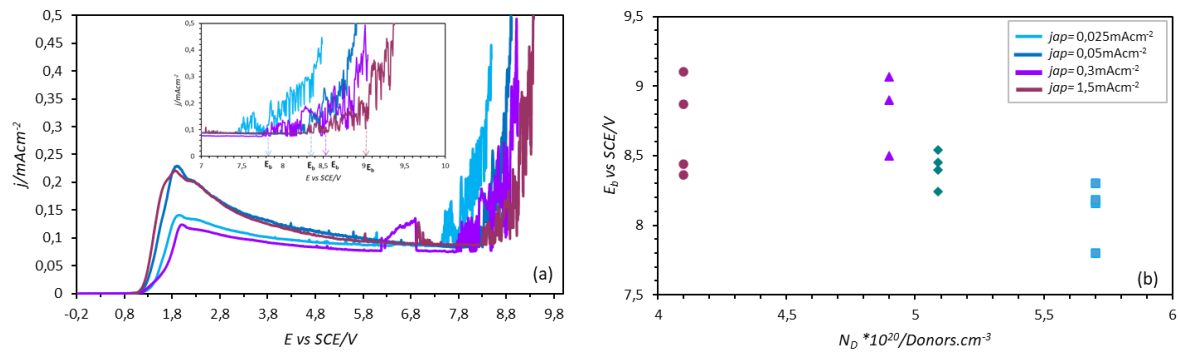


Figure 2. (a) Potentiodynamic current density-potential (j - E) curves traced at a potential scan rate, $v=10\text{mVs}^{-1}$ in 0.5 M KBr for the Nb|Nb₂O₅ ($L\sim 5\text{nm}$) interfaces prepared at various j_{ap} and hence different N_D . (b) Variation of the breakdown potential, as a function of the donor density, $E_b = f(N_D)$.