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OPTICAL PROPERTIES OF ELECTROCHEMICALLY POLISHED AND ANODIZED NIOBIUM SURFACES

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Optical properties of electropolished and anodized Nb surface has been studied using ellipsometric method. The working electrodes were cut from massive cylindrical rod with purity 99.8 % (Alfa Aesar). The discs of Nb with 20 mm in dia and height of 10 mm have been embedded in epoxy resin (Struers), leaving the front area in contact with solution. Prior to each measurement the Nb surfaces were abraded using silicon carbide paper (600 grade) and then electropolished in electrolytic bath consisting: 170 ml HNO₃ (64%) + 50 ml HF (40%) + 510 ml CH₃OH + 5 g citric acid. As a counter electrode was used a Pt grid with large surface. The best electrochemical polishing was obtained for the bath temperature of $t = -5^{\circ}\text{C}$ at voltage of 21 V during 1 min for turbulent stirring of the bath. The cell current was raised with steering speed. The quality of electrochemical polishing was tested ellipsometrically through the reflectivity at normal incidence. The electrochemically polished samples had visually homogeneous mirror brightness over all the surface area. After the electrochemical polishing the Nb surfaces were cleaned in an ultrasonic bath and rinsed with ethanol. The ellipsometric measurements were performed with a "thin film ellipsometer Rudolph Research, type 43602-200" at wavelength of $\lambda = 546.1\text{ nm}$. The incidence angle was determined by searching of principal angle. At this angle the sensitivity of measurements are the highest and for the majority of metal surface moves from 60 to 80^o.

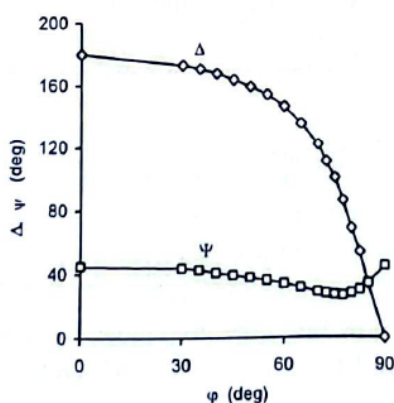


Fig.1. Dependence of ellipsometric parameters Δ and Ψ from angle of incidence:

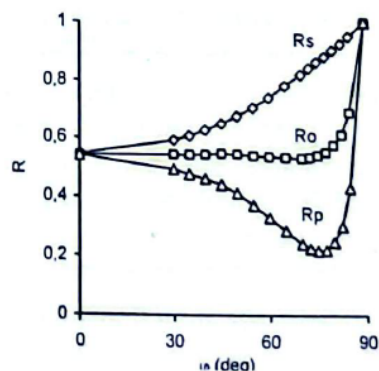


Fig.2. Dependence of reflectivity from angle of incidence: R_s – perpendicular, R_o – normal and R_p parallel to plane incidence

On fig.1. the dependence of ellipsometric parameters Δ and Ψ from the incidence angle in limits from 30^o to 87^o is given. For less values than 30^o it is technically impossible to perform measurements, so values of Δ and Ψ for $\varphi = 0^{\circ}$ are extrapolated to their

theoretical values of 180° and 45° , respectively. As could be seen from fig.1., for $\Delta = 90^\circ$ the corresponding principal angle is 76° and at this angle there is coincidence between point of inflexion of curve for Δ and the minimum of curve for Ψ . On fig.2., R_s increase monotonically from its minimum value at $\varphi = 0$ to 1 when $\varphi = 90^\circ$, whereas R_p exhibits a minimum at the pseudo-Brewster angle of 74° . Taking into consideration the time between electrochemical polishing and performed measurements, on Nb surface it should be built the natural surface layer of about 2 nm, that moves the Brewster angle several degree to higher value. This is the reason why Smith recommends that the measurements should be always taken at the incidence angle which is for several degrees less than the principle angle [1]. All our future measurements were performed at 70° ; several degrees less than the determined pseudo-Brewster angle.

The complex refractive index of metal substrate and anodic oxide films in the potential/voltage region from 0–100 V have been determined by in-situ ellipsometric measurements in 1 M H_2SO_4 . For these measurements the special optical electrolytic cell was adopted, presented previously [2]. The anodization was firstly performed potentiostatically using HEKA potentiostat/galvanostat. The potential was increased stepwise every 30 s by 0.5 V from 0 to 10 V. For potential up to 10 V, a three electrode system was used. For voltage over the 10 V, a two-electrode system was used and the applied voltage was increased in step every 30 s by 2.5 V from 10 to 100 V, using the high-stabilized supplier.

For three component system: medium (1 M H_2SO_4), anodic oxide film (Nb_2O_5) and metals substrate (Nb), the complex refractive index of medium $\bar{n}_m = n_m(1 - i\kappa_m)$ was determined by Abbe's refractometer. The complex refractive index of metal substrate $\bar{n}_s = n_s(1 - i\kappa_s)$ was determined separately [3], and complex index of anodic oxide films $\bar{n}_f = n_f(1 - i\kappa_f)$ was calculated from the ellipsometric measured parameters Δ and Ψ .

Table 1. measured and calculated complex refractive indices.

	\bar{n}_m	\bar{n}_s	\bar{n}_f
1 M H_2SO_4	1.342(1 - i 0)		
Nb		3.62(1 - i 0.993)	
Nb_2O_5 (1-10 V)			2.347(1 - i 0)
Nb_2O_5 (10-100 V)			2.345(1 - i 0.005)

In the potential range from 0 to 10 V the real part of film refractive index has a little higher value $n_f = 2.347$ than in the voltage region of 10 to 100 V, $n_f = 2.345$. Oppositely the value of imaginary part in the potential region from 0 to 10 V is $\kappa_f = 0$, indicating that the film is transparent and homogeneous. For voltage from 10 to 100 V, the imaginary part is $\kappa_f = 0.0005$, indicating that the oxide film is less transparent as a result of film breakdown. During the breakdown process the various defects are generated in the film and it begins to lost in its homogeneity.

[1] T.Smith – J.Opt.Soc.Am. 62, 774 (1974)

[2] Lj.Arsov – Electrochim.Acta 30(12), 1645 (1985)

[3] I.Arsova, A.Prusi and Lj.Arsov – J.Solid State Electrochem. 7, 217 (2003)