Ellipsometric *in situ* study of the titanium surfaces during the anodization

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Abstract. — The titanium surfaces immersed in 0.5 mol.dm^{-3} H$_2$SO$_4$ and anodized in the voltage region from 0 to 100 V have been studied by *in situ* ellipsometric measurements. The thickness, inhomogeneity, and porosity of the formed films rise with increasing applied voltage. A computational method is presented for obtaining both the refractive indices and thickness of an unknown film on a reflecting substrate of known optical constants. The complex index of refraction and thickness of generated films were calculated comparing the theoretical computed curve with experimental loci Δ and Ψ obtained from *in situ* ellipsometric measurements.

Nomenclature.

Δ	relative phase change
$\tan \Psi$	relative amplitude attenuation
n	relative index (real part)
κ	extinction index (imaginary part)
$\hat{n}_1 = n_1(1 - i \cdot \kappa_1)$	complex refractive index of medium
$\hat{n}_2 = n_2(1 - i \cdot \kappa_2)$	complex refractive index of film
$\hat{n}_3 = n_3(1 - i \cdot \kappa_3)$	complex refractive index of metal substrate
φ	angle of incidence
λ	wavelenght
d	film thickness
ρ	ratio of the complex reflection coefficients
r_p and r_s	Fresnel reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively
δ	change of phase of the beam crossing the film
d_c	terminus thickness of the first Δ-Ψ cycle.

Introduction.

The optical properties of anodic oxide films formed on titanium surfaces are of importance in understanding the corrosion stability and photoelectrochemical activity of titanium oxide and its application in solar energy conversion.

Up to now an impressive array of techniques have been utilized for investigating the properties of anodic oxide films formed on Ti surface in various electrochemical conditions [1-5]. However the exact nature and optical properties of these films are still controversial.

Ellipsometry is one of the most convenient and accurate techniques for the measurement of thickness and refractive index of thin films on a solid surface. Winterbottom [6] has described straightforward exact procedures for determining the thickness and optical constants of films on reflecting surfaces. Application of more simple and approximate equations has been discussed by Vasicek [7] and Heavens [8]. For the determination of the exact value of refractive index and thickness of a film grown on a metallic substrate it is necessary to have a good preliminary knowledge of the refractive index of the metal substrate. A number of authors believe that more precise values of the refractive index of a metal substrate could be obtained if the measured surface were to be prepared by evaporation in vacuum and be kept under vacuum conditions [9, 10]. In this manner the risk of surface contamination or oxidation would be prevented during the measurements. According to bibliographical data it seems that these conditions are not always fulfilled. The validity of using the refractive index of evaporated films instead of the bulk metal is questionable.

The purpose of this work is to enlarge the initially studied domain of determination of the refractive index of a film on a titanium surface by ellipsometric measurements under *in situ* conditions during the anodic polarisation and film growth.

Experimental.

ELECTRODES. — Ti discs (U.T. 40 Ugine Kuhlman), 2.5 cm in diameter were cut from an annealed sheet and after that covered in epoxy resin (Struers) leaving front surface area in contact with the solution. Before each measurement, the working surface of the Ti electrode was mechanically polished by 600 grade emery paper and then electropolished. The condition of electrochemical polishing and the way we controlled the quality of the electropolished surfaces are described elsewhere in detail [11].

A Pt grid was used as a counter electrode and a saturated calomel electrode (sce) as a reference electrode.

OPTICAL-ELECTROLYTIC CELL. — The optical electrolytic cell was a quartz tube built in a conventional manner which we have presented previously [12]. The position of the working electrode in the cell could be moved back and forth allowing to adjust the distance between electrode surface and cell wall in order to obtain an optimal collection of the reflected light into the photomultiplier. The cell was placed in an air thermostat at a temperature of 20 ± 1 °C.

SOLUTION. — Analytical grade reagent of H_2SO_4 (Merck) was used for the preparation of the solution in triply distilled water.

APPARATUS. — The ellipsometric measurements were carried out by means of a « Thin Film Ellipsometer » type 43603-200 Rudolph Research at wavelength of 546.1 nm and incidence angle of 70°.

The potentiostatically anodic oxidation was performed every 0.5 V by successively increasing the potential from 0 to 10 V using a Wenking potentiostat type 121. For higher voltage, anodic oxidation was performed every 2.5 V also by successively increasing the applied voltage from 10-100 V utilizing the high supply Drusch 5140.

Experimental procedure.

Before each measurement the solution in the cell was de-aerated by flowing the prepurified N_2 through the fritted glass bubbler. The freshly electropolished Ti electrode was immersed in the cell electrolyte and the working surface was positioned in the cell, under open circuit condition, until maximum photomultiplier response was obtained. The gas flow was interrupted and the electrode was then cathodized at -0.6 V (sce). This is the potential for which the quickest electrochemical dissolution of natural oxide film occurs [12]. The maximum thickness of natural oxide film dissolution was tested ellipsometrically (by variation of Δ and Ψ) and electrochemically (the current change from cathodic to anodic direction) [12]. The electrode was then anodized at various potentials for a period of time of 30 s. In order to prevent the evolution of oxygen bubbles during the ellipsometric measurements in higher voltage anodization the following measures were taken : when the working electrode was anodized at a voltage higher than 2 V, after 30 s the voltage was rapidly diminished and was kept at a constant value of 2 V (small anodic current flowing during the measurements). The ellipsometric measurements were performed under potentiostatic control.

All measurements described in this paper have been repeated three times and good reproducibility was found.

Results.

In ellipsometry measurements the experimentally measured parameters Δ and Ψ are related to the physical properties of the system by the use of Fresnel equation which permits the calculation of the reflective index of a reflecting surface

$$\rho = \frac{r_p}{r_s} = \text{tg } \Psi \cdot \exp(i \cdot \Delta). \tag{1}$$

A typical 3 component system for study by the ellipsometer consists of a film of a refractive index $\hat{n}_2$ and thickness d on a reflecting substrate of index $\hat{n}_3$ immersed in a medium of index $\hat{n}_1$.

In this case the Fresnel equation is more complicated and the complex reflection coefficients at the boundary between the immersed medium and the film, and also between the film and substrate, are related with ellipsometric parameters Δ and Ψ by the equation

$$\text{tg } \Psi \cdot \exp(i \cdot \Delta) = \frac{r_{1,2,p} + r_{2,3,p} \cdot \exp(-2i\delta)}{1 + r_{1,2,p} \cdot r_{2,3,p} \cdot \exp(-2i\delta)} \cdot \frac{1 + r_{1,2,s} \cdot r_{2,3,s} \cdot \exp(-2i\delta)}{r_{1,2,s} + r_{2,3,s} \cdot \exp(-2i\delta)} \tag{2}$$

where

$$\delta = \frac{2 \cdot \pi}{\lambda} d \cdot (\hat{n}_2^2 - \hat{n}_1^2 \cdot \sin^2 \varphi)^{1/2} \tag{3}$$

REFRACTIVE INDEX OF IMMERSED MEDIUM. — In equations (2) and (3) the refractive index of the immersed medium can be most simply determined by Abbe's refractometer. For 0.5 mol dm^{-3} H_2SO_4 in room temperature of 20 °C $\hat{n}_1 = 1.337(1 - i \cdot 0)$ i.e. $n_1 = 1.337$ and $\kappa_1 = 0$. These values are in good agreement with the values of n_1 and κ_1 given in the literature data for 0.5 mol dm^{-3} H_2SO_4 [13].

REFRACTIVE INDEX OF METAL SUBSTRATE. — One of the most commonly used methods for determining the optical constants for strongly absorbing materials is ellipsometry. The conventional ellipsometry with a fixed angle of incidence requires an oxide-free metal surface

to estimate the complex refractive index of the metal. An incorrect determination of optical constants of the oxide-free metal surface is one of the sources of the essential errors in ellipsometric measurements. In this work, the value of $\hat{n}_3$ was taken from our previous ellipsometric *in situ* measurements where the electropolished Ti surfaces were cathodically polarized in a solution of 0.5 mol dm^{-3} H$_2$SO$_4$ [12]. At a potential of -0.6 V (sce) we had shown that the electrochemical reduction of natural oxide film occurred uniformly across the electrode surface. The computed values for clean metal substrate from our ellipsometric measurements were $\hat{n}_3 = 2.94$ $(1 - 1.217 . i$). These values are very close to the literature data for Ti obtained by evaporation in vacuum and measured in high vacuum [10].

REFRACTIVE INDEX OF ANODIC FILM-COVERED METAL SUBSTRATE. — Figure 1 shows the experimentally measured parameters Δ and Ψ for various values of applied voltage.

From this figure it is possible to determine very precisely the voltage difference of 57 V between 0 V (the beginning of the curve, i.e. values of Δ and Ψ for oxide-free metal substrate) and 57 V (terminus of the curve).
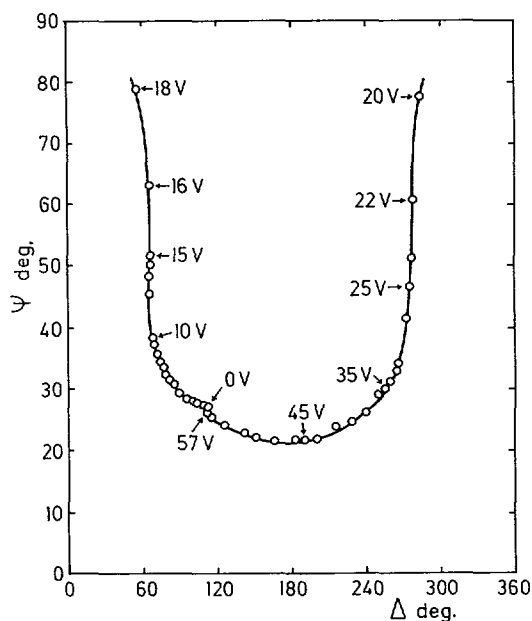

Fig. 1. — *Graphical presentation of dependence between experimentally measured Δ and Ψ for various values of anode voltage.*

The refractive index $\hat{n}_2$ and thickness d of anodic oxide films can be determined most simply by fitting the experimentally obtained points Δ and Ψ (given in Fig. 1) with the theoretical Δ-Ψ curves computed by equation (2) for fixed values of $n_1 = 1.337$ and $\hat{n}_3 = 2.94$ $(1 - 1.217 . i)$. The fitting procedure was performed by special prepared computed program in which $\hat{n}_2$ was searched for prior given values of d in an increasing direction.

The computational method is based on the determination of the distance between two points A $= (\Delta_e, \Psi_e)$ and B $= (\Delta_t, \Psi_t)$. The point A represents any one of the points : A$_1$, A$_2$ .. A $_i$ .. A $_N$ on an experimental function given by the finite set of its discrete values

$$E = \left\{ (\Delta_{e1}, \Psi_{e1}), (\Delta_{e2}, \Psi_{e2}) .. (\Delta_{ei}, \Psi_{ei}), (\Delta_{eN}, \Psi_{eN}) \right\}$$

or

$$E = \{A_1, A_2, .., A_i, .., A_N\}$$

or

$$\Psi_{ei} = f_E(\Delta_{ei}) \quad \text{where} \quad 1 \leq i \leq N . \tag{4}$$

The point B represents any one of the points : $B_1, B_2, .. \; B_j, . \; B_M$ on a theoretical function given with the finite set of its discrete values

$$T = \{(\Delta_{t1}, \Psi_{t1}), (\Delta_{t2}, \Psi_{t2}) .. \; (\Delta_{tj}, \Psi_{tj}), (\Delta_{tM}, \Psi_{tM})\}$$

or

$$T = \{B_1, B_2, .. \; B_j, . \; B_M\}$$

or

$$\Psi_{tj} = f_T(\Delta_{tj}) \quad \text{where} \quad 1 \leq j \leq M . \tag{5}$$

Theoretical function T is one of the family of the functions

$$T \in \{T(n, \kappa) \,|\, n \geq 0 \;\text{and}\; \kappa \geq 0\}$$

for various values of n and κ. The values of n and κ, with prior determined step, are taken from some interval given in advance.

During the computation only one theoretical $T(n_K, \kappa_L)$ function is searched from the family of theoretical functions which has minimal distance to the experimental function E.

The distance D is calculated by the equation

$$D_{\min} = \sqrt{D_1 . D_2} \tag{6}$$

where

$$D_1 = \sum_{i=1}^{N} \min_{1 \leq j \leq M} \{|\Delta_{ei} - \Delta_{tj}| + |\Psi_{ei} - \Psi_{tj}|\}$$

and

$$D_2 = \sum_{j=1}^{M} \min_{1 \leq i \leq N} \{|\Delta_{ei} - \Delta_{tj}| + |\Psi_{ei} - \Psi_{tj}|\} . \tag{7}$$

The searched function $T(n_K, \kappa_L)$ which is given by the equation

$$T(n_K, \kappa_L) = \{[\Delta_1(n_K, \kappa_L), \Psi_1(n_K, \kappa_L)], .. \; [\Delta_2(n_K, \kappa_L), \Psi_2(n_K, \kappa_L)], ..$$
$$[\Delta_i(n_K, \kappa_L), \Psi_i(n_K, \kappa_L)], .. \; [\Delta_N(n_K, \kappa_L), \Psi_N(n_K, \kappa_L)]\}$$
$$1 \leq K \leq N_n ; \quad 1 \leq L \leq N_\kappa$$
$$n_K \in \{n_i \,|\, 1 \leq i \leq N_n\}$$
$$\kappa_L \in \{\kappa_j \,|\, 1 \leq j \leq N_\kappa\} \tag{8}$$

should satisfy the expression for minimal distance

$$D_{\min} = \sqrt{D_1 . D_2} .$$

When the experimentally measured A = (Δ_e, Ψ_e) points are superimposed for minimal distance by computed B = (Δ_t, Ψ_t) points of theoretical $T(n_K, \kappa_L)$ curve the fitting procedure is over.

During the fitting procedure the correct values of searched parameters can be obtained only if $M \gg N$. In our case the number of theoretical points is at least ten times bigger than the number of experimentally determined points i.e. $M \geqslant 10\,N$.

In figure 2 the superposition of computed Δ-Ψ curve (solid line) for values of $\hat{n}_2 = 2.38\,(1 - 0.006 \cdot i\,)$ and experimentally measured Δ and Ψ points (circles) is shown. On the computed curve are also shown the values of film thickness which correspond to experimental points Δ and Ψ for different voltages of anodic oxidation. The number of theoretical points on the computed curves can be regulated with the thickness increments. For smaller values of thickness increments the computed curve has a larger number of theoretical points and is more like a continuous curve. The smallest increments of the real and imaginary parts of the refractive index are 0.001.
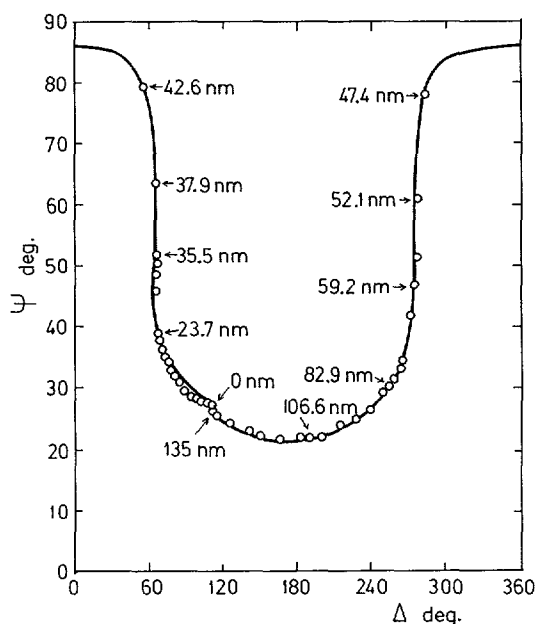

Fig. 2. — Graphical presentation of experimentally measured Δ and Ψ (circle) and computed fitting curve (solid line). The values of $n_1 = 1.337$ and $\hat{n}_3 = 2.94\ (1 - 1.217 \cdot i)$ are given. The values of $\hat{n}_2 = 2.38\ (1 - 0.006 \cdot i)$ and $d_c = 135$ nm are calculated.

The computed curve in figure 2 begins for $d = 0$ and closes the first cycle for thickness of $d_c = 135$ nm. The value for $d_c = 135$ nm corresponds to a voltage difference of 57 V in figure 1. For values thicker than 135 nm the computed curve begins its second cycle, but it does not close on the same point where it begins. Taking into account that the film thickness depends linearly on applied anodic voltage [11] and writing $d = \alpha \cdot V$ where $\alpha = \dfrac{d}{V}$ is the coefficient of film thickness grown per volt, from computed $d_c = 135$ nm value and experimentally determined difference value of 57 V, the value of α can be determined as $\alpha = \dfrac{135}{57} = 2.37$ nm/V. The question is what will be the shape of computed curves for various

values of n_2 and κ_2 ? The answer to this question would be found from the computed curves shown in figure 3 and figure 4.

Figure 3 shows the computed curves for fixed values of $\kappa_2 = 0$ and various values of n_2 from 1.6 to 6.0. For nonabsorbing film $(\kappa_2 = 0)$ the computed values of Δ and Ψ are cycling functions of film thickness and the curves repeat periodically with every 180° change in δ. The arrows on curve show the direction of film thickness growth. The terminus of each curve is the same point as the beginning of the curve. Each curve repeats periodically for every increase of δ by 180°.

Figure 4 shows the computed curves for fixed values of $n_2 = 2.38$ obtained from figure 2 and various values of κ_2 from 0 to 0.3. It is evident that the curve for $n_2 = 2.38$ and $\kappa_2 = 0$ is a cycling function and repeats periodically for every value of $\delta = 180°, 360°, 540°..$ However if $\kappa_2 > 0$ the curves do not quite have a cycling form which repeats periodically. The curve ends are not at the same point as the beginnings. With κ_2 increasing the curves front moves below and the shifting between beginning and terminus point increase in the end of the first cycle. For higher values of κ_2 an exact determination of d_c values is very difficult.
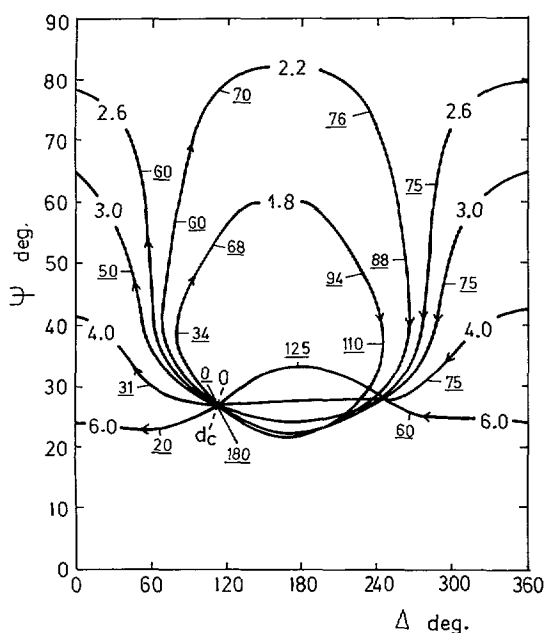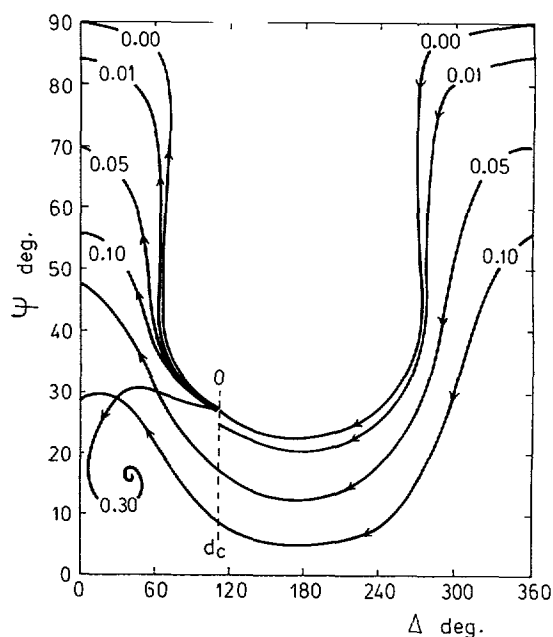

Fig. 3.

Fig. 4.

Fig. 3. — Computed Δ-Ψ curves for fixed prior given values of $n_1 = 1.337$; $\hat{n}_3 = 2.94\,(1 - 1.217 . i)$ and $\kappa_2 = 0$, and various values of n_2 from 1.8 to 6.0. Underlined numbers correspond to values of δ.

Fig. 4. — Computed Δ-Ψ curves for fixed prior given values of $n_1 = 1.337$, $n_2 = 2.38$, $\hat{n}_3 = 2.94$ $(1 - 1.217 . i)$ and various values of κ_2 from 0 to 0.3.

Comparing the computed curves in figure 3 and figure 4 with experimentally obtained curve from figure 2, one can conclude that the refractive index of the anodic oxide films on titanium surface has κ_2 value very close to the non absorbing film case, i.e., zero.

Discussion.

In literature data there exists a very big discrepancy about the values of n_2 (2.00-2.53) and κ_2 (0-0.318) for anodic oxide films on Ti surface [14-16]. This discrepancy can be explained by the variety of deposition methods employed, the different manners of surface preparation and the use of various equations for calculations which provoke very often significant errors. It should be examined in which measure the uncorrect value of d_c influences exact value of n_2 and κ_2 or *vice versa*. For this reason we have studied the influence of n_2 and κ_2 on d_c. In the beginning of this study we have supposed that $\kappa_2 = 0$ and examined the dependence between d_c and n_2. For each Δ-Ψ curve presented in figure 3 and also curves which are not presented in figure 3 (for smaller step of change in n_2) the thickness d_c is determined as terminus thickness of first cycle. If the value of d_c from computed curve is not exactly determined and if it is put in equation (3), the calculated value of δ wouldn't be 180°. The incorrect experimental determination of d_c introduces a significant error in n_2 and film thickness determination with applied voltage.

Figure 5 with curve 1 shows the theoretical function between d_c and n_2 computed by equation (2). From curve 1, it is evident that the experimental determination of d_c should be more sensitive for lower value of n_2. Influence of κ_2 on the values of d_c is given by curve 2. There exists a linear relation between d_c and κ_2 and with increasing the value of κ_2 there is insignificant change in d_c. For values of κ_2 higher than 0.1 there is no cyclic repetition of computed curves (Fig. 4) and determination of d_c is impossible.
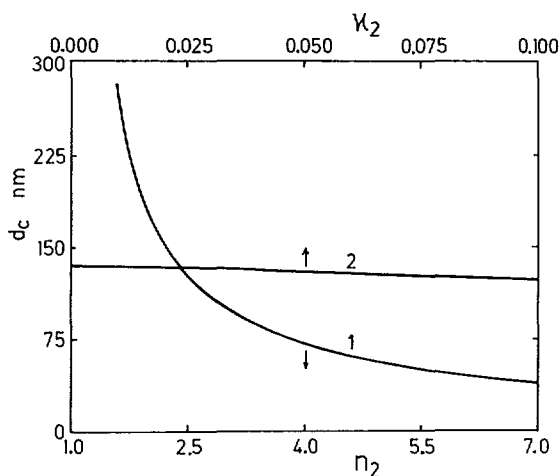

Fig. 5. — Computed dependence between d_c and n_2 (curve 1) and also d_c and κ_2 (curve 2) for fixed, prior given, values of $n_1 = 1.337$ and $\tilde{n}_3 = 2.94$ $(1 - 1.217 . i)$.

In our previous papers we have shown that TiO_2 layers formed at low potentials and small current density have amorphous structure [1, 5]. At higher potentials the evolution of crystallinity in amorphous film and breakdown process begin. Before the beginning of the break the film is homogeneous with grains which reproduce exactly the grains of the titanium substrate. The grains of the film and the grain of the substrate have the same size. When the break formation of microcrystals begins and with the progress of the break there is also progress in the evolution of the crystalline state in the film. The film loses its homogeneity and its structure becomes microporous.

In our fitting procedure we have supposed that the refractive indices n_2 and κ_2 are independent of film thickness. However, with the beginning of the breakdown process there is a rise in film inhomogeneity and crystallisation of the amorphous film. These two processes change the refractive indices. We have shown previously that up to 10 V, n_2 and κ_2 decrease with the film thickness [17]. Over 10 V, n_2 and κ_2 take constant values. This is the main reason why the experimentally measured Δ and Ψ in the beginning (up to 10 V) shift from the computed curve (Fig. 2). For higher voltage all experimental points are well superimposed on the computed curve.

Conclusion.

By ellipsometric *in situ* measurements we have succedeed in determining very precisely the refractive index and thickness of anodic oxide films covering titanium substrate.

The refractive index of $\hat{n}_2 = 2.38 \ (1 - 0.006 \cdot i)$ of anodic oxide films was determined by fitting procedure between experimentally measured Δ and Ψ for various values of applied voltage and computed Δ and Ψ for various values of film thickness. The coefficient of film thickness growth of $\alpha = 2.37$ nm/V is also determined during the fitting procedure. The shift of experimentally measured Δ and Ψ is explained by the change of n_2 and κ_2 with film thickness for lower values of applied voltage. Above 10 V the refractive indices n_2 and κ_2 are independent of film thickness.

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