# 10. Anodic growth of oxide layer.

Theory of anodic oxidation:

Anodic oxidation (or oxide formation) is called the following process: some metal merged in the water solution of a weak acid (phosphorus, oxalic, sulphuric, or chromic acid) and connected in electric circuit as anode (positive pole). In this case decomposition of water takes place and the oxygen is separated on the anode and the hydrogen on the cathode. The formed oxygen immediately reacts with metal connected as anode producing some thin oxide layer on the metal's surface. The oxide can grow further on condition that either the oxygen ions (O_2^-) can get through the oxide to the anode's surface (where the oxidation takes place), and/or the metal ions (M^{m+}) of the anode can move to electrolyte. In this case the reaction of oxidation takes place on the oxide/electrolyte interface. The model of anodic oxidation can be seen in the picture below.
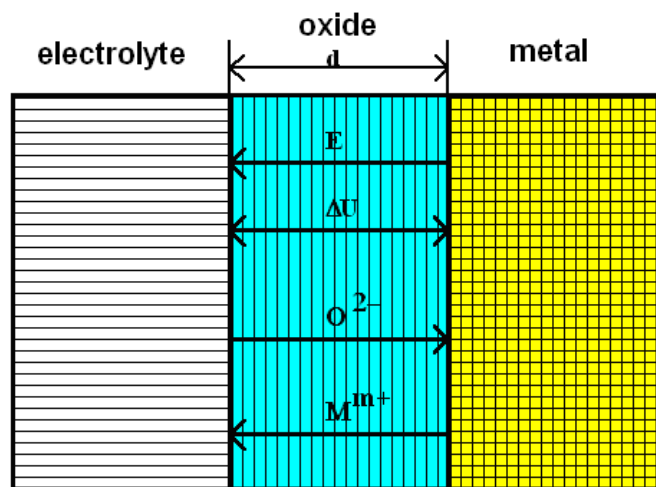

The oxide's growth rate is determined by the velocity of ions crossing the oxide, and as it depends on the electrical field the growth rate depends on voltage drop on the oxide. Usually it is supposed that the voltage connected to the electrodes entirely falls on the oxide layer, but in most cases you can not neglect the voltage drop in the electrolyte and on the electrolyte-oxide phase boundary, especially in case of very thin oxides. The roll of weak acid is to increase the electrical conductance of the electrolyte, and so to decrease the voltage drop in it. The hardness of the oxide layer depends on the temperature and the type of the acid solution. The thickness of the oxide layer depends linearly on the growing voltage:

$$d=(U-U_o)/E \quad \text{where}$$

d	the thickness of the growing oxide
U	the applied voltage
U$_o$	the voltage where the growth of the layer starts, and
E	the strength of the electric field

In the following pictures you can see some typical voltage-time (U_F-t) and current-time (I_F-t) curves of anodic oxidation.

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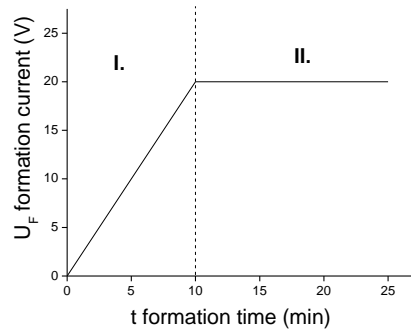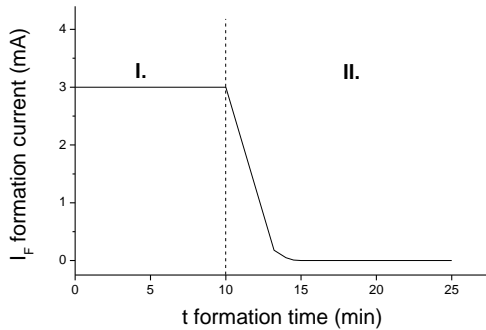
The oxidation takes place effectively in the first (I.) period of oxide formation (the formation current is constant and the voltage on the oxide increases linearly in function of time). In the second (II.) period (the formation current decreases exponentially and the voltage on the oxide is constant) the healing of the oxide defects takes place.

The anodic oxidation is typically used for the following purposes:
- increase of the corrosion resistance (e.g. oxidation of Ti implants),
- increase of the hardness (e.g. Al),
- colouring of the surface (e.g. golden colour can be obtained by oxidation of Ti),
- increasing lubrication of the surface,
- increasing the adhesion, and
- producing very thin dielectrics for the electrolyte capacitors (e.g. Al, Ta, Nb).

Task: grow oxides on 3 different Nb plates in the 1 wt.% aqueous solution of H_3PO_4, at 60°C, with U_F=20, 40, and 80V, and I_F=5 mA. During the oxide growth the U_F, I_F parameters should be collected by computer in function of time, and represent the growth curves. Measure the electrical parameters of the oxide (C: capacity, R: series resistance, I: leakage current) and use it to qualify the grown oxides. Estimate the thickness of the grown oxide with calculations. Draw the capacity C in function of $1/U_F$.

The required data for calculations:

> **Faraday constant** = 96494 C/mol
> **Mass of 1 mol Nb_2O_5** = $2·93+5·16$ =266g, i.e. the sum of the atomic weights of 2 peaces Nb and 5 peaces O
> **Density of Nb_2O_5 ρ**=4,55 g/cm^3
> **Refractive index of Nb and Nb_2O_5** n_{Nb}=2,8-2,9; n_{Nb2O5}=2,3
> **Permittivity of the vacuum:** ε_0=8,85·10^{-12} AsV^{-1}m^{-1}
> **Dielectric constant of Nb_2O_5** ε_{Nb2O5}=41
> **Wavelength of light** λ**(blue)**=400-500nm, λ**(green)**=500-570nm, λ**(yellow)**=570-590nm, λ**(orange)**=590-630nm, λ**(red)**=630-580nm

Sequences of the scheduled measurement tasks:

1. Assembling the experimental setup for anodic oxidation.
Connect the power supply with the sample holder and the METEX type voltage and current meters – which perform the data collection - as shown below. Set the desired current and voltage limits of the growth to the power supply in the following order:

- the current limit should be 5 mA, which can be adjusted by the CURRENT button/key by the "short circuit" of the power supply,
- the voltage limits are 20, 40, or 80 V, which can be adjusted by the VOLTAGE button/key by the "open circuit" of the power supply.
In order to achieve higher accuracy the voltage and current limits should be read not on the power supply, but on the METEX instruments.

After these switch off the power supply and heat up the electrolyte without any sample until 60°C with continuous stirring.
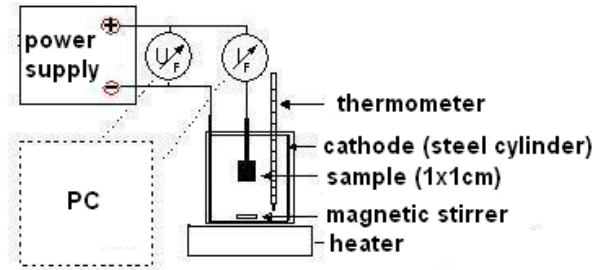
2. Sample preparation (cutting and cleaning).

Cut out 3 peaces of samples from the high purity Nb according to the picture below (1x1 cm squares with 2 mm wide and 1 cm long power supply rails). The samples should be "straighten out" with tweezers, then cleaned in boiling alcohol: take out the samples from the boiling alcohol, dry them in steam of alcohol and put them onto filter paper.
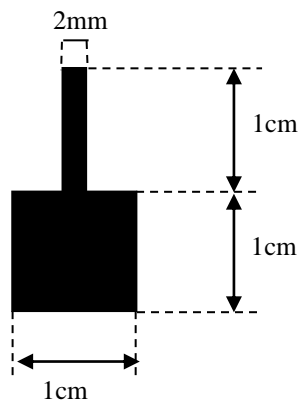
## 3. Oxidation of the 3 Nb plates with 3 different (20, 40, 80 V) voltages.

Fasten the cleaned sample into the sample holder and insert it into the electrolyte until the 1x1 cm surface entirely submerged into solution, but the electrolyte does not reach the sample holder.

Start the date collection of the oxide growing parameters (U_F, I_F) by the computer and perform the oxidation successively on all the 3 samples. The oxidation should be carried out until the current decreases below 0,5 mA (i.e. below one tenth of the set current limit).

The measurement data should be collected with the aid of the programme "METEX.exe". The frequency of the date collection should be 2 seconds (which can be set in menu point MEASURE). The date collection can be start and stop with the menu points START MEASUREMENTS or STOP MEASUREMENTS. The measurement data can be viewed in

tabular form in DATA, and in graphical form in GRAPH menu points. The axis settings of graphical display can be specified in the SETUP menu. The measurement data collected in the FILE / SAVE DATA menu can be saved in ASCII format.
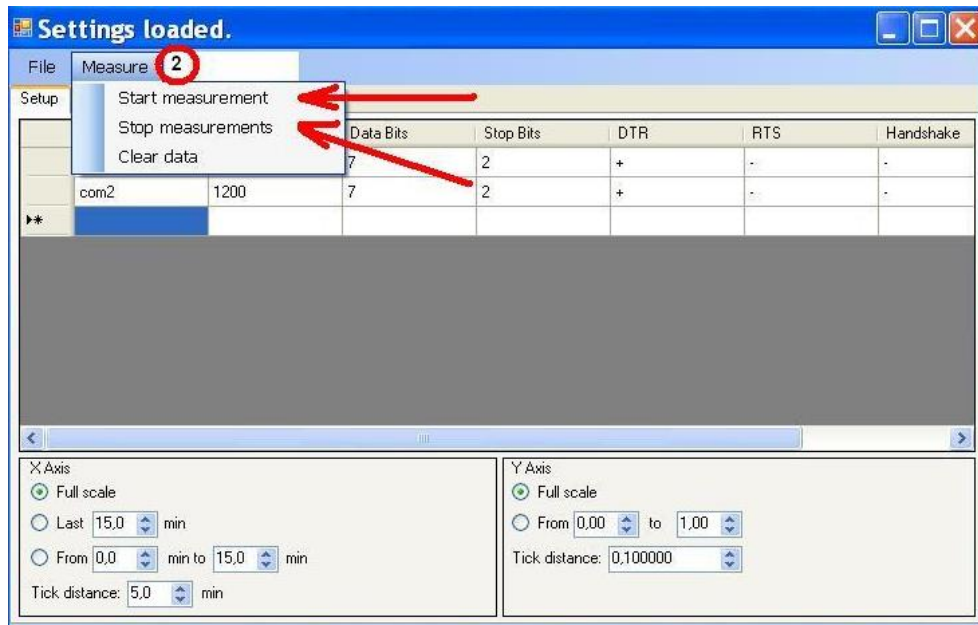
4. Representation of the oxidation curves (U_F-t, I_F-t) by computer with aid of the collected measurement data.

The processing of the saved and collected measurement data can be done by the computer's program called Origin.

## 5. Calculation of the oxide thickness by the charge passed through the growth.

Plot the U_F-t I_F-t-curves for all three samples, then integrate the I_F-t curves to calculate the charge Q flown through during the growth (Q [Coulomb]=I·t [Amper·sec]). Perform the integration of I_F-t curves until the current value reaches the one-tenth of the current limit. Determine the grown oxide thickness by the amount of charge passed through with the aid of the Faraday's law. According to Faraday's law for the formation one mol weight 1 valence material the amount of charge equal to the Faraday constant is needed. Because of the surface roughness use 1,5 times higher surface of the apparent area in your calculations.

Model for calculation: on a Nb with surface A=7 cm^2 violet blue colored oxide increased in 2 minutes by I_F=6,3 mA, the flown through charge Q=6,3·10^{-3}A·2·60sec=7,56·10^{-1}C. 5 pieces of 2 valences oxygen (5x2=10) is required for the formation one molecular Nb$_2$O$_5$, so for one mol quantity i.e. for 266 g oxide formation 10·96494=9,65·10^{5}C charge is needed. In this case 7,56·10^{-1}C/9,65·10^{5}C=7,8·10^{-7} mol amount i.e. m=266·7,8·10^{-7} =2,0748·10^{-4} g mass oxide is formed.
The volume of this amount on the basis of V=m/ρ is V=2,0748·10^{-4}/4,55=4,56·10^{-5}cm^3.
The thickness of the oxide on the basis of d=V/A is d=4,56·10^{-5}/7=6,51·10^{-6}cm=6,51·10^{-5} mm=65,1nm

## 6. Re-cleaning of the samples and assembly of the measuring system for the electrical qualifications.

Rinse the samples in ion exchanged or in distilled water, dry them on a filter paper. Assemble the circuit for leakage current measurement according to the figure below. The 1 k Ω resistor connected in series with the sample has current-limiting role. Fasten the cleaned and dried sample into the sample holder and insert it into the electrolyte until the 1x1 cm surface entirely submerged into the measuring electrolyte (water solution of 30wt.% H_2SO_4), but it does not reach the sample holder.
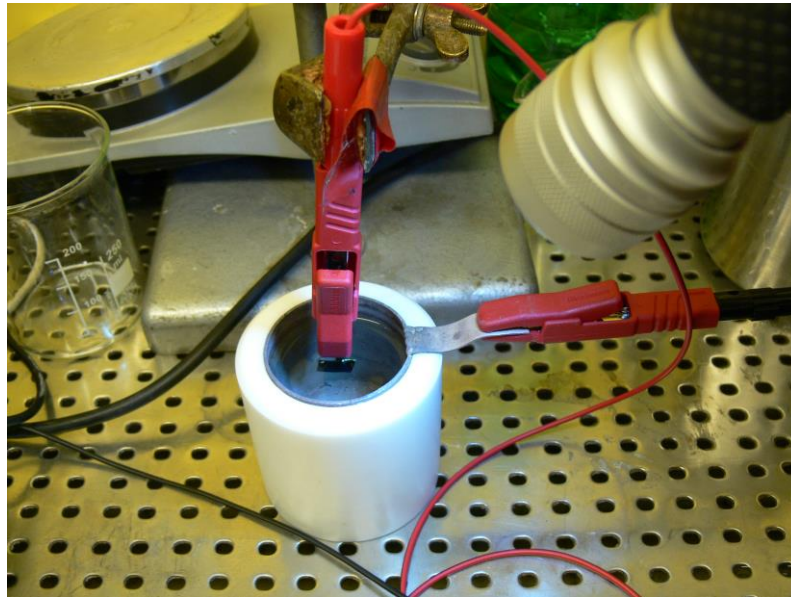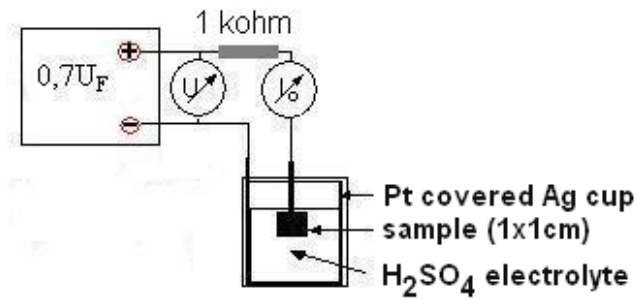
7. Qualification of the oxide (determination of the leakage current, series resistance and capacity).

Measure the I_o leakage current in 1, 2, 5 and 10 minutes after putting $0{,}7 \cdot U_F$ voltage on the sample. After this connect the positive (anode) and negative (cathode) poles of the sample holder to the red and black measuring clamp of the impedance analyser (observe the polarity), and measure the series capacity and resistance of the sample. The equivalent circuit for measurement can be selected with the buttons under the CIRCUIT MODE subtitle (AUTO/series replacement circuit/ parallel replacement circuit). The parameters to be measured (C and R in our case) can be selected by the arrows over the CIRCUIT MODE subtitle. The frequency of measurement should be 120 Hz, which can be selected by the SPOT FREQ button. During measurement use 2 V constant current bias, which can be set by the SPOT BIAS button. The amplitude of the AC power should be 1 V, which can be given with the aid of OSC LEVEL button.
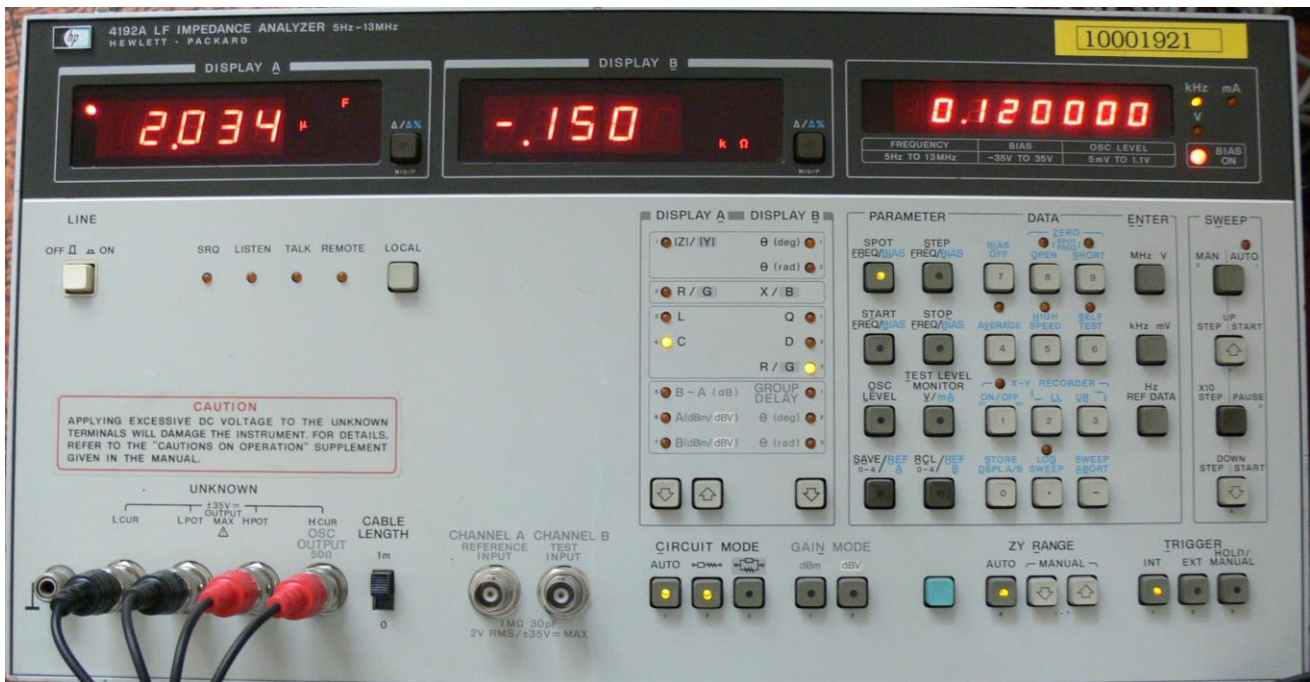
8. Evaluation of the oxide thickness on the bases of oxide capacity.

From capacity calculate the oxide thickness with the aid of $C=\varepsilon\varepsilon_oA/d_{ox}$ formula, where the A is the real surface of the sample (1,5 times higher of the apparent one because of surface roughness).

9. Evaluation of the oxide thickness on the bases of oxide colour.

Thoroughly rinse and dry the samples. Determine their color. The Nb_2O_5 colorless and transparent, the color of the oxidized sample is cased by the interference of the light reflected from the oxide surface and of the light passing through the oxide and reflected from the oxide-metal interface. The waves coming in the same phase reinforce each other, and weaken each other in different phase.
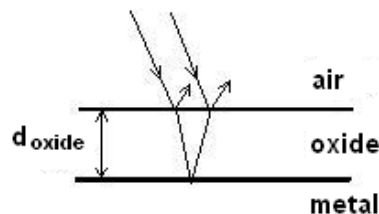
The following context is between the oxide colour and oxide thickness:

$$\text{if } n_{metal}>n_{oxide}>n_{air}$$

$$2\cdot n_{Nb2O5}\cdot d_{ox}=k\cdot\lambda, \qquad \text{where k=1, 2, 3,....}$$

$$d_{ox}=k\cdot\lambda/2\cdot n_{Nb2O5}$$

The oxide thickness of the violet blue oxide $d_{ox}=1\cdot400/2\cdot2,3=86,9$ nm beside λ(violet blue)=400nm, and k=1 (i.e. in the first series of interference colours).