Depth elemental characterization of 1D self-aligned TiO₂ nanotubes using calibrated Radio Frequency Glow Discharge Optical Emission Spectroscopy (GDOES)

Shiva Mohajernia ^a, Anca Mazare ^a, Imgon Hwang^a, Sofia Gaiaschi^b, Patrick Chapon ^b, Helga Hildebrand^a, Patrik Schmuki ^{*a}

^a Department of Materials Science, WW4-LKO, University of Erlangen-Nuremberg,
Erlangen, Germany

^b HORIBA FRANCE SAS Avenue de la Vauve - Passage Jobin Yvon
Palaiseau, France

**Corresponding author email: schmuki@ww.uni-erlangen.de*

Abstract

In this work we study the depth composition of anodic TiO₂ nanotube layers. We use elemental depth profiling with Glow Discharge Optical Emission Spectroscopy and calibrate the results of this technique with X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS). We establish optimized sputtering conditions for nanotubular structures using the pulsed RF mode, which causes minimized structural damage during the depth profiling of the nanotubular structures. This allows to obtain calibrated sputter rates that account for the nanotubular “porous” morphology. Most importantly, sputter-artifact free compositional profiles of these high aspect ratio 3D structures are obtained, as well as, in combination with SEM, elegant depth sectional imaging.

Link to the published article:

<https://www.sciencedirect.com/science/article/abs/pii/S0169433218305403>

1. Introduction

Over the past decade aligned TiO₂nanotube layers have become strongly investigated for a wide range of applications, ranging from electrochemical over photoelectrochemical to biomedical devices[1–4]. Such self-organized TiO₂ nanotube layers can be easily formed by electrochemical anodization of titanium (or titanium alloy) substrates under self-organizing conditions. Their nanoscale morphology (diameter, length, degree of ordering) can be controlled to a large degree by the anodic parameters and their crystal structure can be adjusted via thermal annealing to anatase, or rutile [5–7].

Due to their anodic growth in organic fluoride containing electrolytes, impurities such as carbon or fluoride are usually incorporated in the oxide structure and still uncertainties remain over their depth distribution this is particularly relevant as a number of important properties (namely the electronic properties) are strongly dependent on the chemical composition in microscopic or nanoscopic regions and compositional variations over the tube length may be particularly relevant. Another critical point regarding composition is that for TiO₂ nanotubes grown in many organic electrolytes, a double walled nature of the tubes has been reported[8]. For example, for tubes grown in ethylene glycol (EG)-based electrolytes, an inner shell is present, consisting of Ti-oxy-hydroxide and carbon species mainly incorporated by EG decomposition. The outer shell consists of pure TiO₂. Additionally, a fluoride rich layer at the outside of the tube has also been reported. Gaining reliable depth distribution of these elements is however cumbersome (analytical TEM of the entire tubes). Typical ion beam sputter techniques carry potential artifacts as will be illustrated below. Furthermore, the inner diameter of the tubes varies over the tube length – the tubes have an inner V-shape morphology which leads to non homogeneous sputter rates[9].

Nevertheless, various depth profiling analytical methods have been used to evaluate the elemental distribution in these layers, mainly by sputtering using ion beam-based methods [10], in comparison with X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy

(AES) or time of flight secondary ion mass spectrometry (TOF-SIMS). However, when used for the analysis of TiO₂ nanotubular layers, with lengths of tubes of several micrometers or even several tens of micrometres, all these techniques encounter practical difficulties due to time consuming. They also induce potentially severe artifacts due to sputtering that continuously increase with depth. When using such ion beam sputtering techniques, a reliable sputtering depth for nanotubes is generally limited to a few hundred nanometres only [7,11–13]. It should be noted that, sputter artifacts are particularly severe as TiO₂ nanotube layers have a “porous” morphology. On the other hand TEM (transmission electron microscopy) is incompatible with a rapid parameter screening approach [9]. Other qualitative approaches may rely on cross-section preparation, which is not only lengthy but also prone to artifacts introduced by the sample preparation procedure. It is worth to mention that, GDOES has no lateral resolution - the sputtered area is several mm² – but it is known to be extremely fast compared to SIMS or XPS and it can measure all elements of interest including C, O, H etc. [10,14]. A particular advantage for our work of the Glow discharge (GD) plasma when operated with a pulsed RF source is the possibility to adjust the sputtering rate in order to achieve a “gentle” sectioning of the tubes.

Herein we show that GDOES elemental depth distribution in anodic TiO₂ nanotubes, can be conveniently obtained and be virtually free of sputter artifacts and that quantitative depth profiles can be generated after the instrument has been adequately calibrated for quantification and sputter rate gradients. This provides rapid and unique information on the chemical composition throughout the entire length of the nanotubes. Moreover, after optimization of the plasma conditions, a well defined sectioning of the tube morphology in depth becomes possible (as shown with SEM imaging).

2. Experimental

The TiO₂ nanotubes were grown by anodization of Ti foils (99.6% purity, Advent, England) in an electrolyte consisting of 1.5 M lactic acid (LA, DL-lactic acid, 90%, Fluka), 0.1 M ammonium fluoride (NH₄F) and 5 wt% deionized H₂O at 120V held at a temperature of 60°C for 450 second (22 μm). The formed anodic TiO₂ nanotubes from a first anodization were removed by ultra-sonication and the sample was used in second anodization using the same experimental conditions. A two-electrode configuration was used with Ti foils as the working electrode, and platinum plate serving as the counter electrode (sample area, 0.785 cm²). After the anodization, the samples were dipped into ethanol for 6 h. Subsequently, the TiO₂ nanotubes were annealed at 450 °C in air for 1 h using a Rapid Thermal Annealer (Jipelec Jetfirst 100 RTA), with a heating and cooling rate of 30 °C min⁻¹.

To remove the inner oxide shell (that consists of a carbon containing lower quality oxide) the samples were annealed at 150 °C in air with a heating and cooling rate of 30 °C/min during 1 h using a Rapid Thermal Annealer (Jipelec JetFirst100). Samples then were dipped in a piranha solution (H₂SO₄:H₂O₂ = 3:1) for 70 s at 110 °C. After immersion to H₂O and EtOH, the samples were dried with a nitrogen jet. Etching for significantly longer than the optimized time, the remaining nanotube layer starts to slowly dissolve too. In addition, extended exposure can make the TiO₂ nanotube layer easier to peel off from the Ti substrate. In order to convert the TiO₂ nanotubes to anatase, the samples were annealed at 450 °C in air with a heating and cooling rate of 30 °C/min during 1 h using a Rapid Thermal Annealer. For morphological characterization, a field-emission scanning electron microscope (FE-SEM, Hitachi SEM FE 4800) was used, which is also equipped with EDX. The EDX is also equipped to the FE-SEM. Elemental depth profile analysis was performed using a GD Profiler 2 from HORIBA Scientific. Plasma conditions were optimized using 650Pa for the plasma gas and a standard RF (13.56 MHz) power of 27 W. In order to reduce the sputtering rate, the RF source was pulsed at 3 kHz with a 0.25 duty cycle, giving an average power of 6.75 W. A 4 mm diameter anode was used. For the plasma discharge, a Neon gas was used in order to have enough ionization energy to

excite fluorine atoms. In GDOES the plasma has a double role, on one side it sputters the surface of the sample to be analyzed, on another it excites the sputtered species. The de-excitation of the excited species leads to the emission of a characteristic light which is recorded using an optical spectrometer. All elements are measured simultaneously and independently.

3. Results and discussion

Figure 1a shows SEM images of top view and cross section of typical TiO₂ nanotubes formed in a fluoride containing organic solution (ethylene glycol) as outlined in the experimental section. The nanotubes have a length of ~22 μm and a diameter of ~150 nm. These high aspect ratio nanotubes show a high degree of ordering (top view). Clearly evident is the double-wall tube (inset of Figure 1a) that has been described in a previous work as inner carbon-rich shell [15]. Figure 1b, c shows a XPS depth profile and an EDX characterization of the tubes. The EDX pattern was taken on a nanotube cross section. It shows the average composition of TiO₂ nanotubes with the presence of the elements Ti, C, O in the layer (composition is shown in the inset), and clearly indicates the 2:1 ratio of Ti:O with approximately 5% C (Figure 1b). F cannot be detected because the amount is lower than the detection limit of the EDX. The EDX data also do not give information regarding the depth distribution of these elements. XPS analysis on the top of nanotubes yields around 22 at% Ti, 54 at% O, 15 at% C and 9 at% F. Figure 1c shows the sputter depth profile of the first 400 nm of the tubes containing layer and gives the chemical composition (atomic percentage) of namely Ti, O, C, N and F. This indicates that the outermost part of the tubes has a uniform distribution in depth of Ti, O and F ions and that the amount of C inside the tubes is too low to be detected. However, if a SEM image is taken after Ar⁺ sputtering of these 400 nm of the tubes, it is clear that non-homogenous preferential sputtering of the tube layers takes place (which increases in severity with extended sputtering) – see Figure 1d.

In order to evaluate if the glow discharge erosion can be optimized towards a more uniform and reliable depth profiling, we investigated normal and pulsed RF plasma discharges

(Figure 2). In both cases, profiles were stopped at approximately half of the length of the tube, i.e. after sputtering $\sim 11\text{ }\mu\text{m}$ of the nanotubular structure. Figure 2a shows the top view SEM image of the tube layer after sputtering with normal RF glow discharge operation during 100 s (corresponding to half of the tube length). It can be observed that these conditions (normal RF plasma sputtering) is too harsh for the nanotubes layer and leads to sinter traces and also to unreliable sputtering profiles (Figure 2a, c). In addition, we do not observe a clear interface at the transition oxide/metal with this normal RF plasma condition (Figure 2c). Pulsing the source at ms frequency allows to reduce the average power on the sample while keeping instantaneous conditions energetic enough for proper excitation leading to intense optical signals. Figure 2b shows the SEM plane-view of the tube layer using the pulsed RF operation mode. It can be observed that the smooth and homogeneous structure of the nanotubes is kept. Figure 2d also shows that despite the overall longer time to obtain an elemental depth profile, a sharper interface is obtained, leading to a more reliable elemental depth profile.

The qualitative GDOES depth profile shown in Figure 2d was not only done with pulsed RF but also using Neon as plasma gas rather than the more classical Argon. Neon is needed for F measurement. [16] Under these conditions, the presence of fluoride rich layer can be clearly seen in the magnified GDOES profile obtained in Ne gas, especially a fluoride enrichment is observed close to the interface. This can be ascribed to the anodic growth mechanism of the nanotubes. Tubes grow by a high field oxidation mechanism where oxide growth is governed by Ti^{4+} and O^{2-} ions transport through the bottom oxide of the nanotube, i.e O^{2-} ions (abstracted from water) migrate through the oxide towards the metal interface where they react with Ti^{4+} species to form new oxide. However, fluoride ions are small and compete with O^{2-} inward migration, this leads to a pile-up at the oxide metal interface. In this work this pile-up can clearly be identified also for high aspect ratio tubes due to the high quality sputtering in pulsed RF GDOES [3].

Please note that with the pulsed operation, higher instantaneous power can be applied, while at the same time preventing thermal effects. By comparing the depth profiles of the same TiO₂ nanotube layers measured with RF and RF-pulsed condition (see Figure 2c,d), it can be clearly seen that the overall required time to sputter through the anodic layer is longer in the pulsed mode, however a sharper interface can be achieved and the tubular structure remains clearly visible. In fact, the SEM image in Figure 2b (taken after halve removal of the tube length) shows very clearly not only the individual tubes but also the presence of an outer and inner wall which is a sign that virtually no sputter damage is induced.

There are only very few works reporting compositional depth analysis of high aspect ratio nanotubes. Few reports of XPS depth analysis are limited to short tubes (<1 μm)[17]. With TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy) up to 7 μm long nanotubes were analyzed [18,19] however the results only confirm the presence of elements but do not provide quantitative information. In contrast, the compositional depth profiles obtained with pulsed RF GDOES clearly illustrate that this technique is highly suitable to evaluate the chemical composition of such kind of materials (and the wide range of derivatized structures [20,21]). GD is a comparative technique that requires calibration to derive quantitative compositional depth profiles (concentrations vs depth) from the measured qualitative ones (intensities vs time). The standard calibration method applied in GDOES [22] fails for these samples partly because they are porous and porosity varies in depth. The erosion rate is therefore not constant in the anodized layer.

Figure 3a shows the SEM images of the TiO₂ nanotubes after stopping the sputtering after certain times (200s, 400s, 600s, 800s, 1000s and at the interface). By calculating the sputter rate of the 22μm long TiO₂ nanotubes, we obtained a nonlinear plot of sputtered length vs. time, which is fitted by equation1 (see Figure 3b).

$$y = y_0 + A \cdot \exp(R_0 x) \quad (1)$$

Where y_0 is 24.4138 ± 0.5275 , A is -24.56915 ± 0.39021 , R_0 is $-0.00185 \pm 1.36399E-4$ and the R-square is 0.99914.

This non linearity is in line with the morphology of the anodized TiO_2 nanotubes that shows a gradient in tube-wall thickness from a thinner wall at the top to a thicker wall at the bottom (apparent from the SEM sequence in Figure 3a). The linear calibration of the chemical composition for GD (concentrations vs intensities) is exemplified here by using EDX data as reference. The use of results from a matrix matching sample greatly minimizes the uncertainties.

Figure 3c shows the resulting profile composition vs time and by applying the Equation 1 above the full quantitative depth profile (composition vs depth) (Figure 3d) is obtained that fully takes into account the nanotube morphology. A significant difference at the nanotubes/metal interface is observed, when comparing the depth profile without and with calibration. Namely, when the time-to-depth conversion is achieved the TiO_2 nanotube/metal interface appears sharper. Thus, we show that an optimized and calibrated pulsed RF GDOES can give quantitative compositional elemental depth profiles of high-aspect ratio nanotubes, which is normally not achievable with other sputter-based methods. Moreover, the sequence of the SEM images in Figure 3a shows that the use of the pulse RF GD-erosion allows to obtain a morphological sectioning of the tubes with a quality remaining virtually constant over the entire tubes length revealing the double wall structure at each investigated tube depth.

4. Conclusion

In the present work, we evaluate the elemental depth profile characterization of anodic TiO_2 nanotubes using RF GDOES. In this aim, we use high aspect ratio tubes that are $22\mu\text{m}$ long and 80 nm wide. After optimizing the GD plasma conditions for such nanotubular structures using the pulsed mode operation, we have shown that it is possible to achieve a virtually damage-free depth profiling of the nanotubular structure. This allows extracting

valuable distinct elemental variations as exemplified by identification of a fluorine rich layer at the metal/oxide interface. After calibration of the erosion rate and a calibration of the composition, quantitative elemental depth profiles can be obtained for the nanotubular porous structure without any sputter-artifact.

Acknowledgements

The authors would like to acknowledge the ERC, the DFG, project EXC 315, and the DFG funCOS for financial support.

References

- [1] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C Photochem. Rev.* 1 (2000) 1–21.
- [2] A. Kudo, Y. Miseki, Heterogeneous photocatalyst materials for water splitting, *Chem. Soc. Rev.* 38 (2009) 253–278.
- [3] K. Lee, A. Mazare, P. Schmuki, One-Dimensional Titanium Dioxide Nanomaterials: Nanotubes, *Chem. Rev.* 114 (2014) 9385–9454.
- [4] S.K. Mohapatra, M. Misra, V.K. Mahajan, K.S. Raja, Design of a Highly Efficient Photoelectrolytic Cell for Hydrogen Generation by Water Splitting: Application of TiO₂-xCx Nanotubes as a Photoanode and Pt/TiO₂ Nanotubes as a Cathode, *J. Phys. Chem. C* 111 (2007) 8677–8685.
- [5] X. Feng, J.M. Macak, P. Schmuki, Flexible self-organization of two size-scales oxide nanotubes on Ti₄₅Nb alloy, *Electrochem. Commun.* 9 (2007) 2403–2407.
- [6] H. Tsuchiya, S. Berger, J.M. Macak, A. Ghicov, P. Schmuki, Self-organized porous and tubular oxide layers on TiAl alloys, *Electrochem. Commun.* 9 (2007) 2397–2402.
- [7] W. Wei, S. Berger, N. Shrestha, P. Schmuki, Ideal Hexagonal Order : Formation of Self-Organized Anodic Oxide Nanotubes and Nanopores on a Ti–35Ta Alloy, *J. Electrochem. Soc.* 157 (2010).
- [8] B.P. and W.Z.W. and C.D. and J.Y.H. and S.K. and D.Z.W. and D.B. and G.C. and Z.F. Ren, Formation of crystallized titania nanotubes and their transformation into nanowires, *Nanotechnology*. 16 (2005) 1935.
- [9] S. So, F. Riboni, I. Hwang, D. Paul, J. Hammond, O. Tomanec, R. Zboril, D.R. Sadoway, P. Schmuki, The double-walled nature of TiO₂ nanotubes and formation of tube-in-tube structures – a characterization of different tube morphologies, *Electrochim. Acta*. 231 (2017) 721–731.

- [10] K.R. Marcus, A.B. Anfone, W. Luesaiwong, T.A. Hill, D. Perahia, K. Shimizu, Radio frequency glow discharge optical emission spectroscopy: a new weapon in the depth profiling arsenal, *Anal. Bioanal. Chem.* 373 (2002) 656–663.
- [11] C.E.B. Marino, P.A.P. Nascente, S.R. Biaggio, R.C. Rocha-Filho, N. Bocchi, XPS characterization of anodic titanium oxide films grown in phosphate buffer solutions, *Thin Solid Films*. 468 (2004) 109–112.
- [12] M. Zhao, J. Li, Y. Li, J. Wang, Y. Zuo, J. Jiang, H. Wang, Gradient Control of the Adhesive Force between Ti/TiO₂ Nanotubular Arrays Fabricated by Anodization, 4 (2014) 7178.
- [13] P. Roy, S. Berger, P. Schmuki, TiO₂ Nanotubes: Synthesis and Applications, *Angew. Chemie Int. Ed.* 50 (2011) 2904–2939.
- [14] P. Belenguer, M. Ganciu, P. Guillot, T. Nelis, Pulsed glow discharges for analytical applications, *Spectrochim. Acta Part B At. Spectrosc.* 64 (2009) 623–641.
- [15] S. Mohajernia, S. Hejazi, A. Mazare, N.T. Nguyen, I. Hwang, S. Kment, G. Zoppellaro, O. Tomanec, R. Zboril, P. Schmuki, Semimetallic core-shell TiO₂ nanotubes as a high conductivity scaffold and use in efficient 3D-RuO₂ supercapacitors, *Mater. Today Energy*. 6 (2017) 46–52.
- [16] H. Habazaki, K. Fushimi, K. Shimizu, P. Skeldon, G.E. Thompson, Fast migration of fluoride ions in growing anodic titanium oxide, *Electrochem. Commun.* 9 (2007) 1222–1227.
- [17] S. Bauer, S. Kleber, P. Schmuki, TiO₂ nanotubes: Tailoring the geometry in H₃PO₄/HF electrolytes, *Electrochem. Commun.* 8 (2006) 1321–1325.
- [18] S. Ozkan, A. Mazare, P. Schmuki, Extracting the limiting factors in photocurrent measurements on TiO₂ nanotubes and enhancing the photoelectrochemical properties by Nb doping, *Electrochim. Acta*. 176 (2015) 819–826.
- [19] M. Kulkarni, A. Mazare, J. Park, E. Gongadze, M.S. Killian, S. Kralj, K. von der Mark, A. Iglič, P. Schmuki, Protein interactions with layers of TiO₂ nanotube and nanopore arrays: Morphology and surface charge influence, *Acta Biomater.* 45 (2016) 357–366.
- [20] A. Ghicov, J.M. Macak, H. Tsuchiya, J. Kunze, V. Haeublein, L. Frey, P. Schmuki, Ion Implantation and Annealing for an Efficient N-Doping of TiO₂ Nanotubes, *Nano Lett.* 6 (2006) 1080–1082.
- [21] C. Das, P. Roy, M. Yang, H. Jha, P. Schmuki, Nb doped TiO₂ nanotubes for enhanced photoelectrochemical water-splitting, *Nanoscale*. 3 (2011) 3094–3096.
- [22] T. Nelis, R. Payling, *Glow Discharge Optical Emission Spectroscopy: A Practical Guide*, Royal Society of Chemistry, Cambridge, 2003.

Figure 1a) SEM top view, cross section and double wall structure of the TiO₂ nanotube layers; b) EDX pattern and the elemental composition of the layer, c) XPS depth profile of the first $\approx 400\text{nm}$ of the nanotubular layer and d) SEM top view of the TiO₂ nanotubes after sputtering with XPS.

Figure 2 SEM top view of the half-length sputtered TiO_2 nanotubes with a) RF plasma b) pulsed RF plasma; GDOES depth profile of the same type of tubes sputtered throughout the entire length with c) RF plasma d) pulsed RF plasma, for representation purposes, C and F magnified 500 times. (Noise in the beginning of the spectra is due to a faster acquisition frequency).

Figure 3a) SEM top view of the TiO₂ nanotubes sputtered for a specific time frame, b) sputter rate graph as a function of the sputtering time fitted with the inset equation where, c) the quantified GDOES profile and d) the quantified profile considering the sputter rate equation.