



Comparison of optical models and signals from XPS and VASE characterized titanium after PBS immersion

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ABSTRACT

Here we consider the optical and the chemical effects of a phosphate buffered saline (PBS), to titanium (Ti) surfaces. Compound (Ti, TiO, TiO₂ and Ti₂O₃) analysis was conducted for native surfaces as well as for ultra pure water exposed and for PBS exposed sample surfaces using an X-ray photoelectron spectroscopy (XPS). The reflectance of surface's top layer was modeled by evaluating Bruggeman's model with the particular refractive index spectra. After the reflectance models were gathered, a diffractive optical elements (DOE) based sensor was used to determine coherent and non-coherent reflectance from the Ti samples, while the Ti surfaces were immersed in water or in a PBS solution. The DOE measured samples were also characterized with a variable angle spectro-ellipsometer (VASE). Accordingly to the reflectance models, the oxidation of the titanium surface decrease the overall reflectance of the surface. However, the DOE sensor measurement showed also signals in which the reflectance was observed to increase. This increase of reflectance was interpreted to be caused by effective gas layer. Study also showed, that used PBS solution had similar chemical oxidation effects, and thus optical effects, to the titanium as used ultra pure water.

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1. Introduction

Phosphate buffered saline (PBS) is a commonly used buffer solution for bio-molecules such as different proteins. When a sample surface is measured optically, the surface characterization has great of importance. Thus, the reflectance changes, that the PBS inflicts to a titanium surface, should be evaluated. Here we model (utilizing Bruggeman's model [1]) and analyze such changes on X-ray photoelectron spectroscopy (XPS) and variable angle spectro-ellipsometry (VASE) characterized titanium surfaces, as well as measure the changes, in real-time, from PBS immersed titanium samples with a diffractive optical element (DOE) based sensor [2]. Used PBS was prepared with 8 mM Na₂HPO₄, 1.8 mM KH₂PO₄, 140 mM NaCl, and 2.7 mM KCl.

In our previous work we have analyzed the optical changes (with DOE sensor), which different proteins produce, on surfaces to evaluate the adsorption process on particular surfaces. In these studies we have discovered, that the buffer solution has some effects on the signals. These optical effects have been noted to be minor compared to the effects of the adsorbed proteins. [3–5] Here we study polished titanium surfaces immersed in ultra pure water and in PBS to evaluate the optical effects caused by the chemical reactions.

2. Results and discussion

In XPS measurements, any given surface is excited with X-ray radiation (Al K_α, $E = 1486.7$ eV). The radiation absorbs into an electron orbital of the material and releases the electrons from the particular orbital. The binding energies of these electrons can be detected and assigned to an element's chemical bond in a compound. In this study we analyzed the surface components of a native polished titanium before and after a water and a PBS immersion. Samples were immersed for 10 min. Fig. 1 shows the XPS-determined component (Ti, TiO, TiO₂ and Ti₂O₃) average ratios, with standard deviations, on a polished titanium before and after the liquid exposure. From Fig. 1 one can see, that the ratio of detected titanium decreases when the samples were exposed to water or a PBS.

To estimate the effective complex refractive index (N_{eff}) of the composite of the titanium and it's oxides, one can deploy Bruggeman's model [1], which can be expressed as follows

$$B(\omega, \varepsilon) = \sum_{i=1}^M f_i \frac{\varepsilon_i(\omega) - \varepsilon_{\text{eff}}(\omega)}{\varepsilon_i(\omega) + 2\varepsilon_{\text{eff}}(\omega)} = 0, \quad (1)$$

where the M is the number of the components, f_i is the component ratio (determined with the XPS analysis), ε_i is the complex permittivity ($\varepsilon_i = \varepsilon'_i + j\varepsilon''_i$, where $j = \sqrt{-1}$ denoting imaginary unit) of a component i , ω is the angular frequency (rad/s) at known wavelength λ

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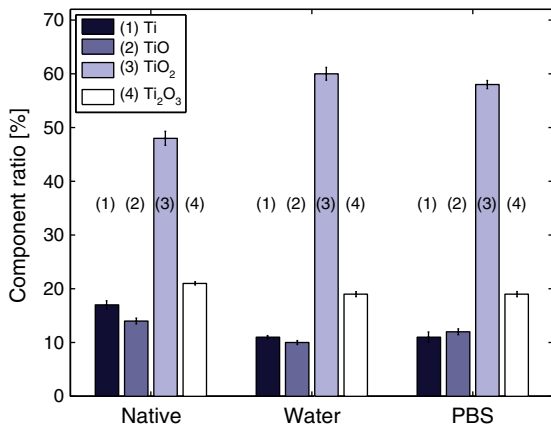


Fig. 1. Chemical component ratios of a native titanium, a titanium after a water treatment and after a PBS treatment determined from the XPS spectra. Vertical lines denote the standard deviations.

($\omega = 2\pi c/\lambda$ and c is the speed of light in vacuum) and ε_{eff} is the effective permittivity of the surface formed by the chemical components.

Solving of Bruggeman's model can be done directly from Eq. (1), analytically, when M is two i.e. there is two mixed substances with ε_1 and ε_2 . However, when M increases, the analytical solution becomes more and more tedious. Here we have four different components to mix ($M=4$): Ti, TiO, TiO₂ and Ti₂O₃. This is why we have solved the effective permittivity with finite element analysis by iterating different possible complex permittivities to satisfy Eq. (1). To describe the iteration procedure, in Fig. 2 is shown an example of $B(\omega, \varepsilon)$ values as a function of the components ($\varepsilon', \varepsilon''$) of the permittivity ε at wavelength of 632.8 nm. Iteration, in the search of the complex permittivity, that satisfies Eq. (1), was done twice. In the first step the iteration area was 50×50 (with increment of 0.5) and possible solution areas in the second iterations step were 2×2 (with increment of 0.02) in the ($\varepsilon', \varepsilon''$) plane.

In next step, solving the effective permittivity, one must find the zero points of the $B(\omega, \varepsilon)$ plane (similar to the Fig. 2). Corresponding permittivity values for these points are then evaluated if they are logical. That is, if potential permittivity (solution for Eq. (1)) has a corresponding reflectance (R) values, which are smaller than 1 and greater than 0.

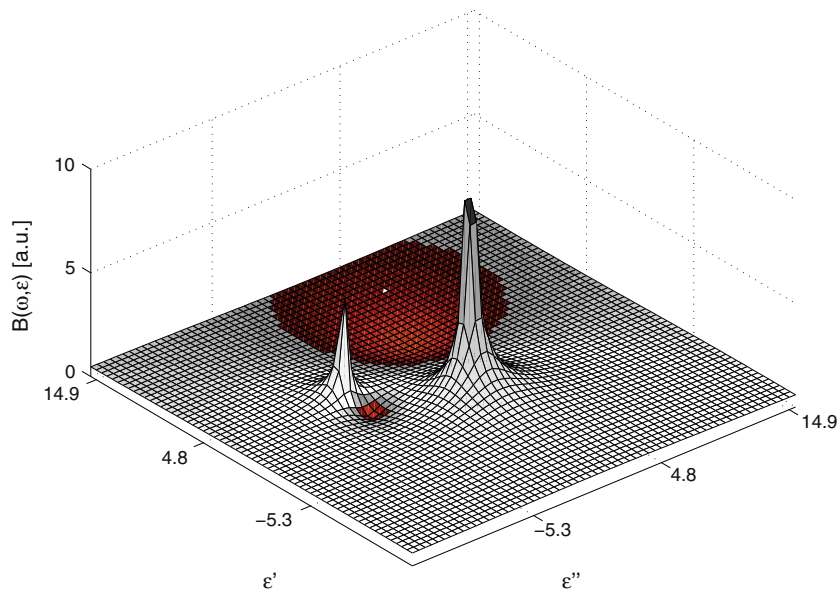


Fig. 2. Example of a characteristic permittivity surface ($\varepsilon', \varepsilon''$) calculated using Eq. 1 for polished titanium after PBS immersion at wavelength of 632.8 nm. Red shadowed areas denote local minimas of B values, which are to be evaluated.

We have calculated the effective permittivities of titanium, without and with water or a PBS immersion. The permittivity connects to the complex refractive index (N) with the relation $\varepsilon = \sqrt{N}$ and to the reflectance (in air) $R = (N-1)/(N+1)$. After quantifying the complex refractive index through the effective permittivity, one can calculate the surface reflectance R . In Fig. 3 is presented the reflectance for the native (R_{effN}), water treated (R_{effW}), PBS treated titanium (R_{effP}) and also the reflectance of an individual bulk titanium and titanium(II, III and IV) oxides. In Fig. 3 variable angle spectro-ellipsometer (VASE) measured refractive indexes (R_{VASE}) are presented for comparison. From the Fig. 3 one can see, that the reflectance of each individual oxide is quite similar. When calculating R by utilizing the effective permittivity, solved from Eq. 1, the ratio of titanium seems to be dominant. This can be concluded for example from the difference of the R_{effN} and the R_{effP} curves in Fig. 3. Underlying spectrum, used in the calculation, mostly define the end results and different literature values might vary from each other. For example, when comparing Ti_{BULK} and Ti_{VASE} in Fig. 3, the differences could be caused from different roughnesses and oxide component ratios, while the spectra were determined.

A DOE sensor setup [2] used in water and in PBS measurements is presented in Fig. 4. The utilized DOE setup is an accurate one-arm interferometer with an accuracy of 0.2 nm and which has been used successfully, also in liquid environments, in our previous studies [4,5]. Thus, we selected this equipment for the water and the PBS *in-vitro* measurements. The XPS measures the surfaces in dry environment, but the DOE has ability to sense the permittivity changes in the surface, caused by a water or a PBS solution, in real time, while the surface is immersed in the particular liquid. In our setup, the DOE focuses a 4×4 dot matrix in its focal plane, when a coherent light wavefront (here $\lambda = 632.8$ nm), reflected from a test surface, is passed through its aperture. The size of the DOE aperture was $4 \text{ mm} \times 4 \text{ mm}$, focal length was 100 mm and dimensions of the dot matrix image in DOE's focal plane was $400 \mu\text{m} \times 400 \mu\text{m}$. Because this reflected wavefront bears information from a surface, the image, which the DOE produces, changes accordingly to the changes on a surface. After recording a DOE image, one can calculate two parameters (gloss G and optical roughness R_{opt} , non-coherent and coherent part of the wavefront) from it.

In Fig. 5 is presented a temporal response, produced by the DOE sensor analysis, from a titanium surface. The reaction, induced by

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