

## BaTiO<sub>3</sub> FILMS DEPOSITED ONTO TiNb AND Ti SUBSTRATES - AMOUNT AND STABILITY OF BARIUM

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**ABSTRACT.** BaTiO<sub>3</sub> films deposited onto TiNb and Ti substrates using hydrothermal synthesis method were studied in the presented work. These films are supposed to improve properties of bone implants due to their ferroelectric behaviour, because ferroelectrics induce improved bone formation. A great question is the chemical stability of the used material. It can be crucial for its biocompatibility and possible in vivo application. We studied chemical composition of prepared samples, especially concentration of Ba and Ti and trends of these concentrations stimulated by a solution saline action. The Ba and Ti concentrations were determined by XPS under ultra - high vacuum condition. The BaTiO<sub>3</sub> films were investigated as received after the preparation procedure as well as after a long - time treatment in solution saline. Every sample was introduced to the solution saline at first for 1 and later for 3 weeks. Ti concentration almost does not change during our experiments while a meaningful Ba decrease is observed. Nevertheless, barium release seems to slow down with respect to the time of solution saline action. Stability of barium titanate films in a period of several months and an absolute amount of the released barium will be a subject of the next research.

**KEYWORDS:** Barium titanate, XPS, concentration, stability.

### 1. INTRODUCTION

Barium titanate could be a promising material for the development of bone implants. This material exhibits ferroelectric properties. If it is polarised, it can improve the bone adhesion to the implant [1–3]. Chemical elements included in barium titanate are biocompatible except for barium which is toxic. We studied chemical composition of thin barium titanate film deposited onto titanium and titanium-niobium alloy substrates using XPS method. We have determined the chemical composition of as prepared samples and after their treatment in solution saline. Barium release is observed and discussed.

### 2. EXPERIMENTAL

Barium titanate films deposited onto TiNb or Ti substrates were prepared by hydrothermal synthesis. Samples were in the form of discs of 10-14 mm diameter and thickness 0.5-1.4 mm. Using calotest, thickness of deposited films was estimated to be about 1-2  $\mu\text{m}$ .

Before the preparation of barium titanate films, the substrates were cleaned (ultrasonic cleaning in acetone, etching in 6M HCl) and annealed in oxygen at 500 °C for 24 hours. After this procedure, the substrate surface is covered by a TiO<sub>2</sub> rutile layer. Barium titanate films were prepared in an autoclave with a Teflon inlet by the hydrothermal reaction of TiO<sub>2</sub> and Ba(OH)<sub>2</sub> at 250 °C for 6 weeks. Using this

procedure, two sets of BaTiO<sub>3</sub> films deposited onto TiNb and one set deposited onto Ti substrates were prepared. These sets are marked BaTiO<sub>3</sub>/TiNb 1st and 2nd series and BaTiO<sub>3</sub>/Ti, respectively. Because the BaTiO<sub>3</sub> films within a given set were prepared in the same run under completely identical conditions, they are identical so only one sample from every set was analysed by XPS. Before XPS measurement, the samples were not specially cleaned except brief rinsing in ethyl alcohol.

XPS measurements were performed in an ultra-high vacuum chamber with a base pressure better than  $1 \times 10^{-9}$  Torr. System is evacuated by titanium ion getter pump and equipped by a quick sample load lock. Working pressure inside of the vacuum system is monitored by a Bayard-Alpert manometer (Varian) and remained about  $3 \times 10^{-9}$  Torr during XPS measurements. Dual anode (Al and Mg) X-ray source (VG) and hemispherical electron energy analyser (Omicron EA -125) equipped with a 5 channel multiplier detector were used to acquire XP spectra. As a primary radiation, Al-K $\alpha$  line of 1486.6 eV energy was used. Distance between the X-ray source and the samples was about 1 cm. Composition of the barium titanate films was determined using the method of relative sensitivity factors. The obtained data describe the surface film of the depth of about  $2 - 4 \times 10^{-9}$  m,

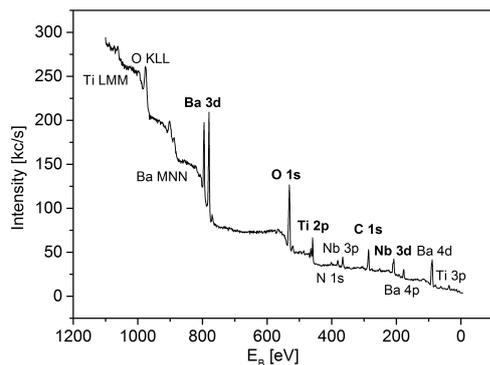


FIGURE 1. Photoelectron spectrum BaTiO<sub>3</sub> on TiNb substrate after preparation of sample. Visible peaks (photoelectron as well as Auger) are marked, those used to calculation of element concentration are in bold.

the relative uncertainty of calculated concentrations should not exceed 20 % of the particular value.

The as prepared samples were characterised by means of XPS and consequently introduced to the solution saline (0.9 mg of NaCl in 100 ml of solution) to check the stability of the BaTiO<sub>3</sub> films in a physiological-like environment. The solution saline was temperature-stabilized at 38 °C, kept under ambient atmosphere and protected against dust and other impurities. The main goal of this treatment was to observe a potential release of Ba. The samples remained in the solution saline for 7 days. After this period, their composition was checked by XPS to determine any possible changes. Subsequently they were re-introduced to a fresh solution saline for next 3 weeks and measured by XPS once more. After every treatment procedure in the solution saline, the samples were rinsed in distilled water.

### 3. RESULTS AND DISCUSSION

Typical electron spectrum of BaTiO<sub>3</sub> is presented in Figure 1. This particular spectrum was obtained for the barium titanate deposited onto TiNb within the first series. We can recognise peaks of Ba, Ti, O, and C. Nb peaks are also visible in the spectrum. They originate from the TiNb substrate. Taking into account the thickness of the barium titanate films, their origin is not clear and is subject of further investigation. A segregation of niobium on the surface or non-completely continuous BaTiO<sub>3</sub> films would explain this observation. Moreover, different samples contain various amounts of carbon. We assume its quantity is influenced by the transfer time between the preparation of the samples and the XPS measurements, by storage conditions etc.

It is, however, out of the scope of this contribution to discuss the chemical forms and concentrations of all the involved elements, we will restrict our discussion

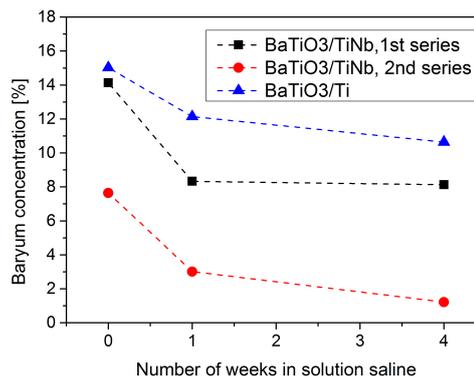


FIGURE 2. Decrease of barium concentration due to an action of solution saline.

only to the barium content with respect to titanium and oxygen.

Oxygen is present in more chemical forms and some of them are obviously included in carbon species. Therefore we only used the so-called lattice oxygen for our calculation of the barium content. It is the oxygen chemically bonded within BaTiO<sub>3</sub>. After fitting O 1s peak, it can be recognised at the binding energy of about 529.5 eV, according to ref. [4], where electron spectra of BaTiO<sub>3</sub> powders exhibit similar features as ours.

The change in the amount of barium is crucial indicator in this study. In Figure 2, relative amount of barium with respect to the total amount of Ba, Ti, and lattice O is presented. It can be seen that the content of barium on the BaTiO<sub>3</sub>/TiNb sample (2nd series) exhibits much lower values. We are currently not able to explain this effect. The most essential, however, is the general trend of barium content decay with the time of sample treatment in the solution saline, which is clearly observed on all the samples. This decrease is more considerable after the 1st week than after the following three weeks. The slowdown of the barium release into the solution saline is the most obvious on the 1st series of BaTiO<sub>3</sub>/TiNb samples. The barium release was independently confirmed by an XPS measurement of NaCl obtained from the used solution saline. Along with Na and Cl peaks, we were able to recognise traces of barium in the XP spectra.

Contrary to barium, the change of titanium concentration is much weaker as can be seen in Figure 3. Generally, it slightly increases except for the 1st series of BaTiO<sub>3</sub>/TiNb where a decrease is observed after the 1st week. Extremely high value of titanium concentration on the BaTiO<sub>3</sub>/Ti sample is probably given by the contribution of the base substrate material. All these results can be identically interpreted as a release of barium to the solution saline. This process could also occur in a human body if barium titanate was used as a material for bone implants. In the follow-up research, we will further investigate if this process fades after some prolonged period of time resulting

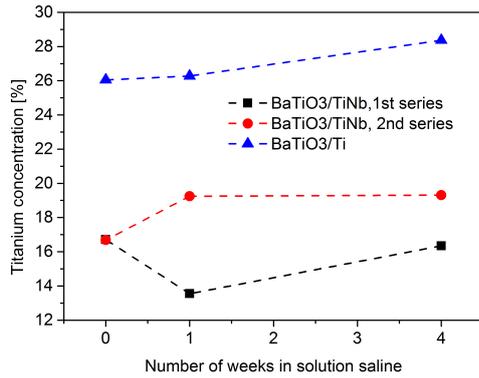


FIGURE 3. Titanium concentration due to an action of solution saline.

in a stable barium titanate thin film. Another topic to be studied on these materials is their ferroelectric properties after the treatment in a solution saline or in a physiological-like environment.

#### 4. CONCLUSION

A depletion of barium concentration in BaTiO<sub>3</sub> thin films under the impact of solution saline was studied. Barium releases into the solution saline, but it can be expected that this effect will become weaker over an extended period of time and the chemical stability of the material will be achieved. Such long-time experiment are currently under the progress.

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