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PLD prepared bioactive $BaTiO_3$ films on TiNb implants

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ABSTRACT

$BaTiO_3$ (BTO) layers were deposited by pulsed laser deposition (PLD) on TiNb, Pt/TiNb, Si (100), and fused silica substrates using various deposition conditions. Polycrystalline BTO with sizes of crystallites in the range from 90 nm to 160 nm was obtained at elevated substrate temperatures of (600 °C–700 °C). With increasing deposition temperature above 700 °C the formation of unwanted rutile phase prevented the growth of perovskite ferroelectric BTO. Concurrently, with decreasing substrate temperature below 500 °C, amorphous films were formed. Post-deposition annealing of the amorphous deposits allowed obtaining perovskite BTO. Using a very thin Pt interlayer between the BTO films and TiNb substrate enabled high-temperature growth of preferentially oriented BTO. Raman spectroscopy and electrical characterization indicated polar ferroelectric behaviour of the BTO films.

1. Introduction

Biomaterials are widely used for replacing irreversibly damaged tissues in the human body. They have to meet requirements for good functioning and long-term durability of the implants, namely biocompatibility, good corrosion and fatigue resistance, wear resistance and biomechanical compatibility [1]. An important requirement of implants designed to replace or interact with bone is a low elastic modulus matching as closely as possible to that of the surrounding tissue [2]. Nowadays, Ti6Al4V alloy is frequently used for construction of implants because of low price and good mechanical properties [1].

Titanium and Ti6Al4V α-β alloys possess the lowest elastic modulus of the currently used surgical metals (~110 GPa); nevertheless, their stiffness is still high compared to that of human cortical bone (~20 GPa) [3]. The β-Ti alloys, and especially those based on Ti and Nb, have significantly lower elastic moduli and can become an attractive orthopaedic material [3].

Elastic modulus decreases to ~60 GPa at about 40 wt.% Nb for TiNb [4,5]. Titanium (Ti)-niobium (Nb) alloys have attracted much attention not only because of their non-toxicity, high corrosion resistance and beneficial mechanical properties [6–8], but also because of their high biocompatibility, i.e. improved cell adhesion and proliferation, particularly on their oxidized surfaces [9].

The electrical activity of biomaterials can improve their integration with the surrounding living tissue. It is well known that bone is electrically active under mechanical loading, due to the piezoelectricity of collagen [10,11] and the movement of ionic fluids within the bone structure (streaming potential) [12]. Electrical potentials in mechanically loaded bone have been linked to the mechanical adaptation of bone in response to loading [12–15], leading to the suggestion that the addition of an electrically active component to an implant material may improve healing and adaptation of the surrounding tissue. Recently, considerable interest has emerged to exploit this phenomenon to develop electrically active ceramics for implantation in hard tissue, which may induce improved biological responses [16,17].

In vivo studies of polarized hydroxyapatite ceramics have shown polarized samples to induce improvements in bone ingrowths [16,18]. Many piezoelectric ceramics proposed for implants are based on perovskite oxide ferroelectric barium titanate $BaTiO_3$ (BTO). In vivo and in vitro investigations have indicated that ceramics of this kind are biocompatible and, under appropriate mechanical load, induce improved bone formation around implants [16]. The mechanism by which electrical activity influences biological responses is not clearly understood, but it is likely to result from preferential adsorption of proteins and ions onto the polar surface.

Our work is aimed at coating TiNb implants (substrates) with ferroelectric $BaTiO_3$. It is known that the formation of the desired perovskite BTO phase requires high temperatures and oxygen-rich atmosphere, i.e., conditions under which intensive oxidation of the TiNb surface takes place. In order to avoid this unwanted oxidation, which prevents

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crystallization of chemically and structurally pure BTO, an appropriate technology should be developed. Here the BTO films were prepared using PLD method. The deposition conditions, post-deposition processing, and multilayer design were varied and optimized with respect to phase composition, morphology, crystallinity, and polar properties of BTO.

2. Experimental

We have prepared BTO thin films using PLD. A high power KrF excimer laser (COMPexProTM 205 F, λ = 248 nm, τ = 20 ns) was used as an external source to vaporize the target material. The pressed BTO target pellet had 25 mm in diameter at a thickness of 5 mm. The films were prepared on one-side polished Ti-39 wt.% Nb, Pt/TiNb, Si (100) and fused silica substrates. β-Ti39Nb alloy samples were prepared by arc-melting 61 wt.% Ti (ingot, 99.55%, Frankstahl, Austria) with 39 wt.% Nb (ingot, 99.85%, TIC, Brussels, Belgium). The melting proceeded eight times at 800–1000 A/23 V with subsequent solution annealing at 850 °C for 30 min and water quenching to achieve the defined homogeneity.

The substrates for the TiNb layer were ground and polished. Using a SiC cutting wheel the as-prepared ingot was sliced into coupons (diameter of 10.5 mm and thickness of ~1 mm). The surfaces of the coupons were ground sequentially with abrasive papers (240, 600, 800, 1000 and 4000 grit) and then polished with a suspension of colloidal SiC (0.05 μm, Colloidal Sillicat, Leco, CR) into a mirror-like sheen, using a Leco machine.

Some films were subsequently post-annealed using rapid thermal annealing (RTA) method (Solaris 75, L&B Semiconductor) to recrystallize the layers after laser deposition.

Thickness and roughness of layers were measured by an Alpha-step IQ mechanical profilometer (KLA TENCOR Co.). The uncertainty in the thickness estimation is about 10% in the examined range of thicknesses, partly due to the fact that the layer thickness in the centre of the sample is higher than at its edges.

Film morphology was checked by scanning electron microscope Jeol JXA-733.

We used XRD in two different arrangements and sources: with divergent beam (Bragg Brentano) and with parallel beam. The reason was to find wider scale of conditions to determine preferred orientations. The first one uses a parallel beam geometry, Cu radiation (0.154056 nm), a detector scan with the stationary sample (rotating around the normal to the surface), and the glazing angle of incidence (GAOI). The second one uses a Bragg-Brentano geometry with a linear X'Celerator detector, the Co radiation (λ = 0.178901 nm). The samples were inclined by 5° from ideal position to avoid diffraction from single crystal substrate. The diffraction patterns were evaluated by Rietveld-like program TOPAS 3 [19]. In this method the measured diffraction pattern is compared with the calculated one and the input parameters are varied on the basis of differences between the measured and calculated diffraction pattern. For the calculation of diffraction pattern, the program is using the so-called "fundamental parameter approach" [20], i.e. the calculated diffraction profile is based on convolution of particular contribution to diffraction profile. Three components of diffraction peak broadening are taken into account: the instrumental broadening, average crystallite size and microstrains. In this way, precise determination of the average crystallite sizes and microstrains is possible. Microstrains e describe the fluctuation of inter-planar distance d and are defined as $\Delta d/d$ [21]. Moreover, the Rietveld base procedure gives also the lattice parameters and eventually phase composition.

The Raman spectra were excited on the optically polished samples with the 514.5 nm line of an Ar-laser at a power of 20 mW and recorded in back-scattering geometry using an RM-1000 RENISHAW Raman Microscope equipped with a Bragg filter. The diameter of the laser spot on the sample surface amounted to 2–3 μm, and the power on the samples was about 4 mW.

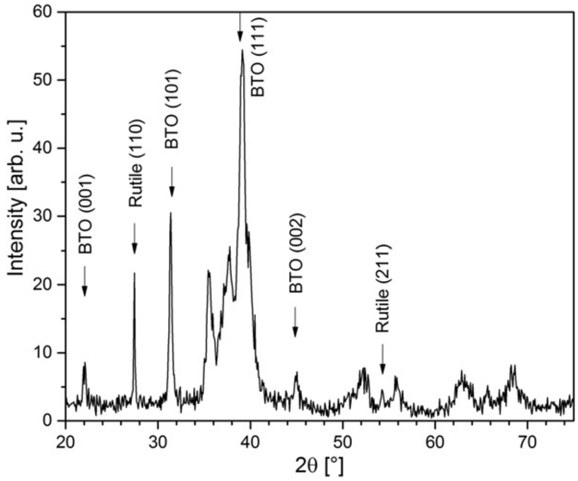

Fig. 1. XRD spectra of BaTiO$_3$/TiNb (1 Pa O$_2$, 2 J cm^{-2}, $d_{\text{T-S}} = 35$ mm, $T_S = 700$ °C, 120 nm).

For electrical characterization of the BTO films, thin-film capacitors were formed by pulsed laser deposition of the Pt top circular electrode pads using shadow masks. As a bottom electrode, either the TiNb substrate itself or additional Pt layer was employed. The area of capacitors was 0.2–12 mm^2. The polarization, leakage current, capacitance, and loss factor were measured by a TF2000 Analyzer (aixACCT Systems GmbH). The capacitance-voltage characteristics were acquired using superposition of dc biasing voltage and small ac probing signal.

3. Results and discussion

The goal was to prepare ferroelectric thin films on TiNb substrates. At first we have tried to fabricate crystalline BTO films on TiNb, for target-substrate distance $d_{\text{T-S}} = 35$ mm and two values of the oxygen pressure (1 Pa and 20 Pa). We varied substrate temperature (T_S) from 200 °C to 900 °C.

Layers were amorphous for deposition temperatures T_S up to ~500 °C. With increasing temperature T_S, the formation of perovskite BTO was achieved, which, however, was accompanied by profound growth of rutile. The X-ray diffraction (XRD) revealed the presence of (001), (101), (111), and (002) BTO diffractions, (110) and (211) rutile (TiO$_2$) diffractions and also some unidentified diffractions. The intensity of the BTO diffractions was the highest at 700 °C and decreased with increasing T_S, whilst the inverse trend was observed for the rutile. With increasing T_S to 900 °C, also oxygen deficient titania phases were detected.

For the best crystallized BTO ($T_S = 700$ °C, oxygen pressure of 1 Pa), the ratio of intensity of diffractions (100)/(111) was approximately

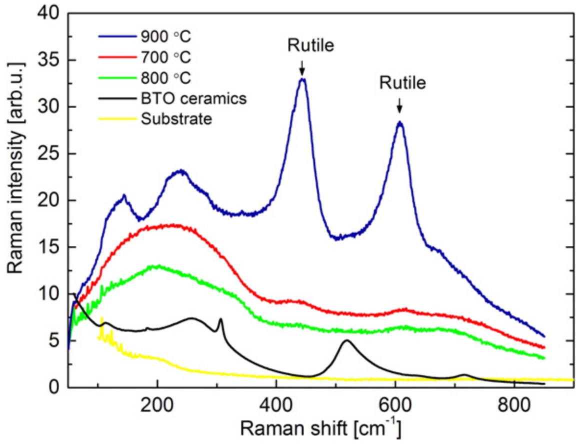

Fig. 2. Raman spectra of BaTiO$_3$/TiNb ($T_S = 700$ °C, 800 °C and 900 °C).