

The Investigation of E-beam Deposited Titanium Dioxide and Calcium Titanate Thin Films

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Thin titanium dioxide and calcium titanate films were deposited using electron beam evaporation technique. The substrate temperature during the deposition was changed from room temperature to 600 °C to test its influence on TiO₂ film formation and optical properties. The properties of CaTiO₃ were investigated also. For the evaluation of the structural properties the formed thin ceramic films were studied by X-ray diffraction (XRD), energy dispersive spectrometry (EDS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Optical properties of thin TiO₂ ceramics were investigated using optical spectroscopy and the experimental data were collected in the ultraviolet-visible and near-infrared ranges with a step width of 1 nm. Electrical properties were investigated by impedance spectroscopy. It was found that substrate temperature has influence on the formed thin films density. The density increased when the substrate temperature increased. Substrate temperature had influence on the crystallographic, structural and optical properties also.

Keywords: electron beam evaporation, titanium oxide, calcium titanate, optical properties.

1. INTRODUCTION

Titanium dioxide, also known as titania, is one the most investigated transition metal oxide due to its remarkable chemical, optical and electronic properties that make it suitable for a variety of applications, such as energy conversion and storage, especially photovoltaics [1–3], photocatalysis [4, 5], optical coatings [6, 7], gas sensors [8] or biomedical uses [9]. Along with its useful applications, TiO₂ provides the benefits of low toxicity, good chemical stability, and ease of fabrication [10]. Titania thin films may be formed using various preparation methods – spincoating of sol gel precursors [11], different physical vapor deposition techniques [12–15], anodic oxidation [9], chemical vapor deposition [16–18] and others [8, 19–20]. With all these thin film preparation methods, titanium dioxide coatings can exhibit largely varying structural and optical properties [21], which are easily affected by the technological conditions of the deposition process such as the substrate temperature and oxygen partial pressure as well as the annealing [22].

Titanium dioxide phase has an important impact to the structural and optical properties of the formed thin films. Titanium dioxide can be in three different phases: anatase, rutile and brookite, though only amorphous, anatase and rutile phases have been observed until now for deposited films [23].

It is important to optimize the preparation process to obtain TiO₂ film with appropriate phase composition and one of the key parameters to influence the microstructure of TiO₂ films is the substrate temperature. Moreover there is little study on titanium oxide and related compounds deposited by electron beam evaporation method. Titanium

based compounds as calcium titanates are thermally and chemically stable, and they are also known for their phase transitions, which strongly affect their physical and chemical properties. CaTiO₃ is being widely used in electronic ceramic materials [24]. Therefore in present study titanium oxide thin films were deposited using electron beam evaporation method and the substrate temperature influence on the microstructure, chemical composition, surface morphology and optical properties of the formed TiO₂ thin films are studied. The properties of titanium compound CaTiO₃ with emphasis to electrical properties were also discussed.

2. EXPERIMENTAL

Two different powder mixtures as e-beam deposition materials were prepared. The initial commercial pure (99.9 %) TiO₂ powder of 25 μm grain size was used for the formation of thin TiO₂ films. The CaTiO₃ powder was prepared by mixing equal molar ratio of initial TiO₂ and CaO (99.99 %) powders. Prepared powders were pressed to pellets and evaporated in the e-beam evaporation system Kurt Lesker 75. Two substrate materials of optical quartz (SiO₂) and Alloy 600 (Ni-Cr-Fe) were chosen to investigate their influence on the growth of thin films. Traditional substrates cleaning routine of ultrasonically cleaning in pure acetone and cleaning in radio frequency (RF) Ar ions plasma was applied. Substrate temperature was changed from room temperature to 600 °C before deposition for the titania thin films and it was kept at the constant temperature of 600 °C for the CaTiO₃ films. The deposition rate was manually controlled and kept at 0.2 nm/s.

The thickness of the formed thin films was measured with an Ambios XP-200 profilometer. Thin films density was calculated from measured films thickness, thin film mass and surface area. The surface morphology of the thin

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formed films was investigated using the scanning electron microscope (SEM) JSM 5600. The elemental composition was analyzed with X-ray energy-dispersive spectroscope (EDS, Quad 5040 Bruker AXS Microanalysis GmbH). In addition, the atomic force microscope (AFM, Bruker Icon SPM, cantilever used ScanAsyst-HR (130 kHz, 0.4 N/m)) was used to investigate surface structure of thin films. All measurements with AFM were done with closed-loop control active, PeakForce QNM mode used. X-ray diffraction (XRD, D8 Discover (Bruker AXS GmbH) standard Bragg-Brentano focusing geometry in a 20° – 70° range using the Cu $K_{\alpha 1}$ $\lambda = 0.1540562$ nm radiation) was used to analyze crystallinity of the formed thin films. Ocean Optics spectrometer was used to obtain the transmittance spectra and the experimental data were collected in the ultraviolet-visible and near-infrared ranges ($\lambda = 300$ nm– 900 nm), with a step width of 1 nm. The electrical properties of the formed ceramics were investigated and impedance spectroscopy measurements were performed using Probostat[®] (NorECs AS) measurement cell. The measurements were done in the frequency range from 10^{-1} Hz– 10^6 Hz under reducing and oxidising conditions. Impedance spectroscopy was performed in temperature range from 200°C to 600°C increasing the temperature by 20 degrees step. The activation energy was calculated using Arrhenius law from obtained conductivity plots at different measurement temperatures.

3. RESULTS AND DISCUSSION

Firstly the thin titanium dioxide films were deposited in order to investigate the influence of substrates temperature during deposition on the formed thin films properties. It was found that the increasing in substrate temperature leads to more stable thin films and enhances electrical properties of the deposited films. Some of the results were published in [25]. Moreover, the deposited titania films surface density, surface roughness and optical properties were influenced by the increasing of substrate temperature as well. Table 1 shows that the density of deposited titania thin films and the CaTiO_3 density increases when the substrate temperature increase. As it is seen from the table the relative density of calcium titanate is obtained higher than for titanium dioxide.

Table 1. Density of the formed thin films

Substrate temperature during the deposition, $^{\circ}\text{C}$	Relative density (theoretical TiO_2 density of 4.23 g/cm ³ , CaTiO_3 – 3.94 g/cm ³)
20°C	77.5 %
300°C	81.2 %
600°C	90.6 %
CaTiO_3 , 600°C	93.5 %

When evaporating metal oxides, the elemental composition of the compounds may vary from the initial material in the crucible. In our case, the elemental composition had small variations from the initial material (Table 2) and the TiO_2 compound stoichiometry was achieved for the samples with higher substrate temperature during the deposition.

Table 2. Elemental composition of the formed thin films

Substrate temperature during the deposition, $^{\circ}\text{C}$	Ti, at. %	O, at. %	
Initial TiO_2	40.00	60.00	
20°C	42.55	57.45	
300°C	43.32	56.68	
600°C	40.00	60.00	
	Ca, at. %	Ti, at. %	O, at. %
CaTiO_3 , 600°C	26.4	21.3	52.3

The thin TiO_2 films deposited on the room temperature substrate had unstable structure and underwent severe deformation and strain-related crumbling off the substrate. The microcracks on the titanium oxide thin film gradually decreased in raising the substrate temperature and the surface became without any visible microcracks as the temperature raised to 600°C (Fig. 1) [25]. From the Fig. 1, d) it can be seen that the thin calcium titanate ceramics were formed with smooth surface and the growing mechanism for these films differs from titanium dioxide and is without columnar grain growth. The bulk material has uniform structure, which indicates that the formed ceramics are dense (see Table 1).

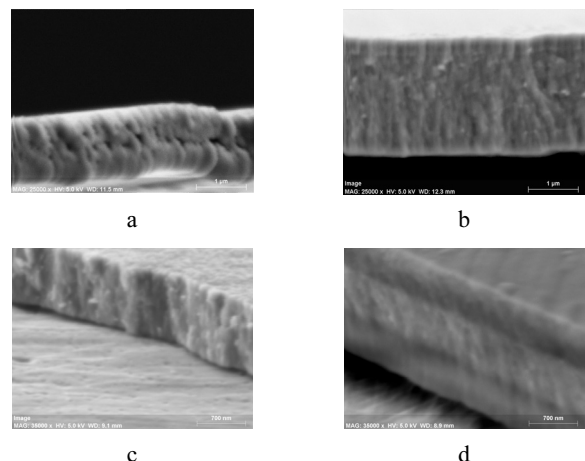


Fig. 1. SEM cross-sectional view of the thin films formed on Alloy 600 substrate: TiO_2 thin films when the substrate temperature during the deposition was (a) room temperature, (b) 300°C , (c) 600°C and (d) CaTiO_3 thin film

Fig. 2 illustrates the XRD diffraction patterns of TiO_2 films, which were deposited at different substrate temperature and the XRD diffraction pattern for CaTiO_3 .

From the figure, it was found that the TiO_2 films deposited at the room temperature substrate and CaTiO_3 thin films had amorphous structure, while the titanium dioxide films deposited at higher temperature substrates are polycrystalline having anatase phase. It's assumable that the amorphous phase was obtained due to the low energy and low mobility of particles impinging on the “cold” substrate, influencing the slow surface diffusion [21] and the lattice deformations occurred due to the microcracks. At higher substrate temperatures the kinetic energy becomes high enough to start the crystallization of the films. When the substrate temperature was 300°C , the crystallization process of tetragonal anatase phase takes place with crystal planes

(101), (004) and (105) appeared, but the intensity of peaks is weak. It was observed that other characteristic anatase peaks appears when the substrate temperature increases. The transition temperature from anatase and rutile range between 350 °C and 1175 °C depending on the method of preparation of the sample, by the presence of impurities or additives for the stabilization of the certain modification, and by the atmosphere present during the transformation [26]. The anatase-rutile transformation in electron beam evaporated thin films starts at 700 °C–900 °C [22, 27], therefore the transformation is not visible in our case.

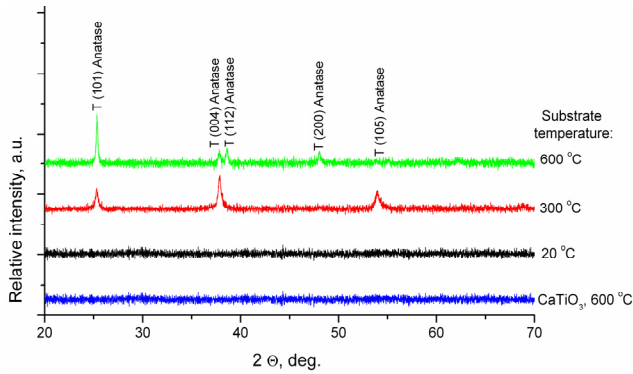


Fig. 2. XRD patterns of the thin films deposited on optical quartz (SiO_2)

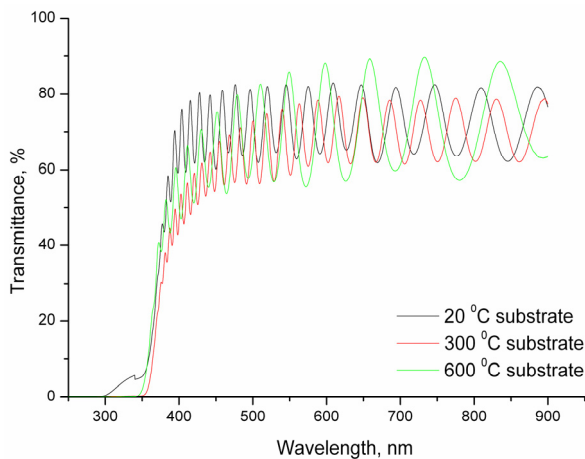


Fig. 3. Transmittance spectra of the TiO_2 films formed with different substrate temperature during the deposition

The transmittance spectra in ultraviolet and visible light of titanium oxide films deposited on different temperature quartz substrate are shown at Fig. 3. It can be seen that all samples exhibit high average transmittance of 77 % in whole UV and visible light region. Anyway, the substrate temperature has a slight influence to the optical transmittance, which slightly decreases in UV area with the substrate temperature increasing. The same phenomenon was observed for titanium and other metal oxides after annealing and great optical losses occurred after annealing at 900 °C [22–23, 28–29]. These optical losses could be explained due to oxygen defects. Tian G. et al. [21] gave the theoretical model, which relates the surface morphology of thin films and optical properties. The transmittance curve shift and transmittivity decrease is resulted by absorption posed by absence of oxygen and scattering of rough surface.

The surface roughness is one of the main mechanical parameters of the thin films. Very rough surfaces could lead to interconnection and other problems. Surface roughness is also influenced by energy of arriving particles, surface temperature, composition of deposited flux, layer thickness [30, 31].

The surface morphologies of the formed thin TiO_2 films were observed by atomic force microscope (Fig. 4) and the influence of substrate temperature was studied. The atomic force microscope results well agree with the optical transmittance properties. It was found that the thin films formed on the room temperature substrate with amorphous structure have uniform morphology as well as relatively small surface roughness. The increasing of substrate temperature influences the surface roughness and a granular morphology appears when the substrate temperature during the deposition is 300 °C. The crystallization process and phase changes of the ceramics at 300 °C substrate temperature influenced the increasing in roughness of the formed films. AFM pictures indicate that the microstructure of thin titanium oxide films is formed by the columnar growth (see Fig. 1) of deposited thin films, which is quite usual growing mechanism for electron beam deposited films. At higher substrate temperature the surface features size develops (“blobs”) besides the grains. The higher substrate temperature results the larger surfaces grains as the crystallinity improves by increasing the substrate temperature as it was shown in XRD patterns.

Undoped titanium dioxide and calcium titanate may exhibit mixed ionic and electronic conduction [32]. Table 3 presents the total conductivity values of the formed ceramics. The total conductivity values are temperature dependent and gradually increase when the temperature increases.

Table 3. Total conductivity under different conditions and their activation energy of the formed TiO_2 (substrate temperature – 600 °C) and CaTiO_3 films

	Wet O_2 conditions			
	σ_{tot} , Sm^{-1} (300 °C)	σ_{tot} , Sm^{-1} (400 °C)	σ_{tot} , Sm^{-1} (500 °C)	σ_{tot} , Sm^{-1} (600 °C)
TiO_2	$2.92 \cdot 10^{-7}$	$8.49 \cdot 10^{-7}$	$1.08 \cdot 10^{-5}$	$5.67 \cdot 10^{-5}$
CaTiO_3	$4.11 \cdot 10^{-8}$	$8.96 \cdot 10^{-7}$	$9.39 \cdot 10^{-6}$	$1.86 \cdot 10^{-5}$
	Wet H_2 conditions			
	σ_{tot} , Sm^{-1} (300 °C)	σ_{tot} , Sm^{-1} (400 °C)	σ_{tot} , Sm^{-1} (500 °C)	σ_{tot} , Sm^{-1} (600 °C)
TiO_2	$7.50 \cdot 10^{-6}$	$1.90 \cdot 10^{-5}$	$9.28 \cdot 10^{-5}$	$2.30 \cdot 10^{-4}$
CaTiO_3	$1.27 \cdot 10^{-7}$	$2.27 \cdot 10^{-6}$	$3.27 \cdot 10^{-5}$	$5.47 \cdot 10^{-5}$

The values of the ionic conductivity increase with the rise of the substrate temperature during the deposition. Total conductivity values shows that titanium dioxide and calcium titanate exhibit higher conductivities under H_2 reducing conditions rather than oxidising O_2 conditions therefore assuming that protonic and electronic conductivity takes place.

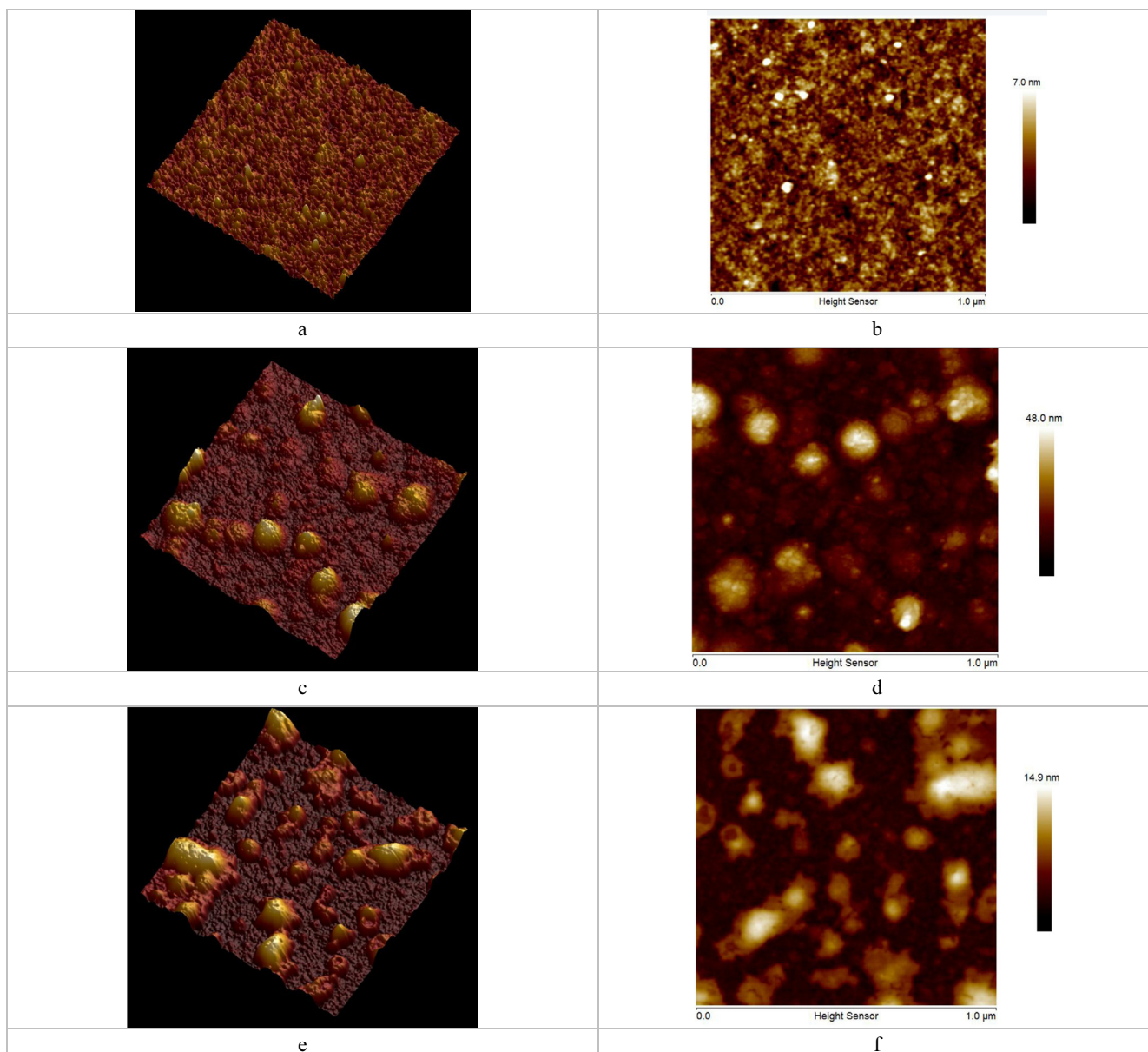


Fig. 4. Surface roughness ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of the formed thin TiO_2 films when the substrate temperature during the deposition was: room temperature (a, b), $300\ ^\circ\text{C}$ (c, d) and $600\ ^\circ\text{C}$ (e, f)

4. CONCLUSIONS

The thin TiO_2 and CaTiO_3 films were successfully deposited by electron beam vapor deposition on Alloy 600 and optical quartz substrates. It was found that substrate temperature has influence on the formed thin films density. The density increased when the substrate temperature increased and reached 90.6 % of relative density when substrate temperature during the deposition was $600\ ^\circ\text{C}$. The density of calcium titanate is obtained higher than for titanium dioxide and reaches 93.5 % of relative density. Substrate temperature had influence on the crystallographic, structural and optical properties of the titanium dioxide thin films. The increase of substrate temperature improved the crystallinity of the films and when substrate temperature reached $300\ ^\circ\text{C}$, the crystallographic anatase phase appeared with better crystallinity at higher temperature. CaTiO_3 films had amorphous structure. Surface morphology studies demonstrated that the surface roughness increase of

$\sim 48\ \text{nm}$ occurred after the crystallization process began when the substrate temperature reached $300\ ^\circ\text{C}$. This increase of the roughness resulted the slight optical transmittance loss when the substrate temperature increased. The total conductivity of the formed films was higher in H_2 reducing conditions and was temperature dependent. The total conductivity is $2.30 \cdot 10^{-4}\ \text{Sm}^{-1}$ for TiO_2 formed on $600\ ^\circ\text{C}$ temperature substrate and $5.47 \cdot 10^{-5}\ \text{Sm}^{-1}$ for CaTiO_3 thin films under H_2 conditions.

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