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Investigation of the properties of Ca-doped TiO₂ thin films formed by e-beam evaporation

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Abstract

Titanium dioxide is considered as one of the most important materials due to its unique dielectric, electrochemical, photocatalytic and optical properties. These properties can be altered by introducing particular amount of dopants. In this work, Ca-doped titanium dioxide was formed by electron beam deposition method and the structural and electrical properties were investigated. For the evaluation of the structural properties the formed thin ceramic films were studied by X-ray diffraction (XRD), energy dispersive spectrometry (EDS) and scanning electron microscopy (SEM). Electrical properties were investigated by impedance spectroscopy. It was found that when the concentration of Ca dopants increases the crystallites size increases as well and follows Vegard's law. The impedance measurements show that the Ca-doping decreased the total conductivity of the formed thin films. The total conductivity varies from 2.7 S/cm in pure TiO₂ to 4×10^{-4} S/cm in 2.5 % Ca doped TiO₂ at 800 °C under wet reducing conditions and from 5.4×10^{-4} S/cm in pure TiO₂ to 3.4×10^{-5} S/cm in 0.5 % Ca doped TiO₂ at 800 °C under wet oxidizing conditions.

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Keywords: Titanium dioxide, electron beam evaporation, calcium doped.

1. Introduction

Over the past decades, titanium dioxide has become one of the most investigated materials due to its wide range of applications ranging from cosmetics [1], food and drugs [2], paints, dyes and varnishes [3] to promising energy

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and environmental applications, such as hydrogen generation by water splitting [4], photocatalytic water purification [5], dye-sensitized solar cells [6], gas sensors [7], polymer proton conducting electrolytes membranes [8] and etc. Due to the use of TiO₂ in many different technological fields, titanium dioxide is formed under diverse forms such as single crystals, epitaxial films, thin films or ceramics, although the applications are generally focused on TiO₂ thin films. TiO₂ thin films are formed using a variety of techniques like chemical vapor deposition (CVD), electron beam evaporation (EB-PVD), magnetron sputtering, pulsed laser deposition; sol-gel method, solvothermal, hydrothermal synthesis and so on. Among all these methods, electron beam vapor deposition was chosen in this work. In contrast to other thin films' formation methods, electron beam vapor deposition has key advantages over the other deposition methods as high and controllable deposition rates, high density and homogeneity of the formed thin film and it is relatively easy to control the stoichiometry of the TiO₂ film. It is known that transition metals as TiO₂ become oxygen deficient at near atmospheric oxygen pressure due to their nonstoichiometry and the oxygen vacancies become the predominant defects in TiO₂. This oxygen deficiency introduces the excess of the electrons which results in an increase of the electrical conductivity [9]. One of the ways to control the oxygen vacancy concentration is to introduce particular amount of charge carriers, e.g. dopants, to the TiO₂ matrix in order to get preferable electrical properties. For example, the doping of TiO₂ with niobium or tantalum will have an increase in the electrical conductivity because these dopants act as electron donors [10-11], and, in contrary, calcium, magnesium incorporated in TiO₂ matrix, act as electron acceptors and decrease the electrical conductivity [12]. These incorporations of dopants do not only modify the electrical conductivity of TiO₂, but also influence the structural and morphological properties of TiO₂.

Titanium dioxide is also known to have the proton conductivity at low - moderate temperature [8, 13-15]. The reported conductivity values depend on the TiO₂ formation method due to the resulting different structure of the TiO₂ layers. In this work, TiO₂ thin films as potential proton conducting electrolyte membrane material were investigated. In order to use TiO₂ as the proton conducting electrolyte material, it is required to reduce the electrical conductivity at oxidizing and reducing conditions, therefore the TiO₂ thin films were doped with different concentration of calcium. Ca - doped titanium dioxide thin films were formed by electron beam deposition method and the structural and electrical properties were investigated.

2. Experimental

Titanium dioxide TiO₂ (99.9 % purity) and calcium oxide CaO (99.9 % purity) powders, both purchased from Sigma Aldrich[®], were used as the initial deposition material. Different concentration of calcium oxide (0.5 %, 1.0 %, 1.5 %, 2.0 %, 2.5 %) was added to the TiO₂ and mixed all together. Prior to deposition process the powder was preheated up to 1200 °C for 8 hours. The resulting powder was pressed to pellets and evaporated by electron beam physical vapor deposition (EB-PVD). Thin ceramic films were deposited on amorphous optical quartz (SiO₂), crystalline Alloy 600 (Fe-Ni-Cr) and high temperature resistant sapphire substrates to investigate their influence for the deposited thin films. To avoid any impurities on substrates, the substrates were carefully cleaned in the ultrasonic bath filled with pure acetone and in radio frequency Ar ions plasma in vacuum chamber before the deposition. The temperature of the substrates was raised to 600 °C at the time of deposition and the deposition rate was 2 Å/s. In order to get the surface homogeneity, the substrates were rotated at constant 8 rpm speed. The thickness of the formed thin films was 1.5 μm.

For the characterization of the formed thin films thickness profilometer Ambios XP-200 was employed. The density of the thin films was calculated from the measured films thickness, thin film mass and surface area. The theoretical density of anatase TiO₂ (3.78 g/cm³) was taken into the calculations. The surface morphology of the films was investigated with scanning electron microscope (SEM) Hitachi S-3400N and X-ray energy-dispersive spectroscopy (EDS, Bruker X FLASH QUAD 5040, Bruker AXS GmbH) was employed to analyze the microstructure and the elemental composition of the formed films. The elemental composition was calculated as the average of 10 measurement points distributed over whole surface of the formed thin film. X-ray diffraction (XRD, D8 Discover (Bruker AXS GmbH), Cu K_{α1} λ=0.1540562 nm radiation) was used to determine the crystallinity of the thin ceramics.

The electrical characterization and impedance spectroscopy measurements were performed using Probostat[®] (NorECs AS) measurement cell in the frequency range from 10⁻¹-10⁶ Hz and under H₂ reducing using pure hydrogen gas and O₂ oxidizing conditions using pure oxygen gas. The electrodes having the geometry 1 x 0.5 cm (L x B) were

made of Pt ink and the sample was mounted in a Probostat[®] cell. Pt ink electrodes were annealed at 800 °C for 2 hours. Impedance spectroscopy was performed in parallel to film surface in the temperature range of 200 °C to 1200 °C with temperature step of 20 degrees. The total conductivity σ of the formed thin films was calculated from impedance spectroscopy via total resistance R_{total} using the relation $\sigma = L/AR_{total}$, where L is the distance between electrodes and A is the area of the electrode.

3. Results and discussion

The analysis of the elemental composition of Ca - doped TiO₂ thin films shows that the concentration of Ca dopant is slightly higher (experimental point 1) or slightly lower (experimental points 2-5) comparing to the initial evaporation material, but the concentration of calcium dopant in the Ca-doped thin films is gradually increasing by increasing the amount of dopant in the initial powder (Fig. 1). This small discrepancy can occur due to the different evaporation rates of Ca, Ti and their oxides. Also this can be due to the different melting temperatures of CaO (2613 °C) and TiO₂ (1843 °C). Calcium oxide sinks down to the bottom of the crucible when the titanium dioxide is melted. This gives the concentration gradient of CaO through the depth of the initial material during the deposition process. The small amount of the initial material (residue) stays in the crucible. The EDS investigation of this residue proves earlier assumption.

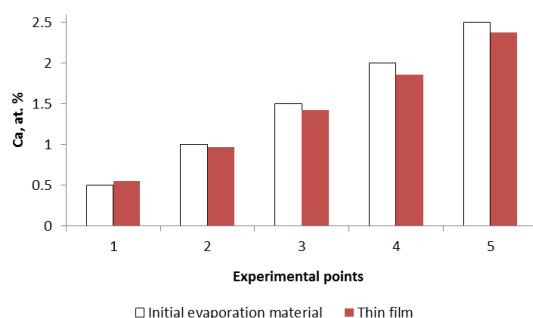


Fig. 1. The calcium concentration in the initial evaporation material (white) and in Ca_xTi_{1-x}O₂ thin films (red).

Thin films that are formed as dense as possible are favorable as the potential electrolytes for solid oxide fuel cells. As it was mentioned above, the evaporation by electron beam vapor deposition method allow to get the high density of the formed thin films. The morphology of the thin films formed using e-beam technology can be described by a Structure – Zone model (SZM) [16] corresponding to Zone T and Zone 2. As the substrate temperature was kept at 600 °C, the surface mobility was high enough to form zone T, i.e. tightly packed fibrous grains with weak grain boundaries, and then transform to a full-density columnar morphology corresponding to Zone 2 [17]. The density calculation reveals that the relative densities of Ca_xTi_{1-x}O₂ thin films are between 99 % and 88.9 % (Table 1). The density of pure titanium dioxide is 3.78 g/cm³. The relationship between relative density and calcium concentration shows that it decreases by increasing Ca concentration in thin film.

Table 1. Relationship between relative density and calcium concentration.

Concentration of Ca doping, mol. %	Relative density (%)
0.0	99.0
0.5	94.9
1.0	92.3
1.5	88.9
2.0	96.9
2.5	89.6

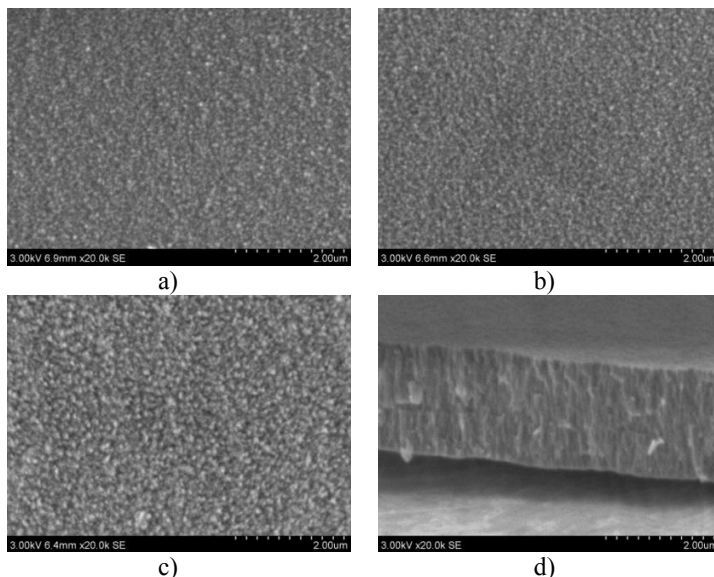


Fig. 2. SEM images of 2 % Ca doped TiO₂ thin films: a) SiO₂ substrate, b) Al₂O₃ substrate, c) Alloy 600 substrate and d) cross sectional view.

The microstructure investigation revealed that Ca – doped titanium thin films are smooth without cracks and pores (Fig. 2). In addition, the surfaces of the thin films have small grains. The morphology is independent on substrate type. The cross section view confirms that thin films are growing in Zone T and Zone 2 under Structure – Zone model. These results agree with other author’s results [18-19].

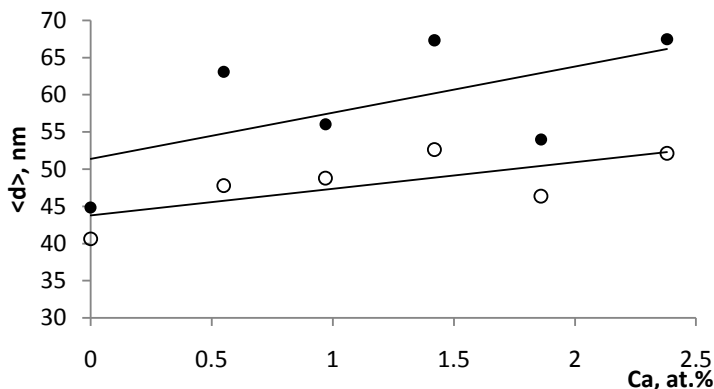


Fig. 3. Relationship between crystallite size and calcium concentration in thin films: ● Ca_xTi_{1-x}O₂ thin films on SiO₂ substrates and ○ Ca_xTi_{1-x}O₂ thin films on Alloy 600 substrates.

The crystallite size calculations revealed that it changes from 44.83 nm to 67.48 nm for the thin films formed on SiO₂ substrate and from 40 nm to 52.63 nm for the thin films formed on Alloy 600 substrates (Fig. 3). The crystallite size increases by increasing dopant concentration in both cases. The linear approximation shows it. The difference between crystallite size of thin films formed on SiO₂ and Alloy 600 substrates could appear due to different surface energies of SiO₂ and Alloy 600 substrates. Alloy 600 substrates have probably lower surface energy than SiO₂ substrates. Therefore crystallites are smaller in the case of Alloy 600. According to XRD (Fig. 4), the increasing doping concentration increases the crystallinity of the formed thin films and the crystallites size increase linearly according to the Vegard’s law. Thin films are comprised of anatase TiO₂ with an exception of 2 % Ca doped TiO₂, where a peak of Ca arise (Fig.4).

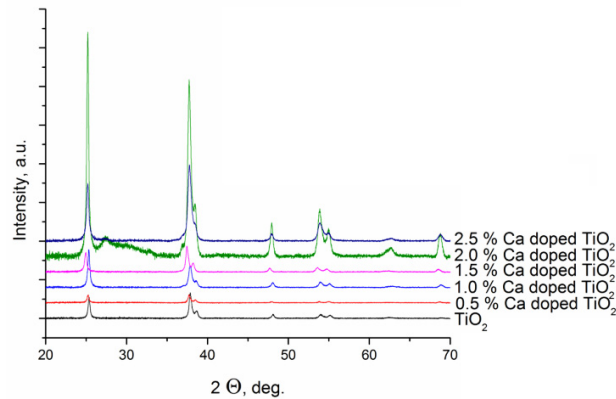


Fig. 4. XRD patterns of the Ca-doped TiO₂ thin films.

Ca-doped titanium dioxide exhibits mixed electronic protonic conductivity, with a reduction of the electron conductivity when the Ca dopants concentration increases. The total conductivity is sensitive to the crystallites size and decreases with the increase in crystallites size. The impedance measurements show that the Ca-doping decreased the total conductivity of the formed thin films. The total conductivity varies from 2.7 S/cm in pure TiO₂ to 4×10^{-4} S/cm in 2.5 % Ca doped TiO₂ at 800 °C under wet reducing conditions (Fig. 5a) and from 5.4×10^{-4} S/cm in pure TiO₂ to 3.4×10^{-5} S/cm in 0.5 % Ca doped TiO₂ at 800 °C under wet oxidizing conditions (Fig. 5b). It is seen that the conductivity in reducing atmosphere is higher than in oxidizing atmosphere. For pure protonic conductors, e.g. LaNbO₄, this behavior would indicate the protons contribution to the total conductivity [20].

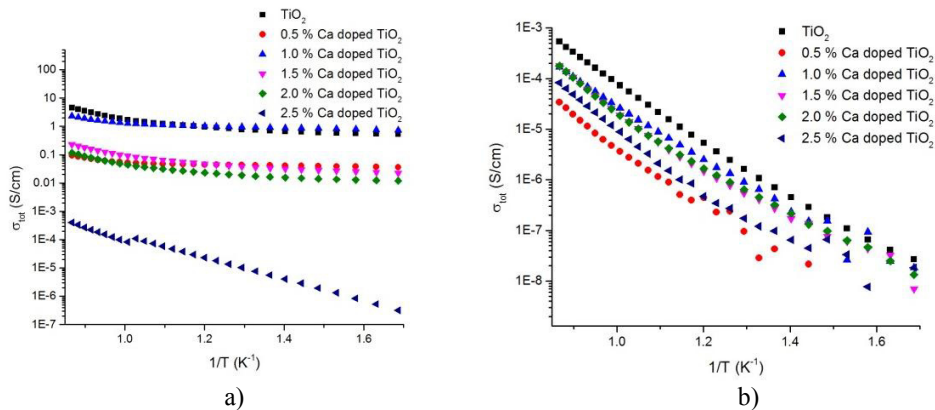


Fig. 5. Total conductivity of Ca-doped TiO₂ thin films under: a) reducing H₂ conditions, b) oxidizing O₂ conditions.

However, for mixed conductors as TiO₂, this increased conductivity could be reflection of an increase in electronic transport. The calculated activation energies for Ca-doped TiO₂ thin films are presented in the Table 2.

Table 2. Activation energies for Ca-doped TiO₂ thin films.

	Pure TiO ₂	0.5 % Ca doped TiO ₂	1.0 % Ca doped TiO ₂	1.5 % Ca doped TiO ₂	2.0 % Ca doped TiO ₂	2.5 % Ca doped TiO ₂
Oxidizing O ₂ conditions	1.05	1.14	0.94	0.99	0.96	0.93
Reducing H ₂ conditions	0.21	0.07	0.1	0.22	0.22	0.73

As one can see the activation energies vary largely each from other in oxidizing and reducing atmospheres. Pure protonic conductor should have higher activation energies in the range of 0.52 – 1.0 eV [21], and much smaller activation energy is probably associated to electron conductivity. Therefore, for the detailed interpretation of the

conductivity results of the Ca-doped TiO₂ system, further work is needed to determine the protonic conductivity part in the formed thin films and hence the conduction mechanism. These issues will be considered in a forthcoming work.

4. Conclusions

Ca-doped TiO₂ films were formed using e-beam evaporation. It was found that increased Ca concentration increases the crystallites size. The impedance measurements show that the Ca-doping decreased the total conductivity of the formed thin films. The total conductivity varies from 2.7 S/cm in pure TiO₂ to 4×10^{-4} S/cm in 2.5 % Ca doped TiO₂ at 800 °C under wet reducing conditions and from 5.4×10^{-4} S/cm in pure TiO₂ to 3.4×10^{-5} S/cm in 0.5 % Ca doped TiO₂ at 800 °C under wet oxidizing conditions.

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