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Nanoporous TiO_2 electrode grown by laser ablation of titanium in air at atmospheric pressure and room temperature

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ABSTRACT

Recently, fabrication of the nanoporous TiO_2 photoelectrode on metal foils by means of sputtering of the Ti film on preheated metal substrate followed by the TiO_2 deposition (doctor blade technique) and sintering represents the frequently applied technique. This is despite the relatively complicated procedure and number of parameters to be controlled in order to fabricate films of required properties. In this work an approach is applied and discussed in which the nanoporous TiO_2 electrode is fabricated under conditions similar to pulsed laser deposition but with the deposit formed directly on the ablated target at atmospheric pressure and room temperature. The titanium dioxide thin film is grown by ablation of the Ti foil with the nanosecond UV laser (266 nm) at fluence up to 1.5 J/cm^2. The rutile–anatase phase transformation takes place during this one-step process and no thermal pre-and post-treatment of the deposit is needed. In samples produced in air, the presence of mixed phases of the non-stoichiometric anatase (>70%), rutile and negligible amount of TiN is consistently confirmed by the X-ray diffraction, energy-dispersive X-ray and Raman spectra. For applications of the reported films as electrode material in the third generation photovoltaic cells, the use of industrial lasers could significantly improve the process efficiency.

1. Introduction

In the research on titanium dioxide electrodes, the use of metal foils evokes much interest because it enables thermal processing of the material at temperatures up to 500 °C required for TiO_2 sintering and the rutile–anatase phase transition. This is of importance for applications such as photocatalysis, sensing and photovoltaics. Recently, it is shown for the foil substrates: Al, Co, Ni, Pt, Ti, W, Zn and stainless steel that during heat treatment these metal foils produce thin n-type semiconductor oxide film which form at the metal–TiO_2 interface and influence positively the short-circuit photocurrent density of the cell [1,2]. Most of the reported results refer to porous TiO_2 electrode obtained by a time consuming multi-step procedure. First, the Ti film is sputtered on preheated metal substrate and next the TiO_2 is deposited using doctor blade technique and sintered. Recent results on fabrication of the nanoporous TiO_2 [3–5] including hierarchically organized nanostructures which ensure enhanced photoreactivity [6], confirm the search on effective production method of this nanostructured photoanode. Among considered techniques the pulsed laser deposition has appeared to be a promising fabrication tool of TiO_2 crystalline films [6–10]. However, the phase growth, the film crystallinity and also the content of anatase and its stoichiometry depend substantially on thermal processing and can be controlled only in a low pressure range of the reactive gas during deposition which limits applications and represents still a challenge. In this work, it is shown that under conditions similar to PLD the nanoporous TiO_2 electrode revealing high anatase content can be produced as thin film in a one-step process (without thermal pre-and post-treatment) and also the film properties are discussed.

2. Experiment

For growth of the nanostructured TiO_2 films on Ti, the 2.5 × 2.5 cm^2 square platelets prepared from 0.1 mm thick α-titanium foil (purity >99.98%, Aldrich) were used as target material for laser ablation. Samples were processed in a chamber filled with dried air and for reference also with O_2 (purity 99.999%) or nitrogen (99.9%) at a pressure of 1060 hPa. The ablation was performed by a pulsed (6 ns, 10 Hz) 266 nm Nd:YAG laser (Quantel) of pulse energy not exceeding 52 mJ and fluence dependent on the beam spot size selected in the range of 520–2100 μm by a quartz lens (f = 300 mm). Films were deposited by multiple scanning of the sample surface by the laser beam along a

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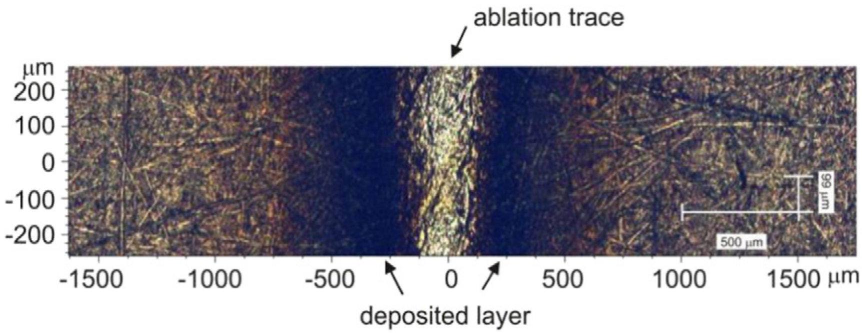

Fig. 1. The microscope image of Ti foil surface ablated for 30 min (18,000 pulses) in air: the bright area surrounded by two dark strips corresponds to ablated trace and deposits, respectively.

circular path of the length of 38 mm. Investigation of the surface topography and elemental analysis were performed by means of the scanning electron microscope EVO-40 (Zeiss) coupled with the Quantax 400 EDX apparatus. For 3D imaging of the sample's surface the confocal microscope LEXT OLS4000 (Olympus) was used. The crystalline phases and composition of samples were investigated by means of the X-ray diffraction (XRD) using the X'Pert (Philips) instrument (Cu Kα line) and the micro-Raman spectrometer InVia (Renishaw, resolution of 2 cm^{-1}, sample excitation at 514.5 nm), respectively.

3. Results and discussion

3.1. Surface structure of the deposit

The ablation performed in air resulted in deposition of the thin film observed as dark strips on both sides of the ablation trace on Ti foil — see Fig. 1. The strip position and width resulted from the short-range travelling distance of the ablation products of kinetic energy strongly dissipated by collisions with particles of the reactive gas due to its high pressure. The film thickness increased nearly linearly with number of laser pulses as observed for process duration up to 60min (36,000 pulses).

From 3D imaging the ablation rate and film thickness were estimated, e.g. in the case of the processing for 30 min at laser fluence of 1.5 J/cm^2 the values of 32 nm/pulse and 760 nm were obtained, respectively. It was observed that processing of the non-polished Ti foil promotes growth of highly porous films characterized by nucleation starting on surface irregularities and formation of inhomogeneously distributed cauliflower-like agglomerates (Fig. 2). Similar structures of TiO_2 films composed mainly of anatase and produced by pulsed laser deposition (PLD) in O_2/Ar mixture or in air at much lower pressure up to 60 Pa and with application of the substrate preheating and film annealing were reported by other authors, too [6,10].

3.2. Crystalline phases

The XRD data of the films and for comparison also the reference reflections of the anatase, rutile, titanium and titanium nitride are shown in Fig. 3. In all recorded patterns the strong reflections observed at 2θ equal to 35.1°, 38.4° and 40.2° can be assigned to the (100), (002) and (101) crystal planes of the underlying metallic Ti, respectively. The XRD peaks corresponding to the films are of relatively low intensity and reveal phase composition which depends on the reactive gas applied. In the case of oxygen the reflection characteristics for titanium oxide at 25.4° and 27.5° (Fig. 3c) indicate that both the anatase and rutile phases are present in the film. On the other hand, in the diffraction pattern obtained for processing in N_2 (Fig. 3b), peaks at 36.7° and 42.7° indicate the presence of Ti_nN_m whereas crystallites of anatase and rutile are not revealed. The presence of the crystalline titanium dioxide

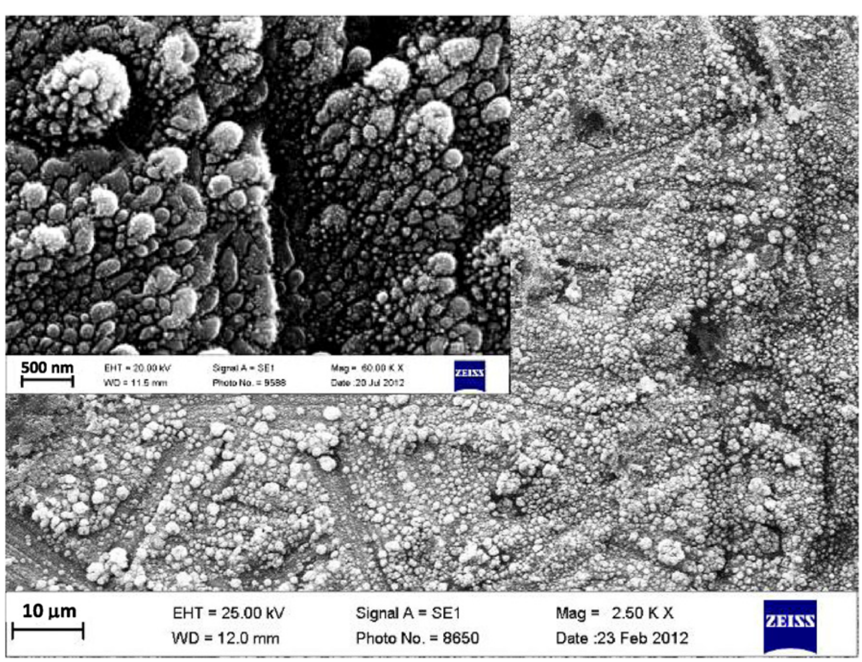

Fig. 2. SEM image of the film deposited in air by application of 36,000 laser pulses on unpolished Ti foil; inset shows magnified surface view.