



Nanopatterned zinc titanate thin films prepared by the evaporation-induced self-assembly process

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ABSTRACT

Nanopatterned thin films prepared by the evaporation-induced self-assembly process have up to now been limited to a few transition metal oxides (i.e. Al_2O_3 , TiO_2 and ZrO_2). Here we describe the formation of zinc titanate nanoperforated thin films with different Zn/Ti ratios using the dipcoating process. Atomic force microscopy and scanning electron microscopy reveal that the structure consists of well-ordered pseudohexagonal nanoperforations in the range of 30 nm in diameter separated by 25 nm wide metal oxide ridges, while the film thickness is close to 2 nm. For films with a zinc precursor content up to 50 mol%, the well-organized structure of the thin film can be maintained, while at higher Zn contents the nanostructure is gradually becoming more disordered, which we have shown is consistent with the partial charge model. Grazing incidence X-ray diffraction measurements on the films calcined at 700 °C indicate that the anatase phase of the pure TiO_2 films is gradually consumed at the expense of a newly formed $\text{Zn}_2\text{Ti}_3\text{O}_8$ phase upon increasing the Zn/Ti ratio in the starting precursor solution. The unique combination of the nanostructure with the zinc titanate composition grants these nanopatterned thin films significant application prospects in for instance optics and catalysis.

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1. Introduction

Nanopatterned metal oxide surfaces have recently attracted a great interest due to their wide applicability associated with emerging nanotechnologies, such as micro- and nanoelectronics, data storage, optics, biosensing and biotechnology, and catalysis [1]. Although having made a lot of progress in the last decade, top-down approaches like lithography [1] or nanoimprinting [2] still have limitations in the preparation of nanopatterned surfaces related to high equipment costs, pattern miniaturization and scale-up for large device applications. On the other hand, various types of solution-based bottom-up approaches have been proven useful to circumvent these drawbacks by utilizing self-assembly of molecules or nanoparticles driven by a reduction in Gibbs free energy of the system [3,4]. Recent approaches, where a careful control of the molecular interactions have been used to design nanopatterned surfaces, include block copolymer lithography [5], colloidal templating [6], and evaporation-induced self-assembly (EISA) [7,8]. The EISA technique utilizes self-organization of surfactants and surrounding metal oxide precursors upon solvent evaporation to form either mesoporous nanoparticles or thin film structures depending on the processing conditions.

By careful control of the film deposition conditions (e.g. by dipcoating), the EISA approach can also be tuned to obtain an open monolayer structure of block copolymer micelles surrounded by the metal oxide precursor of choice, which after template removal gives a nanopatterned metal oxide surface [9]. These metal oxide thin films contain hexagonally arranged nanoperforations (or “nanocraters”) with diameters controlled in the size range of 20–50 nm. Another important feature of these nanopatterned structures is that the substrate is readily accessible at the bottom of the craters. This in turn allows the nanopatterned films to be selectively functionalized making them excellent model substrates in wettability studies [10–12].

In the EISA approach for relatively thick mesoporous thin films, several examples on expanding the concept to include ternary oxide systems have been demonstrated, including SrTiO_3 , MgTa_2O_6 and $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$ [13] as well as WO_3/TiO_2 [14], $\text{Ln}_{0.1}\text{Ce}_{0.9}\text{O}_2$ [15], MFe_2O_4 ($\text{M} = \text{Co}, \text{Cu}, \text{Mg}, \text{Ni}, \text{Zn}$) [16], NbVO_5 [17], MCr_2O_4 ($\text{M} = \text{Co}, \text{Zn}$) [18], and MTiO_3 ($\text{M} = \text{Ba}, \text{Pb}$) [19]. However, the method is still limited to a few pure metal oxides (i.e. TiO_2 , ZrO_2 , and Al_2O_3) for the thinner nanocrater structures [20]. Grosso et al. demonstrated that by changing the dipping conditions in reference [13], a transition from a thicker mesoporous structure to periodically arranged nanoscale islands of SrTiO_3 , MgTa_2O_6 and $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$ mixed oxides took place. However, in this particular case no nanocrater structures could be observed.

In this study, we are demonstrating the possibility of expanding the EISA concept of producing nanopatterned thin films to also include

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ternary metal oxides. As an example, we have here chosen to prepare mixed zinc–titanium oxide films with various Zn/Ti molar ratios. Several zinc titanate phases, including $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 , and Zn_2TiO_4 , have been reported in the literature and the resulting phase or phases are generally dependent on the calcination temperature, the chemical composition and the crystallite size of the precursors [21]. However, pure phases of $\text{Zn}_2\text{Ti}_3\text{O}_8$ are seldom observed because it is a metastable phase that readily decomposes to ZnTiO_3 and rutile TiO_2 at temperatures above 800 °C [22]. Nanostructured zinc titanates have many interesting optical and electrochemical properties and have been put to use in several important application fields, including photocatalysis, microwave dielectrics, gas sensing, catalysis, non-linear optics, and as luminescent materials [23] as well as in lithium-ion batteries [22]. Although highly ordered mesoporous ZnTiO_3 powders have been prepared earlier [23,24] utilizing the EISA method, the formation of zinc titanate nanopatterned thin films by the EISA approach has not been realized until now. These nanostructured thin films are excellent model structures for detailed studies of the zinc titanate crystallization process in a spatially confined system, which is rather different from the crystallization in bulk systems. The open pore structure of the ultra thin nanopatterned films offers the possibility to develop versatile materials with multi-functional properties.

2. Experimental details

2.1. Preparation of dip-coating sols

Titanium(IV) chloride (TiCl_4), zinc(II) chloride (ZnCl_2), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich and used without further purification. Nanopatterned thin films were prepared using the PB-*b*-PEO block copolymer (poly(butadiene)-*b*-poly(ethylene oxide), P2325-BdEO: $\text{MW}_{\text{PB}} = 32000$ g/mol, $\text{MW}_{\text{PEO}} = 43500$ g/mol from Polymer Source Inc.) as templating agent and the preparation of the initial solution followed the same steps as reported earlier [12]. In our experiments, the molar ratios of metal chloride/ethanol/ H_2O /THF/PB-*b*-PEO was always kept constant at $1:274:23:88:5.6 \cdot 10^{-4}$, while the metal chloride composition ($(\text{TiCl}_4)_{1-x} + (\text{ZnCl}_2)_x$ was varied ($x = 0, 0.1, 0.25, 0.5, 0.75$ and 1 , respectively). The different sols were homogenized before dip-coating using an ultrasonic mixer (Covaris Inc., Massachusetts, USA).

2.2. Preparation of metal oxide thin films

Silicon wafers (MEMC Electronic Materials, S.p.A.) were pretreated the same way as described in previous work [12]. The sols for preparing the nanopatterned Zn–Ti oxide films were deposited onto the silicon wafers by dip-coating at a constant withdrawal rate of 1.2 mm s^{-1} within a relative humidity of less than 20% at room temperature, using a KSV Dip Coater DC (KSV Instruments Ltd., Helsinki, Finland). After dipping, the films were transferred onto a heating plate and calcined at 500 °C for 10 min to decompose the organic components, leaving nanopatterned multi-metal oxide networks on the substrates, and then further calcined at 700 °C for 10 min. In order to obtain thicker reference films for grazing incidence X-ray diffraction (GI-XRD) characterization, additional samples were prepared by dip-coating Si wafers 10 times with 3 min 400 °C calcination steps between each dipping followed by a final calcination at 700 °C for 10 min.

2.3. Characterization techniques

Atomic force microscopy (AFM) images of the films were recorded using a Nanoscope V instrument (Veeco Metrology Group, Santa Barbara, CA). All images were recorded in tapping mode using silicon cantilevers (NSG 10, NT-MDT) with a resonance frequency between 190 and 325 kHz. All images (512×512 pixels) were measured in air without filtering, and analyzed by the Scanning Probe Image Processor

software, SPIP 5.1.3. Scanning electron microscope (SEM) measurements were conducted on a LEO Gemini 1530 (Zeiss, Oberkochen, Germany), equipped with a Thermo Scientific UltraDry Silicon Drift Detector (Thermo Scientific, Madison, Wisconsin, USA).

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Physical Electronics Quantum 2000 instrument equipped with a monochromatic Al K α X-ray source. An operating power of 25 W was used with a spot diameter of 100 μm . An electron flood gun and a low energy ion gun were used for charge compensation. The detector position was at an angle of 45° in relation to the sample surface. The pass energy in the high resolution spectral acquisitions was 23.5 eV. Surface concentrations were determined from the high resolution spectra with the Multipak 6.1 software using peak areas to give surface concentrations in atomic percent. GI-XRD measurements were performed on a Bruker AXS D8 Discover instrument (Karlsruhe, Germany). A grazing incidence angle of 0.31° was used for all the measurements. The data was collected between 2 θ and 40° 2 θ using a step size of 0.04° 2 θ . The JCPDS card numbers 00-021-1272, 01-086-0148 and 01-075-0576 were used to identify the pure anatase TiO_2 , rutile TiO_2 and ZnO phases, while $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 and Zn_2TiO_4 were assigned to the 01-087-1781, 01-086-0155 and 01-085-0547 JCPDS cards, respectively.

3. Results and discussion

3.1. Structural properties

Sample 0% Zn, which corresponds to the well-studied pure nanopatterned TiO_2 film with no added ZnCl_2 , was used as the reference composition in this study. From the AFM height image in Fig. 1 it is evident that under the current dipping conditions this composition gives a well-ordered pseudohexagonal nanopatterned structure similar as in previous studies [12]. As seen in Table 2, the extracted nanocrater size and wall thickness are about 30 nm and 25 nm, respectively. The nearest neighbor distance indicates the mean distance between the centers of two nanocraters and can be used to calculate the repeating unit distance in the pseudohexagonal pattern. For sample 0% Zn, this value is estimated to about 57 nm, which corresponds well to the value obtained by adding the nanocrater size and wall thickness together (also ~57 nm). Since the silicon wafer substrate is accessible through the nanopatterned structures, the AFM height images can directly be used to estimate the thickness of the deposited metal oxide layer. For the pure TiO_2 layer, the estimated height is about 2 nm. AFM image analysis has also been used to estimate the area fraction of the thin film which is covered by nanocraters and for sample 0% Zn this is about 18%. Finally, the ordering of the nanopatterned structures can be evaluated by 2-D fast Fourier transforms (2-D FFT) of the AFM height images as shown in the insets in Fig. 1. Similar 2-D FFT analyses for self-assembled block copolymers have been performed previously by other groups [25,26]. The high-intensity domain spacing rings seen in the reciprocal space indicate that the films have a well-defined short-range order and a fairly narrow distribution between the nanocraters. For a long-range hexagonal ordering, six high-intensity spots would be visible instead of the rings [25,26]. The reciprocal distance from the center of the image to these rings can also be used to estimate the pattern periodicity, which coincides with the values obtained from the nearest neighbor distance (i.e. in this case ~57 nm).

As further seen in Fig. 1, replacing equimolar amounts of TiCl_4 with ZnCl_2 in the dipping solution does not seem to alter the nanocrater structure noticeable even up to 50 mol% Zn, although there are some minor fluctuations in the extracted AFM data shown in Table 2. The low sensibility to differences in the chemical composition proves that the EISA process has a good flexibility in the preparation of nanopatterned thin films. However, upon replacing more of the TiCl_4 with ZnCl_2 in the dipping solution, the resulting structure becomes increasingly disordered as seen in the AFM image of sample 75% Zn, as also evidenced by the 2-D FFT pattern. The broader ring suggests that the

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