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Highly inorganic titania based sol–gel as directly patternable resist for micro- and nano- structured surfaces

E. Zanchetta [a,*], V. Auzelyte [b], J. Brugger [b], A.V. Savegnago [a], G. Della Giustina [a,b], G. Brusatin [a]

[a] *Industrial Engineering Department, Via Marzolo 9, 35131 Padova, Italy*
[b] *Microsystems Laboratory, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*

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ABSTRACT

Highly inorganic sol–gel films and patterned surfaces with up to 90% of titania were obtained by hydrolysis and condensation of Titanium(IV) isopropoxide. As a consequence of titania photocatalytic effect, the further treatment of the nanoimprint patterned films by different UV irradiation doses produces highly inorganic micro- and nano-patterns with tunable refractive indexes over a wide range, reaching values over 2.4 at 300 nm. FTIR analysis confirms the degradation of the organic component of the patterns after UV exposure, and TEM analysis shows the presence of crystalline clusters after both thermal treatment and UV exposure. The morphological characterization of the obtained nano-patterned titania structures has been performed by SEM and AFM analysis.

1. Introduction

High refractive index, transparency to visible light and photocatalytic sensitivity make titania thin films suitable for applications in a large number of micro-optical elements and photoelectric conversion devices, such as dye-sensitized solar cells [1], photonic crystals [2], waveguides [3,4] gas and bio sensors, antireflective coatings [5], filters and high-reflectivity mirrors [6]. Thin titania films can be obtained using mainly CVD [7], e-beam evaporation [8], flame hydrolysis [9] and sol–gel methods. Conventional patterning methods of similar inorganic films are made using etching or lift- off processes, usually requiring one lithography step and one pattern transfer step. These methods are expensive, complex and unsuitable for films thicker than a few hundreds of nanometers. The other patterning approach is the use of organic composites containing titanium ions. Lim et al. [10] and Ganesan et al. [11] used metal methacrylate resins combined with alcoxides capable of undergoing in situ thermal free radical co-polymerization during imprinting. However, the most used way to pattern titania films is the sol–gel route.

The advantages of sol–gel bottom-up approach can in fact be combined with top-down methods in order to directly obtain micro- or nano- structured titania surfaces with different lithographic tools (nanoimprint and UV) [12], allowing cost-effective mass production. Many research efforts have been directed toward this route [13–17], however direct patterned and almost inorganic titania films with high refractive index and thickness up to 1 micron and low shrinkage, after imprinting and treatment, have not been obtained yet. Titania sol–gel films described in literature contain an up to 70% Ti molar fraction. The film thicknesses are usually between 100 and 200 nm [18]. The thicker films are obtained with a titania content not higher than 60% [18]. Furthermore, to obtain totally inorganic micro and nano structures, the lithographic step is usually followed by a thermal treatment at high temperatures (over 400 °C), which leads to a high shrinkage (over 50%) of the features [19–21].

In this work we report on direct patterning of a hybrid organic–inorganic (HOI) based sol–gel system with up to 90% of titania, obtained by hydrolysis and condensation of Titanium(IV) isopropoxide. Using nanoimprint the films with thicknesses up to 1 μm were patterned to produce micro- and nano- features. Further film treatment only with UV at different irradiation doses produced highly inorganic patterned surfaces with tunable refractive index and shrinkage up to 30%.

2. Experimental details

2.1. Preparation of TiO_2 sol solution

The titania sol was prepared by hydrolysis and condensation of Titanium(IV) isopropoxide (up to 90% molar ratio) and 3-glycidoxypropyltrimethoxysilane (GPTMS). The monomer bis[4-(glycidyloxy)phenyl]methane was added to improve film elasticity and to increase layer thickness. Precursors and monomer were purchased from Aldrich and used without further purification. The final sol concentration was set at 100 g/l of TiO_2 in methoxyethanol solvent. As synthesized, the solution remains liquid for

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* Corresponding author. Tel.: +39 0498275023.
E-mail address: erika.zanchetta@gmail.com (E. Zanchetta).

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months. Then the solution was filtered through a 0.2 μm filter to remove large particles and improve the resist spin-coating quality. The films up to 1 μm were spin coated and imprinted at temperatures ranging from 80 to 130 °C. Pressures of 20–40 MPa were applied. Stamp materials, silicon (purchased from Silicon materials) and ORMOSTAMP® (purchased from micro resist technology, MRT), with anti-adhesion layer were used. The anti-sticking layer was obtained using 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane 97% (Aldrich).

2.2. Characterization methods

The effects of thermal treatment and UV exposure on the hybrid titania sol–gel films have been analyzed by Infrared Spectroscopy. Infrared absorption spectra were recorded in the range of 400–4500 cm^{-1} by a Fourier Transform Infrared spectrometer (Jasco FT-IR-620) with a resolution of ±4 cm^{-1}. The film structure and titania cluster size was analyzed by TEM. The refractive index and the absorption of the films were characterized by ellipsometric measurements and UV–vis absorption spectroscopy (JASCO V-570) in the range 200–600 nm, respectively. The film thickness has been examined using a profilometer. Finally, the quality of the gratings has been characterized by Atomic Force Microscopy (AFM) and SEM.

3. Results and discussion

Before film irradiation, the absorption edge of the titania film has been compared with the emission spectrum of the Hamamatsu LC5 UV mercury-xenon lamp (with an emission intensity of 3500 mW/cm^2 at 1 cm distance). A small fraction of the lamps intensity is also emitted below 300 nm, where the titania film absorbs. This spectral overlap allows the use of a standard UV lamp for the modification of the sol–gel titania films.

In order to control the degradation of the organic components under UV exposure in the range of 5–216 J/cm^2, the hybrid sol–gel titania films were analyzed by FTIR measurement (Fig. 1).

In the spectrum of the freshly coated film it is possible to identify the C–H stretching vibrations between 3000 and 2800 cm^{-1} and C–H simple bending vibrations between 1500 and 1300 cm^{-1} of the organic compounds. The asymmetric C–H stretch of the methylene groups (2930 cm^{-1}) occurs at slightly higher frequency than symmetric vibrations (2855 cm^{-1}). Moreover, another peak at 2970 cm^{-1} is due to the stretching of the C-H bond that can be ascribed to isopropoxide species, corresponding to the bands of titanium isopropoxide and isopropanol forming after hydrolysis of the Ti precursor [12–23]. The other important set of bands which can be detected are the aromatic ring vibrations (C = C–C stretch bands) of the BFDGE (para-substituted phenyl groups stretching vibrations) centered around 1600 and 1500 cm^{-1}. The bands overlap with other C–H set of vibrations found between 1500 and 1300 cm^{-1} (simple bending vibrations of the methylene C-H bond at 1485–1445 cm^{-1} and asym/sym. bending of methyl –CH$_3$ at 1470–1430 cm^{-1}). Bonded –OH absorption are well visible centered at 3300 cm^{-1}. After UV exposure, all the peaks related to organic species decrease due to the titania photocatalytic effect, with

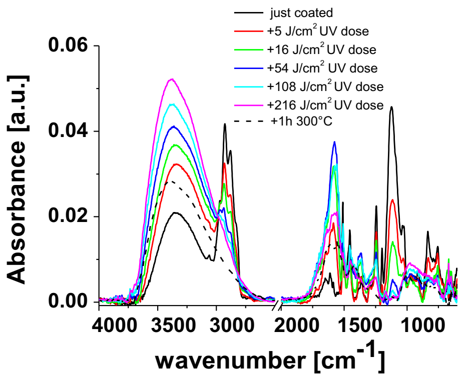

Fig. 1. FTIR spectra of titania sol–gel films: as coated, after UV exposure 5–216 J/cm^2 and after thermal treatment at 300 °C.

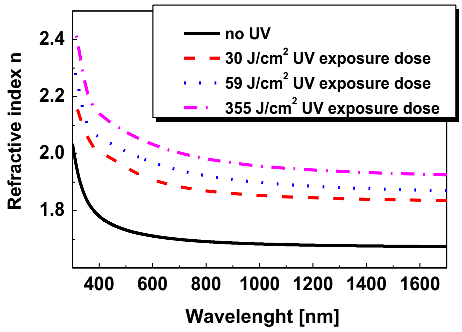

Fig. 2. Titania sol–gel refractive index change after UV exposure from 0 to 355 J/cm^2 in the wavelength range between 300 and 1700 nm.

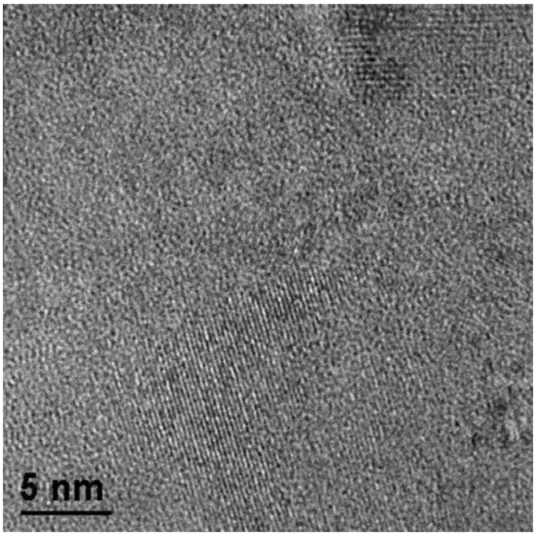

Fig. 3. TEM analysis of the thermally treated (at 500 °C) film.

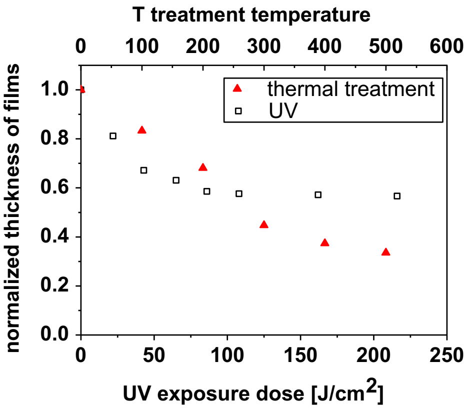

Fig. 4. Normalized thickness of freshly coated and UV (from 0 to 216 J/cm^2) or thermally treated (1 h up to 500 °C) films.