ELSEVIER

Materials Science and Engineering B 129 (2006) 180–185

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Organo-silica–titania nanocomposite elaborated by sol–gel processing with tunable optical properties

J. Franc[a,*], D. Blanc[a], A. Zerroukhi[b], Y. Chalamet[b], A. Last[c], N. Destouches[a]

[a] *Laboratoire Traitement du Signal et Instrumentation, CNRS-UMR 5516, Université Jean Monnet, 10 rue Barrouin, 42100 Saint-Etienne, 18 rue Benoît Lauras, F-42000 Saint-Etienne, France*

[b] *Laboratoire de Rhéologie des Matières Plastiques, UMR CNRS 5156, 23 rue Paul Michelon, F-42023 Saint-Etienne Cedex 2, France*

[c] *Research Center Karlsruhe, Institute for Microstructure Technology, P.O. Box 3640, 76021 Karlsruhe, Germany*

Received 6 December 2005; received in revised form 12 January 2006; accepted 18 January 2006

Abstract

Organically modified silica–titania thin films were elaborated by a sol–gel process and UV assisted photopolymerisation. Two different chelating agents, methacrylic acid (MAA) and a β-diketone (2-(methacryloyloxy) ethyl acetoacetone (MAEA)) were compared in this work. It was demonstrated that the choice of the chelating agent is a key parameter to increase the molar ratio Si:Ti and therefore raise the refractive index of the material. β-Diketone has proven to be a good candidate to stabilise the titanium precursor and its effects were compared to those observed with methacrylic acid. Fourier transform infrared spectroscopy was used to monitor the material formation and modification upon irradiation. M-lines spectroscopy was used to measure the refractive index of the material that varied between 1.51 and 1.59 depending on the titanium molar concentration. Optical properties were analysed in view of applications in the field of micro-optics and optical coatings.

Keywords: Refractive index; Transmission; Organic–inorganic hybrid materials; Sol–gel; Photopolymerisation; Chelating agent

1. Introduction

Organic–inorganic hybrid materials synthesised at room temperature via a sol–gel route are particularly attractive for fabricating micro-optical elements and optical coatings as they combine some advantages of organic polymers (ease of processing, elasticity and organic functionalities) with characteristics of inorganic oxides (hardness, thermal and chemical stability, transparency and large range of refractive index) [1]. For some time, research groups have been exploring the chemistry and physical properties of hybrid materials based on photopolymerisable methacryloxypropyltrimethoxysilane (MAPTMS) to produce optical thin films that are UV-patternable [2–5]. In this context, we were motivated to examine the possibility of expanding the accessible refractive index range of this class of materials, while keeping the material UV-curable. Other relevant properties are the transparency and the possibility to deposit thick films on various types of substrates including plastics. Foreseen applications are in the field of monomode and multimode waveguides for optical interconnections [6] and hard transparent coatings on high refractive index polymers for the ophthalmic industry [7]. It has been shown that the addition of metal alkoxide to a silica network had a direct effect on the refractive index of the resulting material [1,8]. This paper will investigate the use of β-diketone as a chelating agent for titanium isopropoxide (Ti). Its expected ability to control the reactivity of the metal alkoxide in the presence of water should allow to introduce larger Ti concentration into the silicate matrix [9] and lead to higher values of the refractive index. The synthesis of the material and film deposition are described. An insight into the structure of the material is gained through infrared spectroscopy. Optical properties of the coatings are assessed by UV–vis–NIR spectroscopy and M-lines experiments. Finally, conclusions are drawn with respect to the use and limitation of the material for optical applications.

2. Material elaboration

The formation of the organo-silica–titania material described in this paper can be described as a two-step process. The inorganic backbone is produced by hydrolysis and polycondensation of the alkoxides in the solution and during thin film deposition

---

[*] Corresponding author. Tel.: +33 477915826; fax: +33 477915781.
E-mail address: janyce.franc@univ-st-etienne.fr (J. Franc).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.01.011

(sol–gel process). The organic network is formed afterwards by UV-induced polymerisation.

The paper is focused on the role of the chelating agent that is used as a ligand to control the hydrolysis of the titanium alkoxide. The control of the hydrolysis should allow to introduce a higher ratio of metal alkoxide in the silicate matrix without precipitation or early formation of a gel. Larger titanium concentration should lead to a higher refractive index material. In a previous study [5] the use of the widely studied methacrylic acid (MAA) [2] for complexing titanium alkoxide allowed us to reach a Si:Ti ratio of 10:4 and a corresponding refractive index of 1.54. Here we will study the advantage of 2-(methacryloyloxy) ethyl acetoacetone (MAEA) with respect to MAA. The use of a β-diketone for metal alkoxide stabilisation is less frequent and reactions have not been extensively studied. β-Diketone contains a reactive hydroxyl group that forms a complex with titanium isopropoxide of a formula Ti-[O-CH-$(CH_3)_2]_4$, according to a reaction given in Eq. (1), Section 3.1. This reaction produces isopropanol and a modified complexed precursor of titanium alkoxide that has the advantage of being more stable in the presence of water.

Thanks to its strong complexing effect, it was found that a molar ratio Ti:MAEA of 2:1 was sufficient to stabilise the titanium alkoxide. This quantity was four times lower than the necessary amount of MAA and has the advantage to facilitate the hydrolyse step. Furthermore, the Si:Ti ratio can now reach the value of 10:15.

The hybrid organo-silica–titania composite was prepared from combinations of: (a) 3-methacryloyloxypropyltrimethoxysilane (98% purity), (b) titanium isopropoxide (97%), (c) 2-(methacryloyloxy) ethyl acetoacetone (95%) and (c′) methacrylic acid (99%) purchased from Aldrich Ltd. and shown in Fig. 1.

Photoinitiator IRGACURE 651 was acquired from CIBA. Precursors were used as received, without any purification procedure. Silica–titania composite sols were prepared according to the following method previously developed by Blanc et al. [5]: the molar ratios of precursors Si:Ti:MAEA were varied from 10:1:0.5 to 10:15:7.5 to modulate the optical response of the material. Partial hydrolysis and polycondensation of MAPTMS was initiated with 0.75 equivalents of acidified water (0.01 M HCl). Under acidic conditions, silicon atoms are depleted of an electron, making them more electrophilic and thus more susceptible to attack from water. The hydrolysis is consequently faster and more complete. At the same time, Ti was complexed with MAEA before being dispersed into the pre-hydrolysed organosiloxane medium. It was found that a ratio Ti:MAEA of 2:1 was sufficient to prevent the formation of a precipitate. Hydrolysis and condensation of the remaining silicon alkoxide and of the Ti were resumed with additional water (H_2O:alkoxide was equal to 1.5). Photoinitiator in the form of 3 wt% of 1,1-dimethoxy-1-phenyl acetophenone (Irgacure 651) was added to the solution. This photoinitiator was chosen as it has been identified as a stable and efficient molecule for comparable formulations [10]. The free flowing sol was passed through a 0.45 μm filter and allowed to age for 48 h before deposition.

Thin films were dip-coated [11] on glass substrates or silicon wafers with a constant withdraw speed of 5 cm/min. Further condensation due to solvent evaporation during the withdrawing stage contributes to further transformation from sol to gel. The thickness of the coatings which depends on the viscosity of the solution and the withdrawing speed was about 5 μm. Wet films were cured using a mercury lamp mounted with an aluminium reflecting mirror. Although the full spectrum of the mercury lamp was used, the 313 nm emission peak was probably the most active. The power density measured at the sample surface could be varied between 100 and 900 mW/cm^2 and the temperature resulting from the infrared radiation from the lamp varied accordingly between 25 and 80 °C measured on the backside of the substrate. The effect of the thermal assisted UV treatment on the material structure is studied in the next section.

3. Organic and inorganic networks formation

Photoinduced structural changes in the hybrid material were monitored through infrared spectroscopy. More specifically, the titanium complexation mechanism, the development of the organic network during thermally assisted UV curing and the correlated changes in the inorganic backbone were assessed with this technique. Infrared spectra were recorded with a

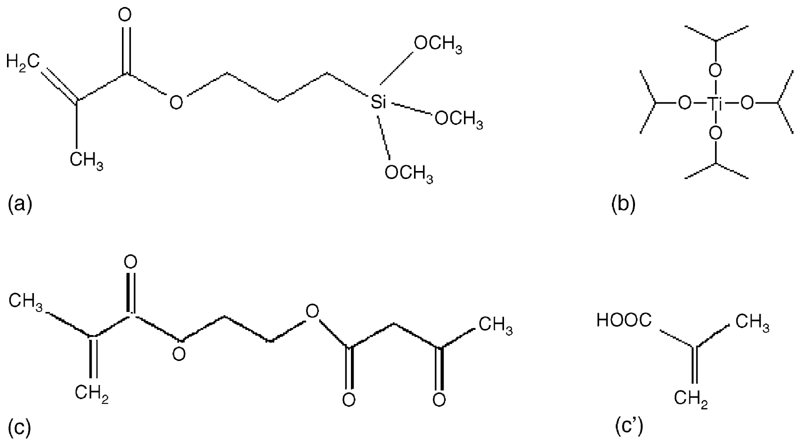

Fig. 1. Chemical precursor formulae: (a) MAPTMS, (b) Ti, (c) MAEA and (c′) MAA.