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Reactive laser-induced ablation as approach to titanium oxycarbide films

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ABSTRACT

The IR laser-induced reactive ablation of frozen titanium ethoxide target was studied. The method involves the laser ablation of titanium ethoxide at −140 °C in gaseous methane (4–50 Pa) atmosphere. This process leads to reactions of the ablative species with hydrocarbon in the gaseous phase. During the ablation of the frozen target excited species interact with methane molecules. The reactive ablation process leads to the formation of a smooth thin film. The thickness of prepared films depends on the number of IR pulses and their composition depends on the pressure of gaseous methane. This reactive IR ablation proceeds as a carbidation process providing nanostructured films with good adhesion to various substrates (glass, metals, KBr) depending on the carbon content in prepared films. Particles are also stabilized by layer preventing their surface oxidation in the atmosphere. The described results are important in the general context for the synthesis of reactive particles in the gas phase. The final products are characterized by spectroscopic, microscopic and diffraction techniques: SEM/EDX, HRTEM, electron diffraction, Raman spectroscopy and XPS.

1. Introduction

Titanium ethoxide is a well-known precursor for the preparation of glass and ceramic materials by sol–gel processes [1]. The combination of titanium ethoxide with water has also been used as a precursor for atomic layer deposition of TiO_2 [2]. The compound is an oily liquid with low volatility and high sensitivity to water vapor. In this work it was used as a precursor in the form of frozen matrix for reactive laser ablation technique used to prepare thin titanium oxycarbide films. Ti/O/C materials are highly desired materials possessing high application potential in advanced technologies.

Several methods were studied for direct synthesis of carbon-doped titanium dioxide. The best known processes of preparing of TiO_2/C composites are thermal oxidation of titanium carbide [3], sol–gel method based on the photocatalytic activity of visible-light-induced C-doped TiO_2 catalyst [4–6], solvothermal and slurry synthesis [7], direct doping of the titanium alkoxide gel by carbon [8], direct burning of elemental titanium powder in highly reductive flame [9] and carbothermal reduction of titanium dioxide to obtain titanium carbides and titanium oxycarbides from mixtures of TiO_2 and carbon [10,11]. Carbon is a great dopant for extending the absorption spectrum of TiO_2 to the visible light region [6]. Therefore it was proposed for photocatalytic destruction of organic pollutants under visible light [12] and for preparation of catalysts where the carbon doping can significantly improve the adsorption of organic pollutants on the catalyst surface thereby increasing the conductivity of TiO_2 that also facilitates the charge transfer [5,8,13]. Recently, titanium oxycarbides TiO_xC_{1-x} have attracted interest due to their promising electronic optical and mechanical resistant applications [14–17]. High temperature strength retention, high melting point, excellent oxidation resistance and low thermal expansion coefficient as well [18] are among the outstanding properties of the titanium oxycarbides. They are considered to be a homogeneous phase of mixed TiO and TiC constituents, which occurs over a wide range of compositions in NaCl type cubic structure [19] and possesses interstitial defects [20,21] and vacancies [21,22] on non-metal TiC lattice and both TiO sublattices. Titanium carbides are known for their outstanding properties such as high wear resistance, TiC compound could be applied in metallurgy, aeronautics, medicine and electronics [23,24], optical films [25], cutting tools, grinding wheels, bullet-proof vests or as seals to turbine engines [11]. Titanium carbide could be used in the reinforcing component in oxides or non-oxides [26] or in polishing pastes [27].

This work is focused on the preparation and study of synthesis of carbon-doped titanium dioxide thin films. The method involves the IR laser ablation of frozen titanium ethoxide in gaseous methane. This process leads to reactions of highly excited species and particles prepared by laser ablation with methane in gaseous phase. Experimental parameters allow for rapid heating of irradiated spot, evaporation and fragmentation of the target molecules, their reaction with background methane and rapid cooling of the emerging products.

2. Experimental part

Pulsed IR laser irradiation experiments of frozen titanium ethoxide target were conducted in a glass reactor (2.2 L in volume) in the

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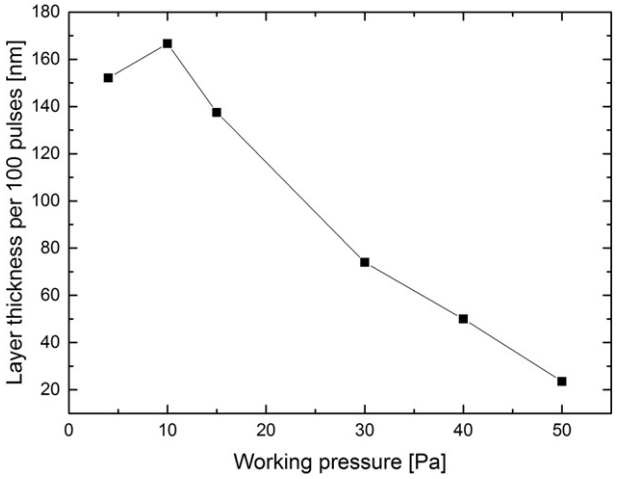

Fig. 1. Dependence of the layer thickness on the pressure of methane after ablation with 100 pulses.

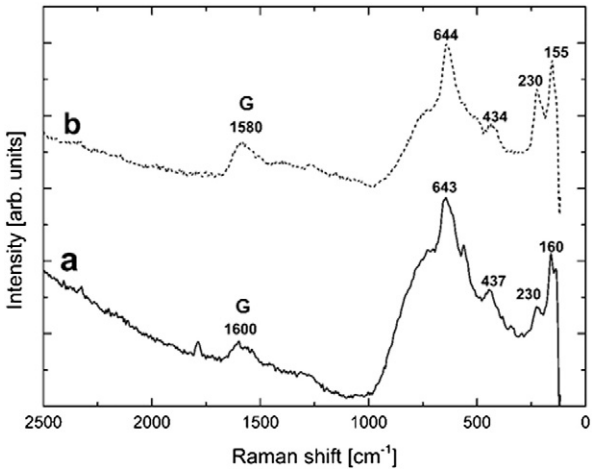

Fig. 3. Raman spectrum of the deposit obtained by laser ablation of Ti $(OC_2H_5)_4$ in the presence of a) 10 Pa and b) 50 Pa of methane.

presence of methane (4–50 Pa) by using a pulsed TEA (Transverse Electrical discharge in gas at Atmospheric pressure) CO_2 laser (model 1300 M, Plovdiv University, Bulgaria, laser pulse duration 100 ns) operating with a repetition frequency of 1 Hz on the P (14) line of the 00°1–02°0 transition (1052.20 cm^{-1}) and a pulse energy of 0.5–0.8 J. NaCl lens (focal length 15 cm) was used to focus the laser beam on the matrix surface. The frozen titanium ethoxide target (Strem Chemicals, USA, Titanium (IV) ethoxide) (99.99%-Ti, CAS# 3087-36-3) was frozen by liquid nitrogen to (−140 °C). The distance of the target and substrate holder was about 4 cm (as substrates, glass, Cu and KBr were used and the deposited layers were analyzed). At the beginning the reactor was efficiently evacuated by a turbomolecular pump to ultimate pressure better than 10^{-3} Pa. The following deposition was carried out in a plug flow set-up. Methane was continuously added to the glass reactor at specific flow rates, which reduced the inflow of ambient atmosphere into the glass reactor. This set-up also limited the oxidation of deposits. The unreacted methane with other by-products was then pumped out.

The deposited films were analyzed with a Nicolet Almega XR Raman spectrometer (resolution 2 cm^{-1}, excitation wavelength 473 nm and power 10 mW) and by the scanning electron microscopy (SEM) (Tescan Indusem). Bulk elemental analysis was carried out on the SE microscope equipped with an energy-dispersive X-ray spectroscopy (EDX) detector (Quantax 125 eV, Bruker) in the range from 5 to 30 kV. By the EDX technique were analyzed films with an accelerating voltage of 10 kV. High-resolution transmission electron microscopy (Jeol JEM 3010 microscope with LaB_6 cathode operated at 300 kV, point resolution 1.7 Å) equipped with an SAED (Selected Area Electron Diffraction) analytical system (INCA Oxford Instruments) for elemental analysis was used for TE microscopy and selective area electron diffraction study.

XPS (X-ray Photoelectron Spectroscopy) spectra were obtained by Kratos ESCA 3400 with base pressure better than 5.0 10^{-7} Pa, using polychromatic Mg X-ray source (Mg Kα, 1253.4 eV). Spectra were taken over Ti 2p, O 1 s and C 1 s regions. Samples were sputtered with Ar^+ ions at 500 V with current of 10 mA for 30 s to remove superficial layer. The overlapping spectral features were resolved into individual components using the damped non-linear least squares method and the lines of Gaussian–Lorentzian shape. Prior to fitting the Shirley background was subtracted.

3. Results and discussion

The method involves the IR laser ablation of titanium ethoxide at −140 °C in the gaseous methane. The pressure was kept during deposition between 4 and 50 Pa. During the ablation of the frozen target excited species interacted with methane molecules. The thickness of the prepared film on the Cu substrate depends on the pressure of gaseous methane (Fig. 1). Thicknesses of prepared films were measured by SEM technique at an angle of 10° from the perpendicular. In Fig. 1 these thicknesses were converted into 100 pulses as a constant value for all measured layers. The layer thickness was observed to increase up to a pressure of 10 Pa of methane, at higher background gas pressure the layer thickness decreases. It is expected that at the high pressure of methane the ablated species are slowed down by collisions with the

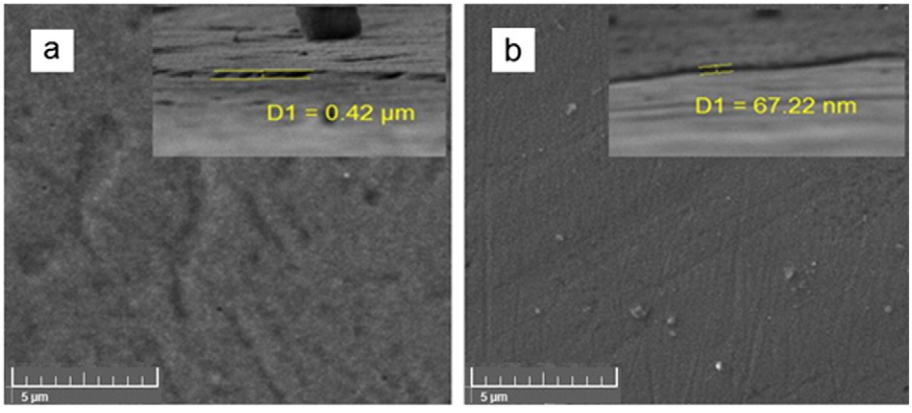

Fig. 2. SEM images of laser-ablated deposit from Ti $(OC_2H_5)_4$ in the presence of a) 10 Pa and b) 50 Pa of methane. Insets represent measurements of the layer thickness.