Applied Surface Science 257 (2011) 6435–6439

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Layer-by-layer deposition of Ti–4,4′-oxydianiline hybrid thin films

Anjali Sood, Pia Sundberg, Jari Malm, Maarit Karppinen*

Laboratory of Inorganic Chemistry, Department of Chemistry, Aalto University, FI-00076 Aalto, Finland

ARTICLE INFO

Article history:
Received 15 November 2010
Received in revised form 4 February 2011
Accepted 4 February 2011
Available online 28 February 2011

Keywords:
Inorganic–organic hybrid
Atomic layer deposition
Molecular layer deposition

ABSTRACT

Features of the two thin-film techniques, atomic layer deposition (ALD) and molecular layer deposition (MLD), are combined to build up a stable novel inorganic–organic hybrid material of the $(–Ti–N–C_6H_4–O–C_6H_4–N–)_n$ type, deposited from successive pulses of $TiCl_4$ and 4,4′-oxydianiline precursors. Depositions in the temperature range of 160–230 °C resulted in unstable films, while the films obtained in the temperature range of 250–490 °C were found stable in atmospheric air. The growth rate increased with increasing temperature, from 0.3 Å per cycle at 160 °C to 1.1 Å per cycle at 490 °C.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Advances in thin film processing techniques are anticipated to open up new approaches to prepare multifunctional materials in which even the distinct properties of inorganic and organic materials may be fused together into a single molecular-scale composite material [1]. The inorganic entity could be selected so as to provide the composite with *e.g.* various useful magnetic or electric functions, while the organic entity would offer *e.g.* structural flexibility and easy processing. Such a fusion of the most attractive properties of inorganic and organic materials could – potentially – be achieved in an elegant way by combining the atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques to deposit coherent inorganic–organic hybrid films from gas phase in a single reaction chamber. The ALD technique is an inorganic layer-by-layer deposition method based on successive self-limiting gas-solid reactions of separately introduced precursor pulses [2]. It produces thin films and coatings with well defined composition, density, thickness, uniformity and conformality under relatively mild deposition conditions. Similarly, MLD is based on sequential and self-limiting surface reactions of purely organic reactants [3–5]. Combination of ALD and MLD techniques was demonstrated recently, and a new class of layer-by-layer grown hybrid inorganic-organic thin films was recognized [6–10]. Earlier examples of the synthesis of hybrid inorganic–organic materials are mostly limited to solution-based chemistries [1,11,12].

* Corresponding author at: Laboratory of Inorganic Chemistry, Department of Chemistry, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.
Tel.: +358 9 470 2 2600; fax: +358 9 462 373.
E-mail address: maarit.karppinen@tkk.fi (M. Karppinen).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.02.022

The first hybrid inorganic–organic polymer films grown by means of combined ALD/MLD were so-called alucones and zincones deposited using ethylene glycol (EG) and trimethyl aluminum (TMA) or diethyl zinc (DEZ) as precursors [8–10]. Apart from aluminum and zinc alkyls, Nilsen et al. [7] have studied the ALD/MLD growth of hybrid films from titanium tetrachloride ($TiCl_4$) and ethylenediamine (EDA) or 4-aminobenzoic acid (PABA) precursors. In all these previous cases, however, the hybrid films were found to be rather air-sensitive. Fortunately, a rich variety of different organic reactants are in our hands to be exploited in combination with various metal precursors for improved hybrid-film fabrication [13,14]. Here we report layer-by-layer growth of stable $(–Ti–N–C_6H_4–O–C_6H_4–N–)_n$ inorganic–organic polymer films employing the ALD/MLD technique.

2. Experimental details

2.1. Thin film depositions

The films were deposited in a commercial flow-type hot wall ALD reactor (F-120 by ASM Microchemistry Ltd.) using $TiCl_4$ (Strem Chemicals Inc.) and 4,4′-oxydianiline (ODA; Fluka >98%) as precursors. The former precursor ($TiCl_4$) was evaporated using an external reservoir held at room temperature and the latter (ODA) from an open glass crucible placed inside the reactor at 150 °C. Nitrogen (>99.999%, Schmidlin UHPN 3000 N_2 generator) was used as a carrier and purging gas. The depositions were carried out under a 2–3 mbar pressure onto Si (1 0 0) and soda-lime glass substrates measuring 10 cm × 5 cm. The substrates were cleaned ultrasonically in ethanol and water *prior* to use. Before the actual hybrid-polymer depositions, 20 cycles of $TiCl_4$ and H_2O were applied to the surface according to the following pulse sequence: 1 s

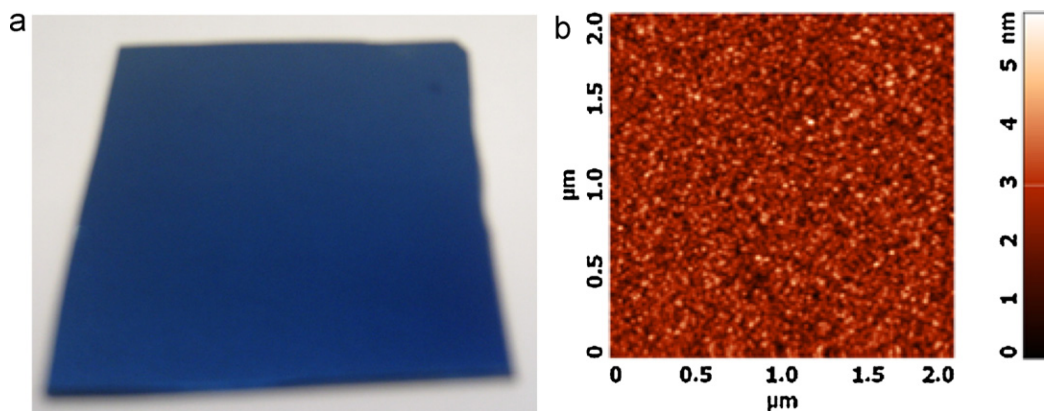

Fig. 1. (a) Photograph of a stable blue Ti–ODA film deposited at 350 °C on a 5 × 5 cm^2 Si substrate, and (b) AFM image of a stable Ti–ODA film deposited at 390 °C; depth scale 6 nm from black to white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

$TiCl_4$/1.5 s N_2/1.5 s H_2O/2 s N_2, in order to coat the surface first with a thin TiO_2 layer. Then, after a long N_2 purge of 60 s, the Ti–ODA film was deposited using a 1.5 s $TiCl_4$ dose followed by a 3 s N_2 purge, a 3 s ODA dose and a 3 s or 30 s N_2 purge. This process was repeated for 1500 cycles to achieve decent film thickness for basic film-property characterization. The relatively long precursor pulsing time for ODA was selected to obtain complete saturation followed by sufficiently long purging time to ensure the complete removal of HCl being released during the chemical reaction between $TiCl_4$ and ODA. Additionally, the behaviour of the process was studied by varying the precursor pulse length and the number of cycles.

2.2. Characterization techniques

A spectrophotometer (Hitachi U-2000) was used to measure reflectance data for calculating thicknesses and refractive indices of the deposited films using the method described by Ylilammi and Ranta-aho [15]. The reflection measurements were carried out in the wavelength range of 190–1100 nm. The film thicknesses were also measured by X-ray reflectivity (XRR; X'Pert MPD PRO Alfa 1, PANalytical). The smoothness of the films was confirmed by atomic force microscopy (AFM) measurements (Ntegra PNL by NT-MDT Co.). Chemical state of the films was investigated by *ex situ* Fourier transform infrared (FTIR) measurements (Nicolet Magna 750). The measurement chamber was continuously purged with purified dry air. A background spectrum was collected using the Si wafer before the deposition. The Ti to Cl ratio of the films was determined using X-ray fluorescence spectrometer (XRF; Philips PW 1480). A rapid thermal annealing (RTA) furnace (601 ATV Technologie GmbH, Germany) was used to anneal selected thin film samples in N_2 atmosphere (>99.999%). The crystallinity of the annealed samples was investigated by X-ray diffraction (XRD; Philips MPD 1880). The solubility of the films was examined using toluene, acetone, iso-propanol, methanol, ethanol, water, 1 M NaOH, 1 M acetic acid, 1 M HCl and concentrated H_2SO_4.

3. Results and discussion

The Ti–ODA hybrid film deposition was studied over the substrate temperature range of 160–490 °C. Depositions in the temperature range of 160–230 °C resulted in unstable films that faded away within few minutes of their exposure to atmospheric moisture, while the films obtained in the temperature range of 250–490 °C were rather stable in atmospheric air. From visual appearance the films were purple to blue in colour after 1500 deposition cycles, homogeneous and shiny in all the cases, see Fig. 1(a). The smoothness of the films was confirmed by AFM measurements. Fig. 1(b) shows an AFM image of a stable Ti–ODA film deposited at 390 °C. The root-mean-square roughness for this 75 nm film is 0.65 nm.

X-ray diffraction was used to evaluate the crystallinity of the films. All the films were found to be amorphous. Post-deposition annealing of the film deposited at 490 °C was investigated in the temperature range of 525–900 °C. No crystallization of the Ti–ODA hybrid was observed, and FTIR measurements carried out for the film after each annealing showed that the film started to decompose at *ca.* 600 °C. Annealing treatments for the film deposited at 250 °C were performed in the temperature range of 300–700 °C. In this case the FTIR spectra collected for the annealed samples showed that the film started to decompose already at *ca.* 500 °C (Fig. 2). The lower decomposition temperature observed for the film deposited at the lower temperature is parallel with our earlier observation that the stability of the films is enhanced with increasing deposition temperature. The hybrid films which were grown at higher temperatures (*e.g.* 490 °C) are more stable even upon further annealing than the films grown at lower temperatures (*e.g.* 250 °C). During the annealing experiments, visual change in colour was observed, when the film started to decompose in both cases.

The presence of Ti in the films was verified by XRF. Some Cl-containing impurity was also observed, apparently due to small amounts of Cl from $TiCl_4$ that has not reacted with ODA or from residual HCl that has absorbed into the film (Fig. 3).

Further information for the chemical state of the Ti–ODA films was obtained through *ex situ* FTIR measurements. In Fig. 4 we show an FTIR spectrum for a stable Ti–ODA film (deposited at 290 °C) together with a spectrum of pure ODA in KBr matrix for refer-

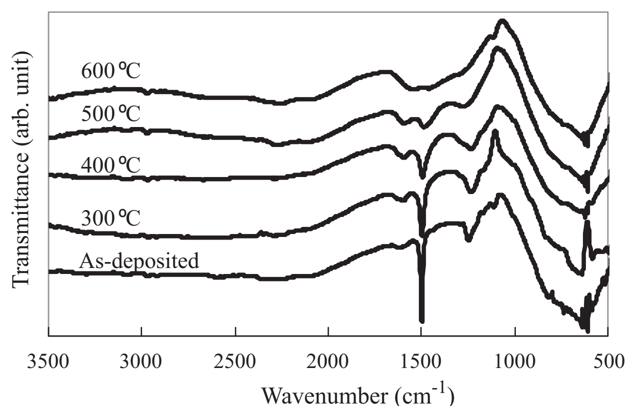

Fig. 2. IR spectra for a 250 °C-deposited Ti–ODA film annealed at various temperatures.

Download English Version:

https://daneshyari.com/en/article/5361801

Download Persian Version:

https://daneshyari.com/article/5361801

Daneshyari.com