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Hydrothermal crystallization of amorphous titania films deposited using low temperature atomic layer deposition

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Abstract

A two stage process (atomic layer deposition, followed by hydrothermal treatment) for producing crystalline titania thin films at temperatures compatible with polymeric substrates (<130 °C) has been assessed. Titania thin films were deposited at 80 °C using atomic layer deposition. They were extremely flat, uniform and almost entirely amorphous. They also contained relatively high levels of residual Cl from the precursor. After hydrothermal treatment at 120 °C for 1 day, >50% of the film had crystallized. Crystallization was complete after 10 days of hydrothermal treatment. Crystallization of the film resulted in the formation of coarse grained anatase. Residual Cl was completely expelled from the film upon crystallization. As a result of the amorphous to crystalline transformation voids formed at the crystallization front. Inward and lateral crystal growth resulted in voids being localized to the film/substrate interface and crystallite perimeters resulting in pinholing. Both these phenomena resulted in films with poor adhesion and film integrity was severely compromised.

Keywords: Crystallization; Titanium oxide; Transmission electron microscopy; X-ray absorption; Atomic layer deposition; Polymer substrates

1. Introduction

Titania enjoys a wide range of uses as a pigment and in photovoltaic [1,2], catalyst [3] and sensor [4] applications. The crystal structure and morphology are critical factors in controlling the associated properties. Anatase titania is often the preferred polymorph for photo-activated applications. A range of methods for depositing anatase in thin film form have been developed. Atomic layer deposition (ALD) (formerly known as Atomic Layer Epitaxy) is one such method [5]. It is a cyclic process which relies upon chemisorption of a (sub) monolayer of a reactive precursor onto a substrate. This is followed by a surface reaction with an oxygen-containing species, in the case of oxide deposition. A wide range of materials have been deposited using ALD, including oxides, sulphides and metals [6]. In the context of the present work, a pulse of $TiCl_4$ vapour is passed into the reactor and chemisorbs onto the hydroxylated surface of the substrate. This is followed by a purge pulse of inert gas to remove unbound precursor, followed by a pulse of water vapour to act as the nucleophilic source of oxygen and form the oxide layer in-situ. It also re-hydroxylates the surface. A final pulse of inert gas purges the reaction product (HCl) and excess water vapour from the system, completing the ALD cycle [7]. The process can be repeated as many times as required to build up the desired thickness. The surface limited nature of the ALD reactions, results in films of exceptional uniformity and conformality, and permits exquisite control over film thickness and chemistry, albeit with relatively slow growth rates [5].

For titania, the ALD method allows pure, highly crystalline anatase films to be deposited at temperatures in the range 165–350 °C [8,9]. ALD of titania can be extended to lower temperatures <165 °C [9–11]. This enables temperature sensitive substrates, such as polymers, to be coated [12]. Such films are amorphous and are generally exceptionally flat and uniform. Crystalline faceting due to preferential development of crystallites in orientations which favour growth can lead to roughening

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of the film [5,8,10,11]. One undesirable aspect of lower temperature ALD is an increased concentration of impurities in the form of retained unreacted and physi-sorbed precursor species or reaction products [10]. Such impurities may retard subsequent crystallization of the film.

Polymers are low cost, flexible materials that can be readily formed into a wide range of shapes. However, they generally exhibit poor stability at elevated temperatures, and are very soft compared with ceramics and metals. Surface properties of polymers can be greatly improved by appropriate surface engineering, such as coating with a hard ceramic layers. Previously, we have demonstrated the feasibility of using ALD for depositing oxide layers on polycarbonate [12,13]. Triani et al. [14] have recently carried out detailed studies of low temperature deposition of TiO_2 on both silicon and polycarbonate substrates, and have demonstrated well adhered stoichiometric TiO_2 film formation (amorphous) at 80 °C. Fabrequette and George [15] have deposited Al_2O_3/W multilayers on a range of polymers. Such coatings can greatly enhance the scratch resistance, reflectivity, photonic and catalytic performance of the material. However, with conventional ALD it is not possible to deposit crystalline titania at a temperature which is compatible with most polymers (≤ 130 °C), and only amorphous films can be grown. In this work we investigate the feasibility of a two stage low temperature process for depositing crystalline titania with good conformality, compositional uniformity and controlled thickness. In the first stage we use the ALD method to deposit an amorphous titania film at 80 °C. In the second stage, we hydrothermally process the film at 120 °C to crystallize it. The nature of the final product is investigated with transmission electron microscopy (TEM), X-ray absorption near-edge structure (XANES) and X-ray photoelectron spectroscopy (XPS).

2. Experimental details

Atomic layer deposition was carried out using a Microchemistry F-120 flow-type reactor system. $TiCl_4$ was used as the source of Ti and H_2O as the nucleophilic source of oxygen. Nitrogen was used as a carrier gas. Each deposition sequence consisted of: 0.4 s pulse of $TiCl_4$; 0.5 s purge with N_2; 0.5 s pulse of H_2O; 0.5 s purge with N_2. Deposition was continued for 1400 cycles to deposit a film of 100 ± 2 nm thickness (as determined via cross-sectional TEM). Ignoring any incubation effects, this corresponded to an average growth rate of 0.07 nm/cycle.

The substrate was Si <100> which was given an RCA clean [16] and a water plasma treatment prior to use. The native oxide layer was still present on the silicon. At the very low deposition temperature used (80 °C), the titania film was almost entirely amorphous and the substrate exerted no influence on the steady-state growth. Silicon was used as a substrate rather than a polymer for these initial feasibility studies, due to greater ease of specimen preparation for TEM. We have previously used ultramicrotomy to section ceramic coated polymers for microscopy examination [12,17]. However, the very large mismatch in toughness and ductility between the ceramic and polymer results in extensive cracking and detachment of the film, which greatly complicates the microscopy analysis. The nature of the films formed on polymer and silicon substrates were found to be very similar at these temperatures.

Films were hydrothermally treated by placing the ALD coated Si wafers in a polytetrafluoroethylene (PTFE) container with 0.15 mL of deionized water . The wafers were held in a PTFE jig above the water line. The PTFE container was housed in a stainless steel autoclave vessel which was heated to 120 °C in an oven and maintained at that temperature for a periods of 1, 10 and 30 days.

TEM specimens were prepared from the coated silicon wafer using methods described elsewhere [8]. Specimens were examined on a JEOL 2010F TEM operating at 200 keV and fitted with a Gatan Imaging Filter and an Oxford energy dispersive X-ray spectrometer (EDS). XANES measurements were performed at beamline 24A, National Synchrotron Radiation Research Centre (NSRRC), Hsinchu, Taiwan [18]. The thin films on Si substrates were mounted directly onto a stainless steel sample holder. The O K- and Ti $L_{2,3}$ edge XANES spectra were measured in both total-electron-yield (TEY) and fluorescence-yield (FY) modes (simultaneously), corresponding to signals from the film surface and bulk respectively. There was a very good agreement between TEY and FY data (except for the O K-edge spectrum of the film treated hydrothermally for 30 days, due to substantial exposure of the substrate — see below). Therefore only TEY data, which have much better signal to noise ratio, are shown here. The interval of data points was 0.1 eV in the near-edge region. The spectra were normalized to the incident photon current as measured from a gold grid, but no background removal was performed. The energy scale was calibrated using the known position of the O 1s and Ti 2p absorption edges in anatase [19]. The anatase reference was a thin film deposited on Si at 300 °C by ALD [6].

XPS analysis was carried out in ultra-high vacuum with a VG ESCALAB 220i-XL system employing a monochromatic Al K_α (1486.6 eV) X-ray source. The X-ray gun was operated at 120 W, and the spectrometer pass energy was set at 20 eV. The diameter of the analysis area was approximately 1 mm, and the thickness of the probed surface layer was less than 5 nm. The surface concentration of different species was determined by integrating the peak area, after subtracting a Shirley-type background, with Scofield sensitivity factors as defined in the software package supplied by VG Scientific.

3. Results

3.1. As-deposited film

Table 1 lists the XPS results obtained from the thin film surfaces, in the as-deposited condition and after various heat treatments. The atomic concentrations were normalized after excluding carbonaceous and hydroxyl contaminants at the surface as well as oxygen contributions from oxidized Si species. In order to eliminate the uncertainties introduced by the normalisation process (which involved peak fitting of overlapping O peaks), the Cl/Ti and Si/Ti concentration ratios were used to monitor the amount of Cl and the extent of pinholes in the film respectively. A high level of Cl was present in the as-deposited film (Cl/Ti = 0.2), while the amount of Si detected was low (Si/