Thin Solid Films 591 (2015) 131–136

Contents lists available at ScienceDirect

Thin Solid Films

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

Atomic layer deposition of Al_2O_3 and Al_2O_3/TiO_2 barrier coatings to reduce the water vapour permeability of polyetheretherketone

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ARTICLE INFO

Article history:
Received 10 May 2014
Received in revised form 23 August 2015
Accepted 24 August 2015
Available online 29 August 2015

Keywords:
Polyetheretherketone
Water vapour permeability
Atomic layer deposition
Thin film coating

ABSTRACT

We demonstrate significantly enhanced barrier properties of polyetheretherketone (PEEK) against water vapour penetration by depositing Al_2O_3 or Al_2O_3/TiO_2 nanofilms grown by atomic layer deposition (ALD). Nanoindentation analysis revealed good adhesion strength of a bilayer Al_2O_3/TiO_2 coating to PEEK, while the single layer Al_2O_3 coating displayed flaking and delamination. We identified three critical design parameters for achieving the optimum barrier properties of ALD Al_2O_3/TiO_2 coatings on PEEK. These are a minimum total thickness dependent on the required water vapour transmission rate, the use of an Al_2O_3/TiO_2 bilayer coating and the application of the coating to both sides of the PEEK film. Using these design parameters, we achieved a reduction in moisture permeability of PEEK of over two orders of magnitude while maintaining good adhesion strength of the polymer–thin film system.

1. Introduction

There is growing interest in the use of polymers to replace metals and ceramics. The low cost, relative ease of fabrication (via injection moulding and extrusion) as well as the physical and chemical stability of polymers are the main drivers for this interest. In the food packaging industry, polymers play a vital role in extending the shelf life of food [1], while the manufacture of organic light emitting diodes on flexible plastic substrates offers limitless possibilities for residential lighting panels [2]. Polymers are revolutionizing the aerospace industry by delivering enhanced safety, reduced manufacturing costs and lower density structural materials that result in improved fuel efficiency [3,4].

A key area in which the applications of polymers are evolving is in the encapsulation of implantable electronic medical devices. For such devices, the electrical conductivity of metals is a disadvantage, due to the requirement for electrical insulation of the conductive feed through wires from the enclosure [5]. While polymers are electrically insulating, their poor barrier properties are a limiting factor in these applications [6]. Polymers allow moisture to permeate through the material, resulting in corrosion and the ultimate failure of the device. The outstanding challenge to the use of polymers for this purpose is the development of an impermeable barrier against moisture.

The polymer chosen for this study is polyetheretherketone (PEEK). PEEK is one of the highest performing thermoplastics, with the ability to retain mechanical structure in harsh environments, a high chemical resistance, a high thermal stability ($T_m \sim 330$ °C), and excellent biocompatibility [7]. As a result, PEEK is a material of choice in many biomedical applications such as total joint replacement, orthopaedic and spinal implants, as well as in fracture fixation [7]. These properties also make PEEK an ideal material for encapsulation of active medical implants [5,8].

The application of barrier coatings on polymers such as PEEK is a potential solution to achieving the required hermeticity. Thin films displaying high barrier performance are characterized by high thermal stability, chemical inertness, dense microstructure with low porosity (as micro-porosities degrade coating adhesion strength) [9], tightly bound grain structure, and most importantly insolubility in water [10]. This directs attention towards coatings with a low density of defects, as achieved in atomic layer deposition (ALD).

Thin films grown by ALD have excellent barrier properties [11–13]. ALD is a surface-controlled, thin film deposition technique, in which films are deposited one atomic layer at a time [14]. ALD offers the advantage of atomic-level control of film thickness, leading to homogeneity, low pinhole density, and conformal growth of the film on the substrate [15]. In a comparative study by Hirvikorpi et al. [11], the barrier properties of thin films deposited by several deposition techniques were compared including magnetron sputtering, electron beam evaporation, sol–gel deposition and ALD. Although significant improvements in barrier performance were found with each technique, ALD was the only technique that produced coatings that were conformal in nature, with dense, pinhole free films with the lowest recorded water vapour transmission rate (WVTR) of the samples tested.

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http://dx.doi.org/10.1016/j.tsf.2015.08.038
0040-6090/

Table 1
Studies on the performance of Al_2O_3 as a barrier coating on various polymers, deposited by ALD.

Authors	Polymer substrate	WVTR of uncoated polymer (mg/m^2/day)	ALD Al_2O_3 configuration	WVTR (mg/m^2/day)	Ratio coated: uncoated
Carcia et al. [19]	PET	18,000	5-25 nm, single-side coating	<0.05	1:360,000
Dameron et al. [20]	PEN	900	26 nm, single-side coating	1	1:900
Groner et al. [21]	PEN	900	26 nm, single-side coating	1.5	1:600
Kim et al. [22]	PEN	900	11.8 nm, single-side coating	<4	1:225
Kim et al. [22]	PES	92,800	11.8 nm, single-side coating	4.1	1:22,634
Langereis et al. [23]	PEN	900	20 nm, double-side coating	5	1:180
Park et al. [24]	PES	92,800	30 nm, double-side coating	30	1:3093
Kääriäinen et al. [25]	PET	18,000	128 nm, single-side coating	100	1:180
Hirvikorpi et al. [26]	PEN	900	50 nm, single-side coating	600	1:1.5
Kääriäinen et al. [25]	PLA	93,000	108 nm, single-side coating	4100	1:23
Hirvikorpi et al. [27]	PLA	93,000	25 nm, double-side coating	33,000	1:3

Thin film Al_2O_3 (alumina) is an ideal candidate as a barrier enhancement material; numerous studies demonstrate significant reduction in water vapour permeation of polymers upon application of Al_2O_3 as a thin film coating. Table 1 presents a summary of the performance of Al_2O_3 as a barrier coating as reported in the literature. Thin film TiO_2 (titanium dioxide) has also been used previously as a protective coating owing to its barrier properties. In addition to its barrier properties, it has superior anti-corrosion properties. The combination of Al_2O_3 and TiO_2 has been shown to be a good choice for a corrosion-resistant barrier coating [16,17]. Abdulgatov et al. [18] showed that while Al_2O_3 and TiO_2 films alone were insufficient to prevent copper corrosion, an Al_2O_3/TiO_2 bilayer coating reduced the overall porosity of the film and enhanced the resilience of copper to corrosion.

Although the barrier properties of ALD Al_2O_3 coatings on PEEK are the focus of this study, measurement of their permeability to water vapour alone is insufficient to assess their suitability for use in medical implants. Enhanced barrier properties may have limited use without a strong and robust interfacial bond between the coating and the substrate. Thus an understanding of the adhesion strength and mechanical stability at the coating–polymer interface is particularly important.

There are currently no studies of the use of ALD coatings on PEEK to improve the barrier against water vapour ingress. In this study, Al_2O_3 and Al_2O_3/TiO_2 nanofilms are investigated for protecting a polymer enclosure against water vapour permeation. We developed a high performance ALD Al_2O_3/TiO_2 moisture barrier coating on PEEK, which enabled us to achieve a reduction of moisture penetration of over two orders of magnitude.

2. Method

2.1. Materials and sample preparation

Untreated semi-crystalline PEEK microfilm (250 μm) (APTIV® 1000 series, Victrex, Lancashire, UK) was used as the substrate for this study. The PEEK film was coated with either a single layer coating of thin film Al_2O_3 (25 nm or 100 nm) or a bilayer coating consisting of thin film Al_2O_3 (25 nm or 100 nm) with a 10 nm TiO_2 top coating. These coatings were deposited either on one or both sides of the PEEK film, producing a total of eight different coating configurations. Coatings were applied by ALD in an Advanced SUNALE™ P-300B ALD reactor (Picosun, Oy). The precursors were trimethylaluminum (TMA) and water for Al_2O_3 coatings, and titanium tetrachloride ($TiCl_4$) and water for TiO_2 coatings. The ALD deposition sequence was carried out as follows:

- TMA + water: TMA pulse 0.2 s → purge 10.5 s → water pulse 0.2 s → purge 10.5 s (total cycle time 21.4 s).
- $TiCl_4$ + water: $TiCl_4$ pulse 0.2 s → purge 10.5 s → water pulse 0.2 s → purge 10.5 s (total cycle time 21.4 s).

The 100 mm × 100 mm samples were cleaned in 50% isopropyl alcohol in an ultrasonic bath, rinsed in deionised water and blown dry with nitrogen prior to deposition of the barrier coatings. Coatings were deposited at 110 °C at 10 cycles/nm of targeted thickness. The thickness of representative coatings (100 nm Al_2O_3/10 nm TiO_2) was measured on silicon wafers using a FilmTec 2000 reflectometer; 100 nm Al_2O_3 was measured to be 99.09 nm–102.8 nm ($n = 2$) and 10 nm TiO_2 was measured to be 13.88 nm on each sample ($n = 2$). Samples for single layer coating were taped to silicon wafers to protect against backside coating. The characteristics of all samples used in this study are displayed in Table 2.

2.2. Water vapour transmission rate

The WVTR of the samples ($n = 3$ per group) was measured using a commercial MOCON Aquatran® 1 Model G, having a sensitivity of ±0.5 mg $H_2O/(m^2$-day) at 37 °C, a detection limit of 0.0005 g/(m^2-day) and 100% relative humidity (RH). Where only one surface of the sample was coated, the coated side was mounted facing the sensor. High performance liquid chromatography grade water was used to wet the sponges and maintained 100% RH.

2.3. Nanoindentation

Nanoindentation tests were conducted using a commercial Hysitron TriboIndenter (TI 900 TriboIndenter, Hysitron Inc). The indenter used was a Berkovich diamond conical indenter having a half semi angle of 42.8°. For each sample, a peak load of 8000 μN was applied at a loading and unloading rate of 20 μN/s, with a hold time of 10 s at the peak load in order to account for stress relaxation.

Table 2
Average WVTR of each coating type arranged in the order of highest to lowest.

Group	Al_2O_3 (nm)	TiO_2 (nm)	Single or double side coating	Total Thickness (nm)	Average WVTR (mg/m^2-day)	Ratio of coated:uncoated PEEK
1	25	0	1	25	959.52	1:3
2	25	0	2	50	464.31	1:7
3	25	10	1	35	341.35	1:9
4	25	10	2	70	258.84	1:12
5	100	0	1	100	88.59	1:35
6	100	0	2	200	50.38	1:62
7	100	10	1	110	27.13	1:115
8	100	10	2	220	24.19	1:129