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ScienceDirect
Thin Solid Films 516 (2008) 4036–4039
www.elsevier.com/locate/tsf

Letter

Protection of polymer from atomic-oxygen erosion using Al_2O_3 atomic layer deposition coatings

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Received 8 April 2007; received in revised form 2 July 2007; accepted 13 July 2007
Available online 21 July 2007

Abstract

Thin films of Al_2O_3 grown using atomic layer deposition (ALD) techniques can protect polymers from erosion by oxygen atoms. To quantify this protection, polyimide substrates with the same chemical repeat unit as Kapton® were applied to quartz crystal microbalance (QCM) sensors. Al_2O_3 ALD films with varying thicknesses were grown on the polyimide substrates. The ALD-coated polyimide materials were then exposed to a hyperthermal atomic-oxygen beam. The mass loss versus oxygen-atom exposure time was measured *in situ* by the QCM. Al_2O_3 ALD film thicknesses of ~35 Å were found to protect the polymer from erosion.

Keywords: Polymers; Polyimide; Ätomic layer deposition; Al2O3; Atomic oxygen; Erosion; Quartz crystal microbalance

Spacecraft in low Earth orbit collide with ambient oxygen atoms with relative velocities of ~7.4 km s^{-1} and fluxes in the range of 10^{13} to 10^{15} atoms cm^{-2} s^{-1}. These high-energy collisions cause oxidation and erosion of materials. Organic polymers used on the external surfaces of spacecraft as structural and thermal-control materials are particularly vulnerable to atomic oxygen [1–4]. Coatings of inorganic oxides, such as SiO_2, have been used to provide protection from atomic oxygen. These coatings are generally applied by plasma enhanced chemical vapor deposition (PECVD).

PECVD is known to produce films that tend to be columnar with a large defect density. Because of the large number of defects, relatively thick coatings have been used to reduce the defect density. Kapton® polyimide surfaces that have SiO_2 coatings with a 1300 Å thickness have been shown to exhibit erosion yields as low as ~0.1–0.2% of the erosion yield of unprotected Kapton® [5,6]. However, handling and thermal cycling of these thick coatings are likely to produce cracks in the coatings and expose the substrate to potential O-atom attack. Atomic oxygen that reaches the substrate through defects may erode large cavities underneath the coating in the vicinity of the defect [6,7].

The PECVD coating technique also requires line-of-sight to the substrate. This requirement may be impractical for shadowed or high-aspect-ratio structures. An approach that is an improvement over PECVD is to attach silicon-containing moieties to the surface through a photochemical reaction. The modified surface may then react with atomic oxygen to form a continuous layer of SiO_2. Although this technique has demonstrated a one hundred-fold reduction in erosion yield for flat samples, there are still line-of-sight limitations when the technique is applied to non-planar surfaces [8].

In addition to protecting existing polymers with inorganic coatings, inorganic/organic copolymers are being developed that take advantage of the reaction of the inorganic component with atomic oxygen to form a passivating oxide layer. This protection strategy has the advantage that the oxide layer can reform after the degradation of the initial oxide layer. An earlier

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doi:10.1016/j.tsf.2007.07.150

class of self-passivating polymers was based on phosphine oxide [9]. More recently, copolymers that include polyoligomeric silsesquioxane have shown great promise as a replacement for Kapton® [10]. However, these polymers exhibit finite erosion by atomic oxygen and may experience damage under vacuum ultraviolet (VUV) radiation in space.

Earlier studies indicate that an ultrathin and flexible inorganic oxide coating may provide an effective barrier. Exposure of a silicon surface to a beam of hyperthermal atomic oxygen leads to the growth of an SiO_2 film with a terminal thickness of ~50 Å [11–13]. The native thickness of aluminum oxide (Al_2O_3) on aluminum has also been measured to be only 30–40 Å [14]. Anecdotal evidence from space flight experiments exists that an Al_2O_3 coating with a nominal thickness of 50 Å protects a reactive substrate [15]. If such thin and flexible oxide coatings can be applied to polymer substrates without line-of-sight restrictions and without defects, then they should be able to protect the substrate even after handling and thermal cycling.

Chemical vapor deposition (CVD) is a well characterized thin film deposition method that does not depend on line-of-sight. However, CVD methods typically require elevated substrate temperatures to grow the desired films. A variation on CVD is atomic layer deposition (ALD). ALD can usually employ more reactive precursor gases than CVD and achieve lower deposition temperatures. ALD techniques can also produce continuous, Angstrom-level-controlled, and defect-free films [16]. ALD is a gas-phase method based on two sequential, self-limiting surface reactions [17]. Each surface reaction allows only ~1 monolayer of deposition.

Al_2O_3 ALD is a particularly robust and well-defined ALD system [18,19]. Al_2O_3 ALD films can be pinhole-free as demonstrated by electrical measurements [20], and they can be deposited on polymer substrates [21,22]. Excellent gas diffusion barrier properties are observed for Al_2O_3 ALD films on polyethylene naphthalate (PEN) and Kapton® polymer substrates [23,24]. Consequently, Al_2O_3 ALD should provide an ideal model system for the systematic investigation of thin-film coatings to protect a polymer from hyperthermal atomic oxygen.

Quartz crystal microbalance (QCM) sensors were used to study the efficacy of thin Al_2O_3 ALD films to protect a polymer. Polyimide substrates were prepared on 0.5-inch-diameter QCM disc sensors. The precursor to the polyimide was Pyralin® PI5878G from HD Microsystems. This polyamic acid as purchased was dissolved in 1-methyl-2-pyrrolidinone. The polyamic acid was diluted and then spin-coated onto gold-coated QCM sensors. Before spin-coating, the QCM sensors were modified by applying an adhesion promoter (HD Microsystems VM651) and heating the substrates in an air oven to 80 °C to remove any residual water. After spin-coating, the samples were allowed to dry in air under a watch glass for two days. The samples were then placed in a vacuum furnace (Centurion VPM) and cured with the following schedule: 2 h at 50 °C, 2 h at 80 °C, 1 h at 200 °C, and 2 h at 270 °C. The chemical repeat unit of the resulting polyimide is equivalent to that of DuPont Kapton®. The polyimide layers on the QCM disc sensors were determined by profilometry to have thicknesses in the range of 800–1000 nm.

Aluminum oxide (Al_2O_3) ALD coatings with various thicknesses were applied to the polyimide substrates using sequential, self-limiting exposures to trimethylaluminum (TMA) (Aldrich) and water (Fisher HPLC-grade). The Al_2O_3 ALD was performed at 177 °C in a viscous flow, hot-wall ALD flow reactor [25]. The TMA and H_2O yield Al_2O_3 ALD according to the following two reactions [18,19]:

$$\text{(A)Al–OH}^* + \text{Al(CH}_3)_3 \rightarrow \text{Al–O–Al(CH}_3)_2^* + \text{CH}_4 \tag{1}$$

$$\text{(B)Al–CH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al–OH}^* + \text{CH}_4 \tag{2}$$

where the asterisks denote the surface species. When performed in an ABAB... reaction sequence, these sequential reactions produce linear, atomic-layer-controlled Al_2O_3 growth. The steady-state Al_2O_3 ALD growth rate after nucleation is ~1.2 Å per AB cycle [19,26]. The polyimide substrates were coated with Al_2O_3 ALD films resulting from 8, 13, 17, 21, 25 and 50 AB cycles, respectively. The reactant exposure sequence was TMA (1.0 s), purge (20 s), H_2O (1.0 s), and purge (10 s). The polyimide surfaces were coated without any prior surface treatment or functionalization.

The coated QCM sensors were exposed to a beam containing hyperthermal atomic oxygen. Mass loss was measured *in situ* versus time using a Maxtek QCM head (Model DSH-200) and a Model RQCM data collection system. The QCM head accommodated two discs, allowing each atomic-oxygen exposure to be conducted with an Al_2O_3-coated polyimide test sample and a polyimide control sample without an Al_2O_3 coating. For each exposure, the atomic-oxygen flux was determined from the mass-loss rate of the polyimide control sample. The oxygen-atom flux did not vary by more than a few percent from one exposure to another. Test and control samples were always placed in the same locations to ensure consistency between the various exposures.

A pictorial diagram of the atomic-oxygen source and experimental apparatus is shown in Fig. 1. This apparatus has

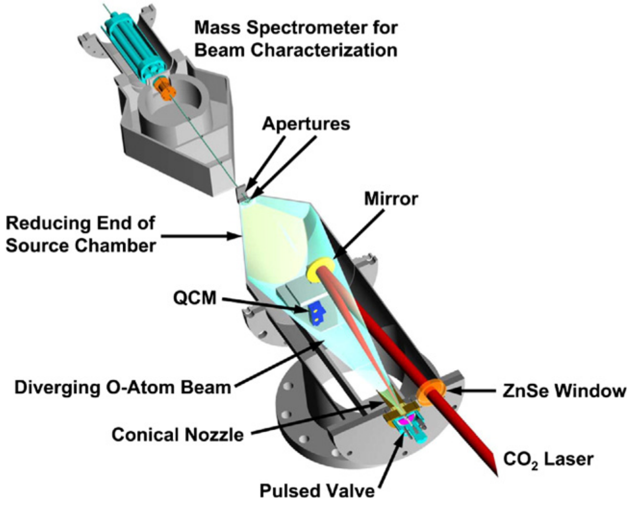

Fig. 1. Experimental apparatus used to measure the mass loss of spin-coated polyimide layers on QCM sensors during exposure to a hyperthermal atomic-oxygen beam.