Applied Surface Science 288 (2014) 98–108

Contents lists available at ScienceDirect

Applied Surface Science

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

Investigating phosphonate monolayer stability on ALD oxide surfaces

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ARTICLE INFO

Article history:
Received 20 May 2013
Received in revised form
20 September 2013
Accepted 21 September 2013
Available online 29 September 2013

Keywords:
Self-assembled monolayer
SAMs
Phosphonate stability
Phosphonate SAMs
Atomic layer deposition
Hafnium oxide ALD
Alumina ALD

ABSTRACT

We report a series of studies aimed at investigating the stability of phosphonate self-assembled monolayers (SAMs) made from octadecylphosphonic acid (ODPA) or a perfluorinated phosphonic acid (PFPA) on hafnium and aluminum oxide surfaces deposited by atomic layer deposition (ALD). The monolayers were deposited by a series of techniques including self-assembly from solution, tethering by aggregation and growth, and the Langmuir–Blodgett (LB) method. SAMs prepared by LB method were primarily used in our stability investigations because they were found to be the most uniform and reproducible. All films deposited on ALD oxide-coated substrates were characterized by means of water contact angle measurements, spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). XPS data conclusively showed covalent phosphonate formation on both substrates. SAMs formed on both Al_2O_3 and HfO_2 were stable upon exposure to water. PFPA SAMs on HfO_2 were found to be the most stable SAMs studied here in either water or phosphate buffer (PBS) at room temperature. We also show that similar silane-based SAMs made from octadecyltrichlorosilane (OTS) on silicon oxide (SiO_2) are less stable in PBS than phosphonate SAMs on atomic layer deposited HfO_2 substrates. These data suggest that phosphonate SAMs should be considered for use in (bio)molecular sensing and actuator devices that utilize ALD and require longer-term stability under aqueous conditions.

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1. Introduction

In the progress of microelectromechanical (MEMS) fabrication techniques the use of ultrathin film, high-dielectric constant oxides, such as Al_2O_3 or HfO_2 has become essential [1]. Among many deposition methods for ultrathin oxide films, atomic layer deposition technique has attracted the most attention due to its excellent thickness and conformity control [2]. Typically ALD processes are based on binary reaction cycles where two surface reactions occur independently and deposit a film containing two distinct elements. This process differs in thermal oxide growth where the oxide is grown at high temperatures through a bottom up process, where oxygen atoms penetrate into the surface and combine to form an oxide layer. Although thermal oxidation can produce high-quality oxide films, ALD can take place at much lower temperatures and is less sensitive to the underlying substrate to form uniform films with the desired electrical properties. The functionalization of oxide layers that are stable under aqueous conditions is important for a number of applications including microelectronics, (bio)sensors, lab-on-a-chip devices and micro-total analytical systems [3–8].

Self-assembled monolayers (SAMs) have been extensively studied as coatings in the above mentioned fields due to their ability to tailor surface properties and relative ease of film formation [9,10]. Molecules capable of forming monolayer-type thin films usually consist of a head group, which binds to the solid surface, a functional tail group that allows the tailoring of the chemical and physical properties of the interface, and a chain group, usually an alkyl chain, which connects the two. SAMs are ordered assemblies of such molecules that are formed spontaneously by the specific adsorption of the head group onto a solid surface while organizing the molecules into dense layers, which is usually due to weaker interactions (hydrophobic attraction, Van der Waals forces) between adjacent chains [11,12].

Thiols deposited on gold surfaces are a model SAM system extensively used due to their ease of preparation and well-defined packing order dictated by the metal lattice [13]. They are used for a wide range of applications, but lack long-term stability due to oxidation under ambient conditions or removal from the surface in aqueous environments over time [14,15], and are limited to certain metal surfaces that react with the thiol head group [16]. For some applications, SAM formation on oxide surfaces is preferred

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0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.09.128

[17–19]. In these cases, alkylsilanes have been extensively studied [20–22]. Silanes have an advantage over thiol-based chemistries because silane terminated molecules and the thin films obtained from them show higher physical and chemical stability [23] and can be deposited on a wide variety of oxide substrates [24]. However, silane-based monolayer deposition can be more complex depending on parameters such as water content, solvent, deposition time and temperature. Silane molecules are also very reactive, thus more care must be taken during deposition [21,25,26].

In an effort to circumvent the disadvantages of silanes, SAMs of organophosphonic acids have more recently been explored [27–30]. Phosphonate SAMs are readily prepared and have affinity toward a variety of oxide surfaces. The formation of an organophosphonate film on an oxide surface is based on a condensation reaction with the phosphonic acid head group reacting with the hydroxyl groups displayed on a hydrated oxide surface that act as reactive sites for covalent attachment after annealing. It is currently believed that organophosphate molecules have up to three sites for attachment [31–33] and that the films conform to the surface topography rather than forming a two-dimensional network above the surface. This attachment chemistry may make phosphonate monolayers on a variety of substrates more suitable than other SAM systems for preparation of films exposed to aqueous conditions. In recent literature, monolayer formation of phosphonic acids have been reported on several oxide surfaces of practical importance including Al_2O_3, TiO_2, NiO, SiO_2, ITO, HfO_2 and ZrO_2 [30,31,33–45]. Although some work has been done to explore the stability of organophosphonate films on a limited number of oxide coatings [46–49], no studies look at these films on ALD coated surfaces. In addition, no long-term stability on oxide-coated substrates in aqueous solutions has yet been reported.

In this study we explored deposition of two phosphonic acids, octadecylphosphonic acid (ODPA) and a perfluorinated phosphonic acid (PFPA), on Al_2O_3 and HfO_2 deposited by ALD. The phosphonic acid SAMs were characterized by water contact angle, ellipsometry, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy. The stability of these monolayers was investigated by immersion in deionized water and a phosphate buffer saline (PBS) solution with periodic characterization of the thin films. The stability of these phosphonate films was compared to an octadecyltrichlorosilane film on SiO_2 substrates. We found that PFPA deposited on HfO_2 ALD substrates were the most stable in water and PBS among the alkylsilane and organophosphonate films studied here. These results provide valuable information about phosphonate SAM deposition and stability on atomic layer deposited oxide films, and indicate that phosphonate SAMs should be considered for device coatings on systems requiring greater stability under aqueous conditions.

2. Material and methods

2.1. Oxide layer preparation

Atomic layer oxide coatings were deposited onto (1 0 0) silicon wafers (Desert Silicon, Glendale, AZ) using a Picosun SUNALE^{TM} R-150B ALD system (Detroit, MI). The surface of the silicon wafers used displayed a native oxide (SiO_2) with a thickness of ~1.9 nm as determined by spectroscopic ellipsometry before ALD deposition. Liquid trimethylaluminum (TMA, SAFC Hitech (USA)) and deionized water (resistivity 18 MΩ/cm), both preheated to 25 °C, were used as precursors for the deposition of a 25 nm Al_2O_3 film. TMA was introduced into the reaction chamber at a rate of 150 standard cubic centimeters per minute (sccm) with a pulse time of 0.1 s and water followed at 200 sccm for 0.1 s with a purge of nitrogen at 150 sccm for 6.0 s between each pulse of precursor. The chamber temperature was maintained at 300 °C during the completion of 250 cycles, where one cycle consisted of TMA and water pulses with nitrogen purges in between. Tetrakis-dimethylamido hafnium(IV) (TDMAH, SAFC Hitech (USA)) was used as the hafnium metal precursor with deionized water as the oxygen source for the 250-cycle ALD deposition of a 25 nm HfO_2 film. TDMAH preheated to 75 °C was delivered to the reaction chamber heated to 200 °C at 100 sccm with a pulse time of 1.9 s. The water precursor and nitrogen purge conditions were the same as those used for the Al_2O_3 deposition.

2.2. Synthesis of 4,5,6,7,8,9,10,11-perfluoroundecyl phosphonic acid (PFPA)

Iodofluoroalkane (1.0 g, 2.05 mmol, FluoroFlash) and triisopropylphosphite (0.85 g, 4.1 mmol, Sigma-Aldrich) were combined in a microwave vial with a stir-bar. The vial was capped and sealed, heated to 170 °C (30 min) with microwave irradiation (Biotage Initiator, Charlotte, NC) and cooled to room temperature. The crude reaction mixture was filtered through a FluoroFlash column using their published procedure [50]. Briefly, the column was equilibrated with water/methanol (1:4) and loaded with the reaction mixture. The column was eluted with water/methanol to remove non-fluorinated reagents and products, followed by elution with 100% methanol to remove fluorinated products from the column. The methanol wash was concentrated and the residue was reconstituted in chloroform. This solution was dried over solid Na_2SO_4, filtered and concentrated to yield the isopropyl protected intermediate product shown in Scheme 1. ^{1}H NMR ($CDCl_3$) d 1.31 (d, 12*H*), 1.77 (m, 3*H*), 1.92 (m, 3*H*), 2.20 (m, 3*H*), 4.72 (m, 2*H*. ^{31}P NMR(CDCl3) d 29.1 (s). MALDI-MS: M + 1 calc'd: 627.29, found: 627.02. The isopropyl protected phosphonate and trimethylsilyl bromide (TMS-Br, 2.5 g, 16.4 mmol, Sigma-Aldrich) were dissolved in CH_2Cl_2 in a microwave vial. The vial was capped and sealed, heated to 100 °C (10 min) with microwave irradiation (Biotage Initiator) and cooled to room temperature. The reaction mixture was concentrated, evaporated twice from CH_2Cl_2 to remove residual TMS-Br, reconstituted in 1:4 water/methanol and filtered through a FluoroFlash column as described above. The methanol was concentrated to the final PFPA product as a white solid. ^{1}H NMR (CD_3OD) d 1.80 (q, 2*H*), 1.95 (m, 2*H*), 2.35 (m, 2*H*). ^{31}P NMR (CD_3OD) d 29.2 (s). MALDI-MS M + 1 calc'd: 543.13, found: 542.94. PFPA was used without further purification for the investigation of monolayer formation (Scheme 2).

2.3. Silane monolayer preparation

In all cases substrates were cleaned prior to deposition by sonicating in methanol (ACS, 99.8%) for 10 min, drying under a stream of air and exposure to deep-UV light for 30 min to remove residual organic contamination. A film of *n*-octadecyltrichlorosilane (OTS, Gelest Inc., Morrisville, PA) was deposited by immersing cleaned silicon wafers into vials containing a solution of 1 mM OTS dissolved in *n*-hexadecane (99%, ACROS Organics) [51]. The vials were sealed and allowed to incubate for 24 h at room temperature. Samples were removed and promptly rinsed first for 10 min in chloroform (HPLC, 99.9%), followed by isopropanol (ACS, 99.5%) and deionized water. The samples were then heat treated at 115 °C for 10 min [52,53].

2.4. Phosphonate monolayer preparation

Three different deposition techniques were used to coat a monolayer of octadecylphosphonic acid (ODPA, Sigma-Aldrich) or the perfluorinated phosphonic acid. Films were initially deposited onto SiO_2 to determine the most uniform and reproducible deposition technique. This technique was then used to deposit onto Al_2O_3 and

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