Solid State Sciences 55 (2016) 8–12

Contents lists available at ScienceDirect

Solid State Sciences

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

Influence of composition and processing parameters on the properties of solution-processed aluminum phosphate oxide (AlPO) thin films

Kevin M. Norelli [a], Paul N. Plassmeyer [a], Keenan N. Woods [a], Benjamin A. Glassy [a], Christopher C. Knutson [b], Matt Beekman [c], Catherine J. Page [a], *

[a] Department of Chemistry, University of Oregon, 1253 University of Oregon, Eugene, OR 97403, United States
[b] Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331, United States
[c] Department of Natural Sciences, Oregon Institute of Technology, Klamath Falls, OR 97601, United States

ARTICLE INFO

Article history:
Received 19 December 2015
Accepted 28 January 2016
Available online 2 February 2016

Keywords:
Amorphous
Aqueous
Dielectrics
Solution-processed
Thin films
Aluminum phosphate

ABSTRACT

The effects of precursor solution concentration, composition, and spin-processing parameters on the thickness and electrical properties of ultra-smooth aluminum oxide phosphate ($Al_2O_{3-3x}(PO_4)_{2x}$ or “AlPO”) thin films prepared using aqueous solutions are reported. Compositions were verified by electron probe micro-analysis and range from $Al_2O_{1.5}(PO_4)$ to $AlPO_4$ ($x =$ P:Al from 0.5 to 1.0). Film thicknesses were determined using X-ray reflectivity measurements and were found to depend systematically on solution concentration, P:Al ratio, and spin-speed. Metal-insulator-semiconductor devices were fabricated to determine electrical properties as a function of composition. As the P:Al ratio increased from 0.5 to 1.0, the dielectric constant decreased from 6.0 to 4.6, leakage currents increased from 0.45 to 65 nA cm^{-2} at 1 MV cm^{-1} and dielectric breakdown (defined as leakage currents >10 μA cm^{-2}) decreased from 9.74 to 2.84 MV cm^{-1}. These results establish composition, concentration, and spin-speed for the production of AlPO films with targeted thicknesses and electrical properties.

1. Introduction

Metal oxide thin films are essential components in a variety of electronic device structures, including dielectric and channel layers in thin-film transistors (TFTs) [1] and metal-oxide-semiconductor field effect transistors (MOSFETs) [2], charge trapping layers for memory devices [3], and as passivation or catalyst layers for photovoltaics [4,5]. In most of these applications the film morphology, composition, and the electrical properties are critical to the performance of the devices.

In principle, a thin film of a given chemical composition should have a well-defined set of properties. To a first approximation this is true, but many secondary factors impact thin film chemical and physical properties and device performance. These include the concentration and nature of defects and impurities [6], the extent or lack of crystallinity, crystallite size and orientation [1,7], overall thickness, morphology, and porosity. In general, these secondary factors are strongly influenced by the synthetic route and processing parameters used to fabricate a particular film.

The techniques for fabricating metal oxide thin films can be broadly divided into either vapor-phase or solution-phase deposition. In general, the vapor-phase deposition techniques tend to yield films of higher quality [8] and, in some cases, these films can be made to conform to complex substrate architectures [9]. However, vapor-phase routes often require reactive precursors [10,11] and specialized deposition equipment, resulting in high cost and low atom economy due to wasted reactants. By contrast, solution-phase deposition techniques are relatively inexpensive, require relatively simple deposition equipment, and allow for reduced waste.

Most solution-deposited metal oxide thin films are produced using the sol-gel route, which employs metal alkoxides or other precursors with organic ligands [12,13]. The sol is deposited onto a substrate, typically via spin- or dip-coating, and thermally processed to remove organics and promote condensation to the desired metal-oxide. Because of the high volume fraction of organic ligands and solvent which must be expelled during processing, the resulting films often suffer from relatively low density, high porosity, and unwanted electronic defects [14].

A related paradigm, “prompt inorganic condensation” or PIC

---

* Corresponding author.
E-mail address: cpage@uoregon.edu (C.J. Page).

http://dx.doi.org/10.1016/j.solidstatesciences.2016.01.009
1293-2558/

[15–21], has been developed using aqueous solutions of metal inorganic salts. PIC minimizes the number and size of counterions in thin film precursor solutions while simultaneously forming solubilized polynuclear metal-oxo or -hydroxo species. Prompt heating of spin-cast solutions enables a relatively smooth transition to thin film metal oxides [22]. PIC has been used to make a variety of amorphous semiconducting and insulating metal oxide (as well as metal sulfate and metal phosphate) thin films, including aluminum phosphate oxide films [15,19,21,23]. Generally, this technique produces films which meet or surpass the quality of sol-gel derived films and frequently rival that of vapor-deposited films [15,22,24–27].

Aluminum phosphate oxide ($Al_2O_{3-3x}(PO_4)_{2x}$ or “AlPO”) is of interest as a catalyst for the conversion of methanol to dimethyl ether [28], as a cathode coating material for lithium-ion batteries [29], and as a dielectric component for thin-film devices [15,19,30]. Previously, vapor phase methods (atomic layer epitaxy (ALE) [31] and atomic layer deposition (ALD) [32,33]) have been used to prepare AlPO films. Solution-phase PIC has also been employed to prepare amorphous AlPO films with dielectric properties comparable to thermally grown SiO_2 [15,19,21,23]. These AlPO films have been successfully employed as gate dielectrics in high-performing thin-film transistor (TFT) devices that are competitive with a-Si TFTs [24]. For the latter application, incorporation of phosphate into an aluminum oxide matrix suppresses crystallization, yielding desirable amorphous films over a range of firing temperatures (up to 600 °C in the current study). Additionally, the simple PIC solution preparation allows for facile manipulation of the P:Al ratio (x) and of the resulting thin film properties.

In this contribution, we examine the impact of the precursor solution concentration, P:Al ratio, and spin-speed on the thickness and electrical properties of resultant amorphous AlPO thin films. We show that film thickness is approximately linearly dependent on solution concentration. This relationship, while not unexpected, has not been explicitly shown previously for PIC-produced films. In addition, the stoichiometry of P:Al in the films is shown to closely match that of the precursor solutions, enabling precise control of film composition. The studies reported here allow the production of AlPO films with specified thicknesses and electrical characteristics based on simple manipulation of concentration, P:Al ratio, and spin processing parameters.

2. Experimental section

2.1. Materials

$Al(OH)_3 \cdot xH_2O$ (Alfa Aesar, 76.5%) was standardized through thermal conversion to the oxide (Al_2O_3) in a tube furnace in air and gravimetric analysis to determine the degree of hydration for accurate mass calculations. Trace metal grade HNO_3 (Fisher, 70% w/w) and H_3PO_4 (EMD Chemicals, 85% w/w) were used as received.

2.2. Solution synthesis

1.00 M Al^{3+} precursor solutions of various P:Al ratio were made by adding two equivalents of nitric acid drop-wise to a suspension of $Al(OH)_3$ in 18 MΩ water and heated to 95 °C. The solution was stirred overnight to achieve complete dissolution. The appropriate amount of phosphoric acid was added drop-wise, followed by dilution to the final volume. The stock solution was then diluted to achieve the desired precursor solution concentrations reported below.

2.3. Film preparation and characterization

Polished, conductive n-type silicon substrates (100) supplied by SumCo-Oregon were exposed to an oxygen plasma in a March CS-1701 generated by a 150 W RF field for 120 s at 300 mTorr and 74.6 sccm of pure O_2. The oxygen plasma treatment generates a hydrophilic SiO_2 layer which promotes solution adhesion and uniform wetting.

AlPO films were produced by coating a freshly plasma-treated silicon substrate with precursor solution deposited using a syringe fitted with a 0.45 μm PTFE filter. The coated substrate was spun at the desired rate (2000–5000 RPM) for 30 s, immediately transferred to a pre-heated hotplate at 300 °C for 60 s, and subsequently annealed in a box furnace at 600 °C for 10 min.

Film thicknesses were determined by X-ray reflectivity (XRR) measurements on a Bruker D8 Discover diffractometer with a Cu-Kα radiation source ($\lambda_{avg} = 1.5418$ Å). Reflectivity data were analyzed using the EVA software package to locate Kiessig fringe positions and a modified form of Bragg's Law (corrected for refraction). Because AlPO and SiO_2 have similar electron densities, thicknesses determined by XRR include contributions from both the AlPO film and the underlying SiO_2 layer. Ellipsometry measurements to determine native SiO_2 thicknesses were conducted using a J. A. Woollam Co., Inc. EC-270 Spectroscopic Ellipsometer equipped with a LPS-400 75W Xenon Light Source. The AlPO film thicknesses reported in the Results section have been corrected for the SiO_2 thickness and reflect the thickness of only the AlPO layer. X-ray diffraction experiments were also performed on the Bruker D8 Discover diffractometer to qualitatively evaluate the crystalline or amorphous nature of the films.

FT-IR experiments were performed on a Nicolet Magna 560 spectrometer using a spectrum collected from a bare, plasma treated silicon substrate as the background. Electron probe microanalysis (EPMA) was performed on films deposited from 1.00 M Al^{3+} solutions with a Cameca SX-50, referencing alumina and apatite as elemental standards. The resultant raw X-ray intensities were corrected as outlined by Donovan and Tingle [34]. Electron micrographs were obtained using a Zeiss Ultra-55 FESEM with a 20 μm aperture and 5 kV accelerating voltage.

2.4. Electrical characterization

Metal-insulator-semiconductor (MIS) devices were prepared by depositing AlPO films onto degenerately-doped silicon substrates and thermally depositing aluminum top contacts (~100 nm thick, 1.10 mm^2 dots) using an Edwards E306A Coating System. Contact to the underlying degenerately doped silicon was achieved by scratching through the insulating layers and applying indium-gallium eutectic. All MIS devices used films which had been annealed at 600 °C for 30 min, and resulting thicknesses ranged from 78 to 100 nm.

Capacitance and loss tangent measurements on films deposited from 1.00 M Al^{3+} solutions were made using an HP Agilent 4284A LCR connected to a two-point probe station. All capacitance measurements were performed at 50 mV AC oscillating at 10 kHz with 0 V DC bias. Breakdown measurements were made using a Hewlett-Packard 4140B picoammeter with a 1 V s^{-1} ramp. Breakdown is herein defined as the applied field strength at which the leakage current density meets or exceeds 10 μA cm^{-2}.

For comparison, a standard device was fabricated using a 100 nm thermally grown silicon oxide on degenerately-doped p^+ silicon (resistivity <1 Ω cm^{-1}) with a chromium gold back (supplied by Hewlett Packard, Corvallis). Aluminum top contacts were thermally deposited on the silicon oxide sample by the procedure outlined above.