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Aqueous process to limit hydration of thin-film inorganic oxides

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ABSTRACT

Aqueous-processed aluminum oxide phosphate (AlPO) dielectric films were studied to determine how water desorbs and absorbs on heating and cooling, respectively. *In-situ* Fourier transform infrared spectroscopy showed a distinct, reversible mono- to bidentate phosphate structural change associated with water loss and uptake. Temperature programmed desorption measurements on a 1-μm thick AlPO film revealed water sorption was inhibited by an aqueous-processed HfO_2 capping film only 11-nm thick. The HfO_2 capping film prevents water resorption, thereby preserving the exceptional performance of AlPO as a thin-film dielectric.

1. Introduction

Solvent and solute transport through porous and gel media and interfaces fundamentally affects many materials functions and processes, ranging from the mechanics of biological soft tissues [1] to semiconductor lithography [2,3] and printed electronics [4]. Processing electronic materials with water, either in aqueous solutions or humid environments, presents challenges for residual water removal and passivation, as associated mobile water and hydroxyl protons commonly degrade electronic and device performance [5–12]. Consequently, understanding how to systematically affect and control both liquid and vapor water transport and its antecedent dehydration reactions in gels and solids is essential to produce many functional materials—especially at low temperatures.

Recently, Anderson and co-workers showed the properties of aluminum oxide phosphate (AlPO) dielectric thin films, deposited from water, could be enhanced by capping them with an ultrathin HfO_2 layer, also deposited from water [13]. The HfO_2 cap reduced the relative transient capacitance of a comparable uncapped AlPO film by a factor of 70 in sweeps covering ±1.5 MV/cm. Simultaneously, zero-bias hysteresis decreased from 7000 to <100 ppm. The bilayer dielectric also suppressed V_{on} drift in thin-film transistors. These electrical results suggested the existence of mobile protons in the uncapped films and their diminution in the capped analogs. The presence of these protons was confirmed by chemical analysis via forward hydrogen scattering. To improve understanding of this unique process, we examine here film dehydration, hydration, and H_2O transport dynamically via *in-situ* Fourier transform infrared (FTIR) spectroscopy, temperature-programmed desorption (TPD), and transmission electron microscopy (TEM). We find water sorption after film annealing critically affects water and mobile charge concentrations in single layer AlPO films. On heating, AlPO films coated with a thin Hf-based gel cap readily desorb H_2O. By 350 °C, the Hf layer converts to a dense, continuous HfO_2 film, which then limits water resorption. Hence, solution deposition produces an effective ultra-thin HfO_2 moisture barrier at modest process temperatures that simultaneously renders performance stability to the AlPO dielectric. The approach yields novel features for creating highly effective barrier and encapsulation coatings via aqueous processing.

2. Experimental

Solution precursor synthesis has been described previously [14,15]. The AlPO solution was prepared with a 0.85-M Al concentration and an aluminum:phosphorus ratio of 1:0.6. The water-based peroxide HfO_2 precursor was prepared in two different concentrations—0.250 and 0.124 M for the thick and thinner films, respectively.

Prior to thin-film deposition, all substrates were cleaned by sonication in a deionized water bath. Following this cleaning, they

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were treated in a low-energy O_2 plasma to create a clean, hydrophilic surface. The films were deposited onto either *p*-type Si (for the TEM experiment) or 100-nm thermally grown SiO_2/Si (for TPD-MS). Films were deposited by spin coating the aqueous precursors at 3000 rpm for 30 s. Each coat was soft baked at 230 °C for 1 min prior to deposition of additional layers. In each case, two coats of 0.85-M AlPO were deposited to produce film thicknesses of 140–150 nm. For the thicker HfO_2 films, three coats of the 0.250-M HfO_2 precursor were deposited to produce a film thickness near 45 nm. One coat of the 0.124-M solution produced the 11-nm HfO_2-capping layer.

Spectroscopic ellipsometry data were collected with a J. A. Woollam M-2000 spectroscopic ellipsometer to determine film thickness. Film thicknesses of the HfO_2 and AlPO layers were determined with a Cauchy model via the CompleteEASE software package [16].

In-situ FTIR spectroscopy studies were carried out using a nitrogen-purged home-built ALD reactor with a Thermo Nicolet 6700 infrared spectrometer equipped with a liquid nitrogen-cooled broadband mercury cadmium telluride (MCT-B) detector [17]. A single-pass transmission at Brewster incidence (~74°) was used to minimize the substrate phonon absorption in the low frequency region (<1000 cm^{-1}) and to increase detection sensitivity of all film chemical components. After heating in flowing N_2(g), the films were cooled to 80 °C for data collection. A K-type thermocouple spot-welded onto a tantalum clip was attached at the center of the long edge of the substrate to monitor the sample temperature during analysis. Two gate valves were used to isolate the KBr windows used in the analysis chamber for IR transmission during annealing.

FTIR data analysis involved two parts. To measure water (hydroxide) content in the films, the relative absorbance was integrated from the spectra; all films were referenced to a spectrum of a clean SiO_2/Si (100) wafer. The amount of water desorbed after annealing was calculated by measuring the integrated area in the range of 3740–3000 cm^{-1} of the absorbance spectra. The baselines of the spectra before and after annealing were not consistent; therefore, absorbance values at 3740 and 3000 cm^{-1} were assumed as the baseline. Similar to the water content, the initial and final amounts of phosphate binding after the 350 °C anneal were quantified by integrating the area between 1300 and 1250 cm^{-1}. To quantify the phosphate content of the 20-nm HfO_2-capped AlPO film, changes from the HfO_2-cap were subtracted from the spectrum using the band at 1576 cm^{-1} as the reference.

The TPD study was performed on a Hiden Analytical TPD Workstation with a quadrupole mass analyzer (3F PIC) to monitor gas-phase products released from the thin films upon heating. The measurement was performed with a base pressure $<5 \times 10^{-9}$ Torr. Mass spectra were obtained using electron impact ionization with 70 eV ionization potential and 20-μA emission current. The *m*/*z* of 18 was selected to monitor water desorption. Thin films on 2.54×2.54 cm^2 substrates were cleaved into 1×1 cm^2 for the TPD analysis. To test the amount of water in each of the samples, the films were heated from room temperature to 550 °C with a ramp rate of 30 °C/min and a dwell time of 5 min at 550 °C. The samples were then allowed to sit open in air in preparations for tests of water resorption and then ran TPD again heating to 900 °C. Relative peak areas were integrated to specific temperatures to establish % water loss.

In-situ TEM experiments were performed with an FEI Titan 80–200 TEM/STEM transmission electron microscope operated at 200 kV. Carbon and chromium coatings were deposited on HfO_2/AlPO bilayers for protection and to enhance sample contrast. After adding a final protective layer of platinum *in-situ*, a thin cross section of the HfO_2-capped AlPO film was selectively machined with a focused gallium ion beam on an FEI Quanta 3D SEM. The lamella was welded to a copper TEM grid and thinned to approximately 100 nm with the ion beam. The films were heated *in-situ* with a ramp rate of 20 °C/min. Micrographs were collected at 50 °C increments to study effects of heat.

3. Results and discussion

Fig. 1 shows a TEM micrograph of a typical HfO_2-AlPO bilayer structure examined in this study. The AlPO film is homogeneous, the AlPO/HfO_2 interface is sharp, and the HfO_2 surface is atomically smooth. The films are deposited from aqueous solutions comprising oxo-hydroxo metal clusters accompanied by nitrate counter ions [14,15,18]. On spin coating, partial condensation occurs to produce continuous films. The AlPO film must be heated to 230 °C prior to deposition of the Hf precursor to prevent its dissolution. At this temperature, the films are heavily hydroxylated, and they retain nitrate. We focus here on dehydroxylation and hydroxylation and associated desorption and sorption of water, respectively, for both uncapped and capped AlPO to understand the effects of the HfO_2 top layer.

3.1. AlPO dehydration

We performed *in-situ* heated FTIR and TPD measurements to examine thermal dehydration of AlPO and HfO_2-capped AlPO films. Three different films—single layer AlPO and HfO_2 and bilayer AlPO/HfO_2—were investigated. For the FTIR studies, films were heated from 80 to 350 °C in 50 °C increments and held at each temperature for 5 min. In each case, samples were cooled to 80 °C prior to data collection. Fig. 2 shows IR absorption between 3740 and 3000 cm^{-1}, which corresponds to −OH and H_2O vibrations. The dashed lines represent absorption, and the solid lines represent difference between spectra for samples heated at 80 and 350 °C. The dips represent dehydration. Percent signal loss is determined from the difference in integrated areas of the dashed-line and solid-line spectra; results are summarized in Table 1. The single-layer AlPO film loses 84% of its −OH signal after annealing to 350 °C. A similar reduction, 90%, occurs for the HfO_2 and HfO_2-capped AlPO films.

Fig. 3 shows H_2O TPD spectra for AlPO and HfO_2-capped AlPO films heated to 550 °C. Substantial water evolves below 350 °C; AlPO loses 80% of its initial H_2O content, while HfO_2-capped AlPO loses 87%. These results match the FTIR measurements. Fig. 3(a) shows data for a thick, 46-nm HfO_2 capping layer, while Fig. 3(b)

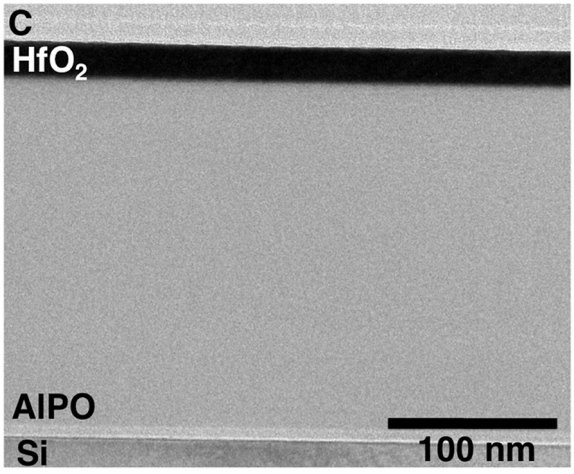

Fig. 1. TEM micrograph of AlPO-HfO_2 bilayer heated to 550 °C.