Thermal Atomic Layer Etching of Amorphous and Crystalline Hafnium Oxide, Zirconium Oxide, and Hafnium Zirconium Oxide

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ABSTRACT

Thermal atomic layer etching (ALE) using the fluorination and ligand-exchange mechanism was employed to etch amorphous and crystalline films of hafnium oxide, zirconium oxide, and hafnium zirconium oxide. HF was the fluorination reactant and dimethylaluminum chloride (DMAC) or titanium tetrachloride was the metal precursor for ligand-exchange. The amorphous films etched faster than the crystalline films. The differences were most pronounced for hafnium oxide. At 250 °C, the etch rate was 0.03-0.08 Å/cycle for crystalline HfO_2 and 0.68 Å/cycle for amorphous HfO_2.

INTRODUCTION

ALE is a method to remove thin films with Ångstrom level precision using sequential, self-limiting surface reactions [1]. ALE can be accomplished with either plasma [1] or thermal [2] ALE methods. Plasma ALE is anisotropic and involves energetic ions or neutrals to remove material. Thermal ALE is isotropic and is viewed as the reverse of atomic layer deposition (ALD).

Thermal ALE can be performed using the fluorination and ligand-exchange mechanism [2]. For metal oxides, the fluorination reaction converts the surface of the metal oxide to a surface fluoride layer. The ligand-exchange reaction can then volatilize the metal fluoride layer. Many metal oxides have been etched including Al_2O_3, ZrO_2, and HfO_2 [3]. Metal nitrides such as AlN can also be etched using a similar approach [4]. Other mechanisms for thermal ALE also are possible including oxidation and fluorination to a volatile fluoride. This mechanism has been demonstrated for TiN ALE [5].

The thermal ALE of amorphous ZrO_2 and HfO_2 has been demonstrated using HF for fluorination and dimethyl aluminum chloride (DMAC) or $SiCl_4$ as metal precursors for ligand-exchange [3]. In contrast, there have been no reports for the thermal ALE of crystalline ZrO_2 and HfO_2. The thermal ALE of crystalline AlN has been demonstrated using HF for fluorination and $Sn(acac)_2$ as the metal precursor for ligand-exchange [4]. There have been no reports for the thermal ALE of amorphous AlN.

This study focuses on the thermal ALE of amorphous and crystalline phases of ZrO_2 and HfO_2. The amorphous films were deposited using ALD. The crystalline films were obtained by annealing. The temperature of crystallization for thin films of ZrO_2 is between 200-550 °C and for thin films of HfO_2 is between 300-800 °C. The etching of crystalline materials is important because etching is required to obtain ultrathin crystalline films. Films may not crystallize easily when they are too thin. Consequently, films may have to be grown thicker, crystallized, and then etched back to obtain the desired ultrathin thickness [6]. A schematic illustrating this processing sequence is shown in Figure 1.

Differences between the thermal ALE of amorphous and crystalline films may also be important for selective ALE. Selectivity is obtained when two different materials have different etch rates under the same conditions or when one material etches while the other does not etch [3]. Selective thermal ALE has been observed for a variety of metal precursors and materials [3]. Selectivity could also be observed between amorphous and crystalline phases of the same material.

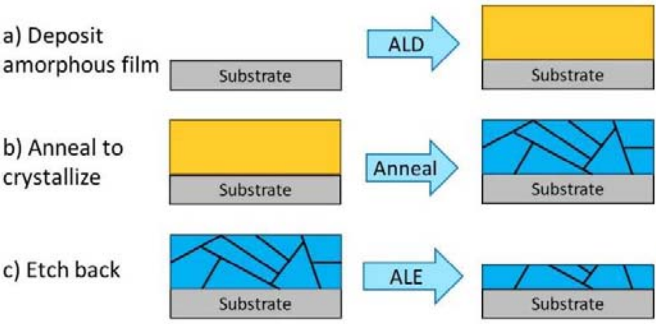

FIGURE 1. Schematic detailing processing sequence to obtain an ultrathin crystalline film.

This work used ZrO_2, HfO_2, and $HfZrO_4$ thin films on silicon coupons provided by the Tokyo Electron Limited (TEL) Technology Center, America, LLC in Albany, NY. The as deposited films were deposited using ALD methods at 250 °C. These as deposited, amorphous films were used without further modification. These films had a thickness of approximately 100 Å. The anneal 1 and anneal 2 films were both annealed at 800 °C in an N_2 environment. The anneal 1 films had a polycrystalline morphology. The anneal 2 films were fiber textured. The annealed ZrO_2 materials were tetragonal. The annealed HfO_2 materials were monoclinic. The annealed $HfZrO_4$ materials were a mixture of monoclinic and tetragonal. The crystal structures were verified using grazing incidence x-ray diffraction (GIXRD).

Thermal ALE experiments were performed in a viscous flow reactor. Each thermal ALE cycle included one exposure for 1 second of HF and one exposure for 2 seconds of DMAC or $TiCl_4$. There was a 30 second purge between each reactant exposure. N_2 was employed as the viscous flow carrier gas. The reactor pressure with flowing N_2 carrier gas was 1 Torr. The reported film thicknesses were measured using ex situ spectroscopic ellipsometry (SE) measurements.

RESULTS

Hafnium Oxide: Figure 2 shows the results for the hafnium oxide films. SE measurements were used to measure HfO_2 film thicknesses over 400 thermal ALE cycles using HF and DMAC at 250 °C. The amorphous HfO_2 film was etched completely after 150 cycles. The amorphous HfO_2 film had an etch rate of 0.68 Å/cycle. In contrast, the anneal 1 and anneal 2 HfO_2 films had much lower etch rates of 0.03 and 0.08 Å/cycle, respectively.

Results with HF and $TiCl_4$ as the reactants at 250 °C showed similar differences between amorphous and crystalline HfO_2. The etch rate for the amorphous HfO_2 film was 0.36 Å/cycle with HF and $TiCl_4$.

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The etch rate of the amorphous HfO_2 film was 14-24 times higher than the etch rate for crystalline HfO_2 films.

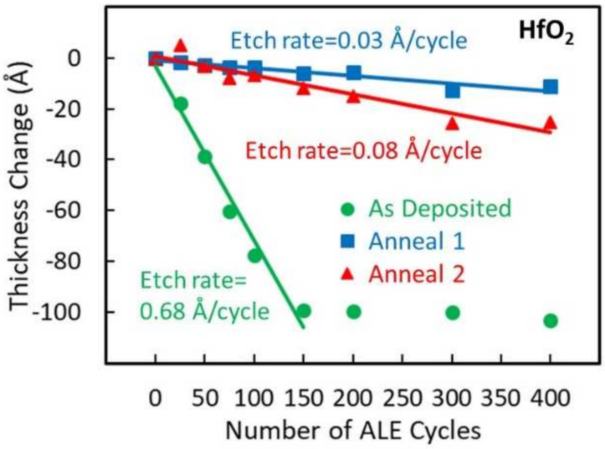

FIGURE 2. ALE for three different hafnium oxide films using HF and DMAC at 250 °C.

Zirconium Oxide: Figure 3 displays the results for the zirconium oxide films. The amorphous ZrO_2 films and the crystalline ZrO_2 films were etched with HF and DMAC at 250 °C. Under the same reaction conditions, all three ZrO_2 films etched faster than any of the HfO_2 films. The etch rates were 1.11, 0.74, and 0.82 Å/cycle for the amorphous, anneal 1, and anneal 2 ZrO_2 films, respectively. In contrast to the results for the HfO_2 films, the etch rates for the amorphous and crystalline ZrO_2 films were similar. The ZrO_2 films were completely etched away after 75 cycles for the amorphous ZrO_2 films and after 100 cycles for the anneal 1 and anneal 2 ZrO_2 films.

The ZrO_2 films were also etched with HF and $TiCl_4$ as the reactants at 250 °C. The etch rates using HF and $TiCl_4$ were lower than the etch rates using HF and DMAC. The amorphous ZrO_2 film had an etch rate of 0.68 Å/cycle. The crystalline anneal 1 and anneal 2 ZrO_2 films had etch rates around 0.2 Å/cycle.

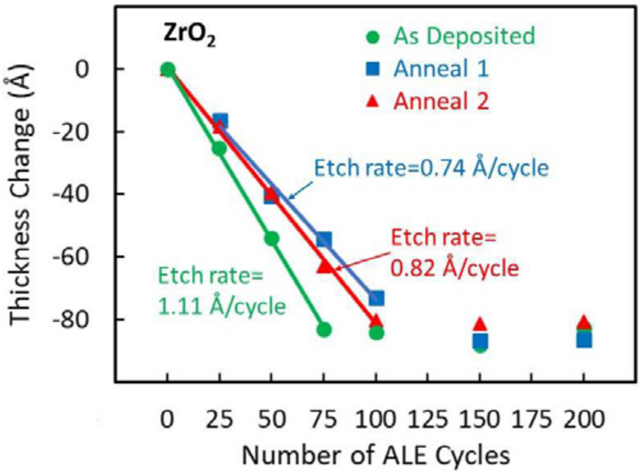

FIGURE 3. ALE for three different zirconium oxide films using HF and DMAC at 250 °C.

Hafnium Zirconium Oxide: Figure 4 shows the results for the composite $HfZrO_4$ films. The amorphous $HfZrO_4$ films and the crystalline $HfZrO_4$ films were etched with HF and DMAC at 250 °C. These measured etch rates were between the HfO_2 and ZrO_2 etch rates. The amorphous $HfZrO_4$ film was etched completely in 150 ALE cycles. The amorphous $HfZrO_4$ film had an etch rate of 0.69 Å/cycle. The etch rates for anneal 1 and anneal 2 $HfZrO_4$ films were 0.13 and 0.16 Å/cycle, respectively.

Etch results for the $HfZrO_4$ films using HF and $TiCl_4$ as the reactants at 250 °C displayed similar results. The amorphous $HfZrO_4$ film had an etch rate that was faster than the two annealed $HfZrO_4$ films. The etch rate for the amorphous $HfZrO_4$ film was 0.35 Å/cycle. The etch rates for the two annealed $HfZrO_4$ films were 0.03-0.04 Å/cycle.

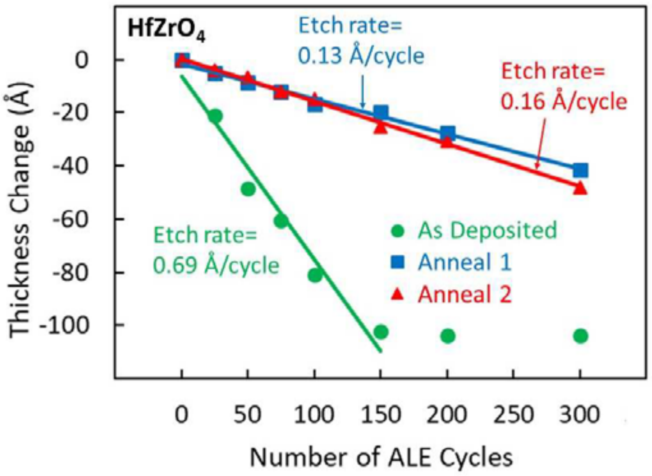

FIGURE 4. ALE for three different $HfZrO_4$ films using HF and DMAC at 250 °C

CONCLUSIONS

The etching of amorphous and crystalline HfO_2, ZrO_2, and $HfZrO_4$ films by thermal ALE was studied at 250 °C. All amorphous films etched faster than the crystalline films for each material. The difference was the most dramatic for the HfO_2 films where the amorphous HfO_2 films etched 8-22 times faster than the crystalline HfO_2 films. The thermal ALE of crystalline films should be useful to produce ultrathin crystalline films by depositing thicker films that can crystallize via annealing and then etching back to obtain ultrathin crystalline films.

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