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Vapor−Liquid Hybrid Deposition Process for Device-Quality Metal Oxide Film Growth

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Metal oxides with a high dielectric constant are attracting serious consideration as an alternative gate insulator to SiO_2 in future generation metal-oxide-semiconductor (MOS) transistors. Extensive studies are ongoing to explore vapor-deposition chemistry that is suited for formation of ultrathin (typically less than 5 nm) metal oxide layers.[1] Among the potential vapor-deposition processes is atomic layer deposition (ALD), which enables atomic-scale control of film thickness over a large substrate area.[2,3] When used to form metal oxides, ALD generally consists of two half reactions: (i) adsorption of metal-organic or metal-halide precursor molecules and (ii) reaction of the adsorbed species with oxygen-containing species such as water vapor, O_2, O_3, or metal alkoxide.[4] Self-limiting adsorption of the half reaction (i) is essential for the above-mentioned thickness controllability. It is achieved, however, at relatively low temperatures (ca. 600 K) because thermal decomposition of precursors dominates at higher temperatures. This limitation on the process temperature tends to result in incomplete conversion of the half reaction (ii) above, preventing fabrication of films free of residual impurities.[5]

To overcome this shortcoming, we propose a new growth concept in which the half reaction (ii) above is carried out by exposing the substrate surface to liquid water rather than water vapor or a gaseous oxidant as used in conventional ALD. Adsorption of the metal precursor is carried out by exposing the surface to precursor vapor. We thus refer to this process as *vapor−liquid hybrid deposition* or *VALID*. Because of the large availability of H_2O molecules in the liquid phase, conversion of the adsorbed metal precursor layer to oxide or hydroxide should readily proceed even at low temperatures. Solvation effects and ionized species such as H_3O^+ and OH^- may also facilitate the hydrolysis reaction. Since half-reactions are self-terminating as in conventional ALD, VALID preserves the thickness controllability of ALD.

p-type Si(001) wafers with resistivity of 1−10 Ω·cm were cleaned by the RCA method followed by etching in 1% HF solution. The wafer was loaded into a high-vacuum chamber where the hydrogen-terminated Si surface was oxidized to 0.3-nm thickness by UV−O_3

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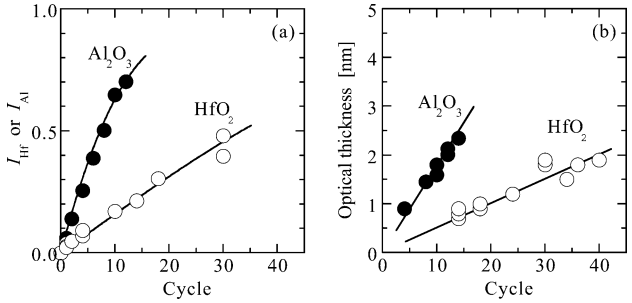

Figure 1. Changes of normalized Al 2p and Hf 4f photoelectron intensities (a) and optical thickness (b) of the Al_2O_3 and HfO_2 films with the number of growth cycles. See text for definition of I_{Al} and I_{Hf}. Optical thickness was estimated for PDA-treated samples by spectroscopic ellipsometry taking into account the thickness of the SiO_2 interface layer.

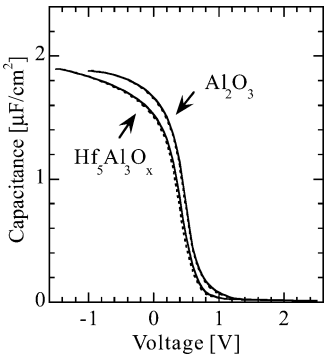

Figure 2. $C-V$ curves for MOS capacitors incorporating Al_2O_3 (1.5-nm thickness) and $Hf_5Al_3O_x$ (2.0 nm). These curves were obtained using the two-frequency correction method with $C-V$ data measured at 1 MHz and 200 kHz. Solid and dotted curves are for accumulation-to-inversion and inversion-to-accumulation sweeps, respectively. Flat-band voltage shifts were +0.75 and +0.63 V for Al_2O_3 and $Hf_5Al_3O_x$, respectively, indicating the presence of negative fixed charges in the oxide layers.

oxidation[6] to facilitate metal precursor adsorption. Thickness of this SiO_2 interface layer was unchanged by the VALID processing described in the following. Immediately after forming the interface layer, a metal precursor was introduced into the same vacuum chamber to initiate the VALID process. In this study, we investigated Al_2O_3 and HfO_2 deposition, as these oxides remain to be candidate gate dielectrics after the materials selection investigation in past years.[7] Metal precursors used in this study were $Al(CH_3)_3$ and $Hf(OC_4H_9)_4$. Exposures to precursor vapor were performed at room temperature and were continued until adsorption reached saturation (typically 10^4-10^6 L), as judged by chemical analyses using X-ray photoelectron spectroscopy (XPS). Samples were then removed from the chamber through a loadlock. Hydrolysis was carried out at room temperature by either immersing the sample in ultrapure water or by placing the sample on a spin processor and supplying ultrapure water on the sample. The sample surface was in contact with liquid water for approximately 2 s. The liquid-phase hydrolysis ensures complete decomposition of the adsorbed precursors, while exposure to the ambient moisture by itself leads to partial decomposition of the adsorbates.

Figure 1a shows changes of Al 2p and Hf 4f photoelectron intensities measured by XPS, I_{Al}, and I_{Hf}, respectively, with increasing number of growth cycles. I_{Al} is defined as $I_{Al} = S_{Al}/(S_{Al} + S_{Si})$, where S_{Al} and S_{Si} are, respectively, integrated area of Al 2p and Si 2p peaks divided by the photoelectron emission cross-section for each element. I_{Hf} is defined similarly for the Hf 4f peak. Both I_{Al} and I_{Hf} increase with increasing number of cycles, indicating that film growth indeed takes place.

An unavoidable consequence of room-temperature aqueous processing is that deposited films contain hydrated H_2O molecules and/or OH groups. Thermal desorption spectra for the as-deposited samples showed a large desorption peak of H_2O at ~500 K. To convert the as-deposited films into metal oxides with useful insulation properties, dehydration and densification by postdeposition annealing (PDA) was carried out in a vacuum using a rapid thermal annealing furnace. Sample temperature was first kept at 473 or 573 K for 2 min for dehydration and then increased to 1023 K and held for 30 s. This PDA treatment decreases film thickness by approximately 30% while increasing the refractive index to 1.7 and 2.0 for Al_2O_3 and HfO_2, respectively, as measured by spectroscopic ellipsometry. PDA also induces growth of the SiO_2 interface layer to approximately 0.7- and 1.0-nm thickness for Al_2O_3 and HfO_2 samples, respectively, as estimated from the Si 2p photoelectron peak.

In Figure 1b, optical thickness of the Al_2O_3 and HfO_2 films after PDA is plotted as a function of the number of growth cycles. The slope of the regression lines gives growth rates of 0.18 and 0.05 nm/cycle for Al_2O_3 and HfO_2, respectively.

Carbon concentrations in as-grown Al_2O_3 and HfO_2 samples were lower than the detection limit of XPS (~1 at. %). Analyses for the PDA-treated samples by secondary ion mass spectroscopy indicated that the films grown by VALID contain less carbon impurities than those grown by typical ALD processing; however, quantitative evaluation was confounded by the carbon-containing surface contaminants. Ichinose et al. reported that various metal oxides can be formed by the surface sol−gel technique in which adsorption of metal precursors was carried out in organic solvents.[8] They reported that the obtained films contain a relatively large amount of carbons species (more than 10 at. %). Vapor-phase adsorption as used in VALID is therefore advantageous to form metal oxide films with less carbon impurities.

Electrical properties of VALID-grown Al_2O_3 and $HfO_2-Al_2O_3$ alloy were evaluated in metal-oxide-semiconductor (MOS) capacitor structures. The $HfO_2-Al_2O_3$ alloy samples were grown by depositing six cycles of HfO_2 followed by one cycle of Al_2O_3. This seven-cycle sequence was repeated until films of desired thickness were obtained. The Hf:Al atomic ratio was tentatively estimated from the growth rates for HfO_2 and Al_2O_3 (see Figure 1b) to be 5:3; consequently, we denote this alloy as $Hf_5Al_3O_x$ in this article. MOS capacitors were fabricated by performing PDA as described above and then evaporating Au electrodes. For the $Hf_5Al_3O_x$ samples,

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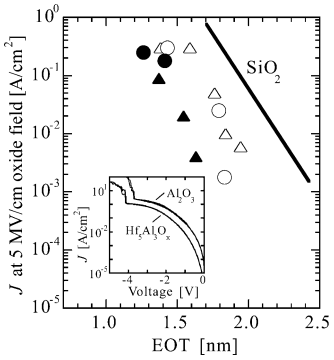

Figure 3. *J* at an oxide field of 5 MV/cm. Triangle and circle symbols are for Al_2O_3 and $Hf_5Al_3O_x$ MOS capacitors, respectively. Open and filled symbols are for capacitors with SiO_2 and SiO_xN_y interface layers, respectively. Literature data for thermally grown SiO_2 with n^+ poly-Si gate is also shown for reference. Inset shows typical $J-V$ characteristics for Al_2O_3 and $Hf_5Al_3O_x$ capacitors of 1.8-nm EOT, which were prepared on the UV−O_3 interface layer. Both the Al_2O_3 and $Hf_5Al_3O_x$ capacitors show a dielectric breakdown near −4 V.

the PDA treatment was followed by a second anneal in 1% O_2 (Ar balance) for 30 s at 673 K.

The electrical responses for both Al_2O_3 and $Hf_5Al_3O_x$ MOS capacitors yield well-behaved capacitance−voltage ($C-V$) behavior as shown in Figure 2. Hysteresis between the trace and retrace curves was as small as 9 and 24 mV for Al_2O_3 and $Hf_5Al_3O_x$, respectively. Effective oxide thickness (EOT) estimated from the $C-V$ curves[9] was 1.4 nm for both the Al_2O_3 and the $Hf_5Al_3O_x$ capacitors in Figure 2. Dielectric constants estimated from the $C-V$ and growth-rate data were 9 and 17 for Al_2O_3 and $Hf_5Al_3O_x$, respectively.

Leak current density, *J*, is an important index in assessing the insulator quality. In Figure 3, *J* at oxide field of 5 MV/cm are shown for Al_2O_3 and $Hf_5Al_3O_x$ MOS capacitors of various EOTs. Examples of the current−voltage ($J-V$) traces are shown in the inset of the figure. Some of the capacitors were fabricated on a SiO_xN_y interface layer of 0.5-nm thickness, which was formed by exposure to remote plasma of N_2 gas at 523 K.[10] Figure 3 shows that *J* for the Al_2O_3 and $Hf_5Al_3O_x$ capacitors are smaller by 1−2 orders of magnitude than those for thermally grown SiO_2.[11,12] Capacitors with SiO_xN_y interface layers show lower *J* than those with the SiO_2 interface layer, which we ascribe to the larger physical thickness of the SiO_xN_y interface layer than that of the SiO_2 interface layer.

In summary, Al_2O_3 and HfO_2 films have been successfully formed by combining vapor-phase precursor adsorption with liquid-phase hydrolysis. Electrical characterization of the MOS capacitors has shown that this hybrid process is a viable approach for forming gate-quality dielectric films.

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