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Growth of Crystalline Gd_2O_3 Thin Films with a High-Quality Interface on Si(100) by Low-Temperature H_2O-Assisted Atomic Layer Deposition

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Downscaling of complementary metal oxide semiconductor (CMOS) devices requires the replacement of Si-based gate dielectrics with a material exhibiting a much higher dielectric constant ($\varepsilon_r > 10$). Many metal oxides have been investigated, but only a very few meet all the criteria that are indispensable for the CMOS process line.[1] Rare-earth oxides have shown great potential in this respect, exhibiting higher dielectric constants, higher thermal stabilities, large band gaps, and most importantly, large band offsets with respect to both the valence and conduction bands of Si.[2] Recently, Gd_2O_3 has been shown to be highly promising for application in next-generation CMOS transistors with superior electrical properties.[3] Nevertheless, all reports to date have been based on physical deposition techniques such as molecular beam epitaxy, which have not been welcomed by industry.

For applications in microelectronics, atomic layer deposition (ALD) is the method of choice, as it allows excellent layer thickness control and uniform step coverage on complex device geometries. The strict self-limiting nature of such a deposition process contributes to the superior crystalline quality of the layers obtained, even in the case of quite complex geometries.[4] Thus, ALD is highly dependent on the precursor surface chemistry. To date, only a very few examples of ALD-like growth of Gd_2O_3 have been reported, including that from $[Gd\{N(SiMe_3)_2\}_3]/H_2O$, but the growth was not truly self-limiting.[5] Other precursors were $[Gd(CpCH_3)_3]$ (Cp = cyclopentadiene) and the Gd alkoxide $[Gd(DMB)_3]$ (DMB = 2,3-dimethyl-2-butoxide), but the ALD characteristics with H_2O were poor.[6,7] $[\{Gd(thd)_3\}_2]$ (thd = 2,2,6,6-tetramethylheptane-3,5-dione) was found to be incompatible with H_2O, which necessitated the use of a strong oxidant like O_3, but the reported growth rates (Å/cycle) were low.[6] There is a clear need for alternative precursors with adequate thermal stability and optimal reactivity toward H_2O to facilitate higher growth rates.

Herein, we report the water-assisted ALD growth of Gd_2O_3 thin films using the homoleptic gadolinium guanidinate precursor $[Gd(DPDMG)_3]$ (DPDMG = $(^iPrN)_2CNMe_2$). The synthesis and characterization of this compound were recently reported.[8] $[Gd(DPDMG)_3]$ was found to possess all of the crucial requirements for an ALD precursor in terms of volatility and thermal stability as well as high and selective reactivity with water. When this precursor was employed, surface-controlled, self-limiting ALD-type growth with a nearly constant growth rate of ~1.1 Å/cycle was observed within a broad temperature window of 175−275 °C on Si(100) substrates (Figure 1a). The obtained growth rate is nearly 4 times higher than that reported for $[\{Gd(thd)_3\}_2]/O_3$ (~0.3 Å/cycle, ALD window 250−300 °C).[6] The superior performance of $[Gd(DPDMG)_3]$ is attributed to the increased basicity of the guanidinato ligand relative to thd, which facilitates a fast and selective reaction with the OH surface functionalities and the adsorbed water in the next pulse, respectively.

The ALD growth for $[Gd(DPDMG)_3]/H_2O$ was further verified by investigating the influence of the precursor pulse length on the growth rate of Gd_2O_3 at 225 °C (Figure 1b). Saturation of the growth rate was achieved with 2.5 s metal precursor pulse duration. An increase in pulse duration had no impact on the growth rate, confirming the self-limiting character of the film growth. The other characteristic feature of an ALD process, namely, the proportional relationship between film thickness and the number of deposition cycles, was also substantiated. The linear dependence of the film thickness on the number of deposition cycles at 225 °C (Figure 1b inset) suggests an ideal ALD process.

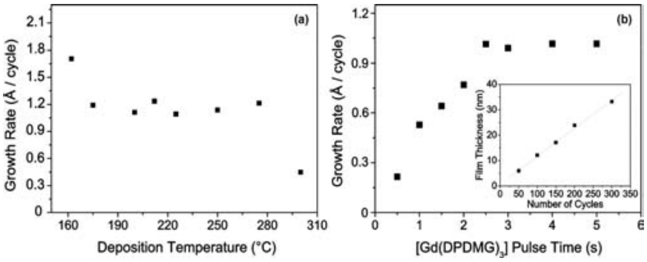

Figure 1. Gd_2O_3 growth rate as a function of (a) deposition temperature and (b) $[Gd(DPDMG)_3]$ pulse time. The dependence of the Gd_2O_3 film thickness on the number of deposition cycles at 225 °C for the $[Gd(DPDMG)_3]/H_2O$ process is shown in the inset.

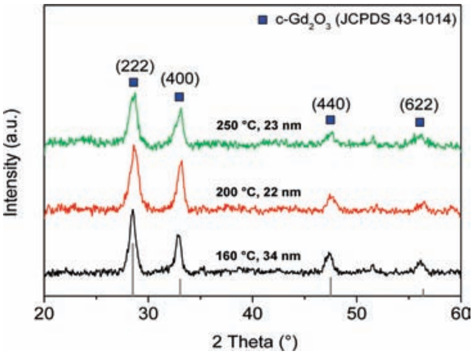

Figure 2. GIXRD patterns of Gd_2O_3 films deposited on Si(100) by ALD at 160−250 °C. substrates.

Grazing-incidence X-ray diffraction (GIXRD) measurements were performed on the Gd_2O_3 films deposited in the temperature range 160−300 °C to investigate their crystallinity (Figure 2). The GIXRD measurements show that at temperatures as low as 160 °C, polycrystalline films with 222, 400, 440, and 622 reflections

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characteristic of cubic Gd_2O_3 were obtained. The films were very uniform and smooth (rms roughness 0.3−0.7 nm, as estimated by atomic force microscopy; SI 2 in the Supporting Information) irrespective of the deposition temperature. The stoichiometry (O/Gd ratio) of the films grown in the temperature range 175−250 °C, as determined by Rutherford backscattering spectrometry (SI 3), was found to be 1.60 ± 0.1, which is close to that of bulk Gd_2O_3 (O/Gd = 1.5). The morphology of the layers was further investigated by high-resolution transmission electron microscopy (HRTEM) measurements (Figure 3).

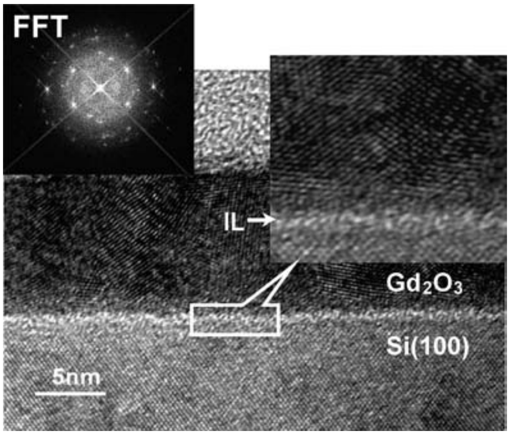

Figure 3. HRTEM cross-sectional images of Gd_2O_3 thin films deposited by the $[Gd(DPDMG)_3]/H_2O$ process at 225 °C.

The cross-sectional HRTEM image clearly reveals crystalline grains with different orientations; these were further analyzed by fast Fourier transform (FFT) analysis (Figure 3 inset), which showed the polycrystalline ring. The employed ALD process conditions resulted in a nearly sharp and abrupt interface between the Gd_2O_3 and the Si(100) substrate. This could be achieved even without any special surface treatment of the substrate. Furthermore, in contrast to all of the earlier work cited above, these films do not exhibit a pronounced interfacial SiO_x layer (Figure 3 inset), and this result is particularly encouraging. In order to achieve optimum electrical properties of any high-*k* oxide, the interface plays a significant role, and any secondary layer at the interface significantly degrades the overall electrical performance. Figure 4 depicts the hysteresis behavior in the capacitance−voltage (*C*−*V*) characteristics of a Pt/Gd_2O_3/Si(100) capacitor with a 10 nm thick Gd_2O_3 layer measured at a frequency of 200 kHz.

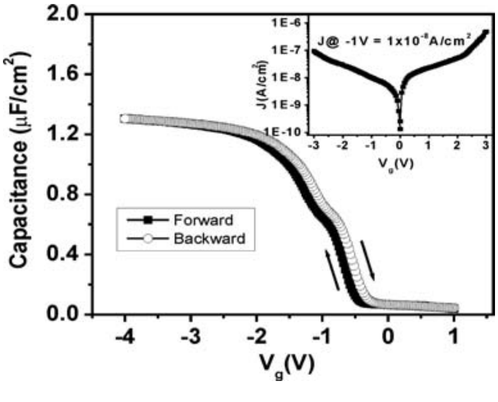

Figure 4. Capacitance−voltage (*C*−*V*) hysteresis characteristics measured at 200 kHz for Gd_2O_3 thin films deposited at 225 °C. The inset shows the leakage current (*J*−*V*) behavior from the same MOS structure.

The dielectric constant estimated from the accumulation capacitance was ∼15, which is in agreement with the previously reported values.[9] The as-deposited oxide layers showed reasonably small hysteresis (∼50 mV), but the same samples after forming gas annealing at 450 °C for 15 min showed almost no hysteresis in the *C*−*V* sweep (not shown). The inset in Figure 4 shows the leakage current behavior of the same MOS capacitor measured at room temperature. The leakage current density estimated at $V_g = -1$ V was found to be 1×10^{-8} A/cm^2. These data surpass the strongest requirements for low standby power applications predicted for 2015 in the latest edition of the ITRS roadmap.[10] The ultralow leakage current is attributed to the superior structural and morphological quality of high-*k* materials grown by a true ALD process, as outlined above. The electrical properties of the Gd_2O_3/Si(100) interface were evaluated by the conductance method.[11] The mid-gap interface trap charge density for Gd_2O_3 layers estimated from the conductance peak was found to be 3.2×10^{12} eV^{-1} cm^{-2}, which is comparable to that obtained for MBE-grown oxides.[9]

In summary, Gd_2O_3 thin films of superior structural quality with very low leakage current were deposited at growth rates of 1.1 Å/cycle in a surface-controlled, self-limiting ALD process. On the basis of the electrical characterization of the Pt/Gd_2O_3/Si(100) structures, it appears that the Gd_2O_3 films could be potential candidates for the replacement of SiO_2-based gate dielectrics in future CMOS devices. The key to this success was the use of a tailored all-nitrogen-coordinated tris(guanidinato)gadolinium precursor that combines several advantageous properties, including high and selective reactivity toward water at low temperatures. This precursor concept is extendable to other oxide and nitride binary materials as well as ternary materials containing f-block elements for ALD and metal−organic chemical vapor deposition applications.[8,12,13]

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Supporting Information Available: ALD process parameters, including reactor details, and Gd_2O_3 thin film characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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