

Composition Modulation in High-*k* Hafnium Silicate Films

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The search continues for high dielectric constant (high-*k*) gate materials to replace silicon dioxide in complementary metal-oxide-semiconductor (CMOS) technology. Among the possible candidates, pseudobinary systems such as $(\text{ZrO}_2)_x(\text{SiO}_2)_{1-x}$, $(\text{HfO}_2)_x(\text{SiO}_2)_{1-x}$, $(\text{Gd}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$, $(\text{La}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ and $(\text{Y}_2\text{O}_3)_x(\text{SiO}_2)_{1-x}$ have advantages over pure metal oxides since they have higher crystallization temperatures allowing them to remain amorphous during high-temperature processing. The silicates might provide a better interface with Si than the metal oxides, and they may also be less susceptible to B, Si or O diffusion. Moreover, the use of pseudobinary systems provides a large flexibility in selecting the film composition to tailor the electrical properties. However, a common problem encountered in the silicate films is the phase separation: pseudobinary systems tend to separate into two phases with each phase enriched in one of the two components [1].

In this work, phase separation in thin films with composition $(\text{HfO}_2)_{0.25}(\text{SiO}_2)_{0.75}$ and thickness from 4 nm to 20 nm grown on *p*-type Si (100) substrates by atomic layer deposition (ALD) using the precursors tetrakis(diethylamido) and tris(2-methyl-2-butoxy)silanol (details on growth methodology can be found in ref. 2) was studied by high resolution transmission electron microscopy (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive x-ray spectroscopy (EDX). For films with thickness less than 8 nm, the composition modulation with alternate SiO_2 -rich and HfO_2 -rich layers parallel to the substrate-film interface was observed. The typical film structures with the composition modulation are shown in Fig. 1 and 2. Two layers with a HfO_2 -rich layer near the surface and a SiO_2 -rich layer close to the Si substrate are shown in an HRTEM image of an as-grown 5 nm film [Fig. 1]. As shown in an HAADF-STEM image (Fig. 2a), a 6 nm film after rapid thermal anneal (RTA) in N_2 at 800 °C for 6 seconds consists of four layers, starting from the substrate: SiO_2 -rich, HfO_2 -rich, SiO_2 -rich and HfO_2 -rich. To verify the composition modulation in the films, the O, Si and Hf distributions of the film shown in Fig. 2a were determined by EDX. An EDX line scan was performed from the Si substrate to the surface to record the O-*K*, Si-*K* and Hf-*L* edges simultaneously. The scan path is perpendicular to the interface. Fig. 2b shows the O, Si and Hf profiles. The intensity of each element shown in Fig. 2b has not been corrected to reflect the relative concentration in the film. The profiles clearly show the composition modulation in the film. More interestingly, the HfO_2 -rich layer near the surface has a higher Hf concentration than the HfO_2 -rich layer close to the Si substrate. A closer look at the profiles reveals that there is a ~0.5 nm thick pure SiO_2 right above the Si substrate, which is the thermal oxide SiO_2 layer formed during the substrate oxidation process prior to the film deposition. For films with thickness greater than 8 nm, instead of continuous layered structure, the $(\text{HfO}_2)_{0.25}(\text{SiO}_2)_{0.75}$ separated into HfO_2 -rich and SiO_2 -rich nano-clusters in the center part of a 19 nm as-grown film (Fig. 3). The composition modulation in the $(\text{HfO}_2)_{0.25}(\text{SiO}_2)_{0.75}$ films has been discussed in relation to the surface-directed spinodal decomposition [3].

References

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 [2] J. Liu et al., *J. Electrochem. Soc.* 156 (2009) G89.
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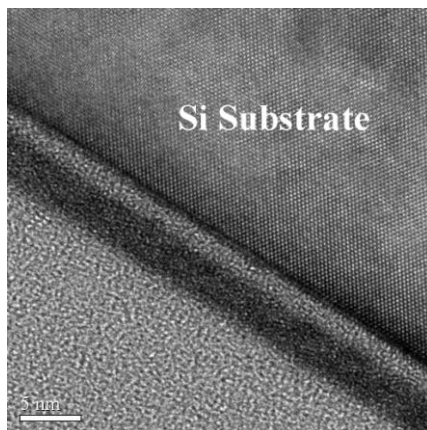


FIG. 1. HRTEM image of a 5 nm as-grown film.

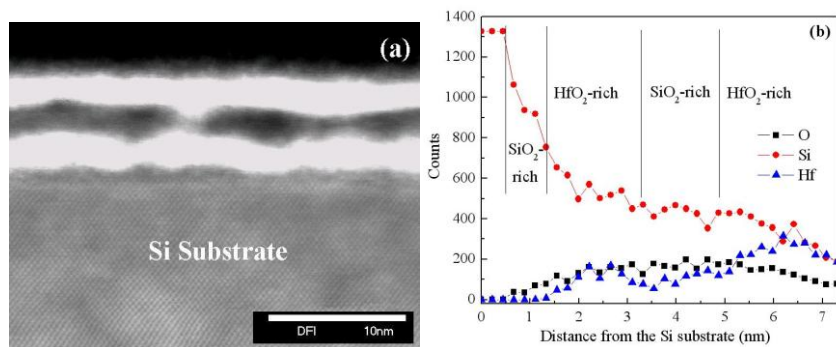


FIG. 2. (a) HAADF-STEM image of a 6 nm film after RTA in N₂ at 800 °C for 6 seconds. (b) EDX line profiles of O, Si and Hf of the film in (a).

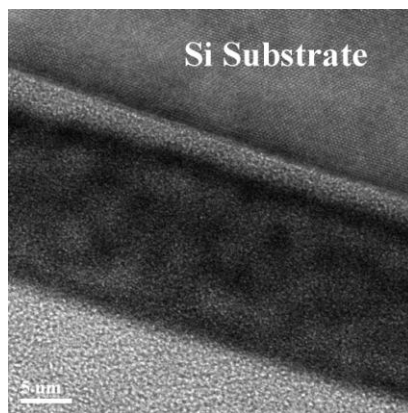


FIG. 3. HRTEM image of a 19 nm as-grown film.