DOI: 10.1017/S1431927603442530
Microsc Microanal 9(Suppl 2), 2003
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Thermal Stability of Hf-based High-κ Dielectric Films on Si(100)

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As the scaling of silicon integrated circuits continues, the problem of direct tunneling leakage current due to the reduced thickness of current gate dielectric films such as SiO_2 and SiO_xN_y should be resolved [1]. For this, high-κ gate dielectrics become one of the solutions in providing increased capacitance without remarkable increase in gate leakage current. This poses a very important technological problem whose solution depends on the structure, chemistry, and properties of new alternate gate dielectrics exhibiting higher κ. Some important requirements include thermal stability, smooth interfaces, dopant diffusion resistance, etc. For this study, we present results on the thermal stability of Hf-based films that have been proposed as suitable candidates for advanced gate dielectric applications [2].

Current gate dielectric SiO_2 thin films are thermally stable as shown in Figure 1. The as-deposited gate oxide is amorphous and is about 1.5 nm thick. Its structure is unchanged after rapid thermal annealing at 1050ºC for 60 sec, as expected. A thicker SiO_2 gate oxide is also thermally stable at this temperature. Hf-silicate ($HfSi_xO_y$) films deposited by chemical vapor deposition methods on Si(100) are shown in Figure 2. The as-deposited film is amorphous and contains a thin SiO_x interfacial layer. No crystallization was observed in Hf-silicate films after RTA annealing up to 60 sec below 950ºC. However, early stage of crystallization is observed after RTA anneal at 950ºC for 60 sec. Crystallization becomes more evident upon further annealing at 1050ºC, as shown in Figure 2b. The observed nano-crystals appear to be HfO_2, not Hf-silicate, which is consistent with the fact that the crystallization temperature of HfO_2 is lower than the one of $HfSi_xO_y$. Our earlier results showed an enhanced B diffusivity in these annealed films [3], suggesting enhanced diffusion along newly formed grain boundaries of HfO_2 nanocrystals.

The incorporation of N is known to be useful in improving thermal stability as well as minimizing dopant diffusion [4]. Figure 3 illustrates the effects of N incorporation into $HfSi_xO_y$ where no crystallization is observed after the annealing at 1050ºC for 60 sec. $HfSi_xO_yN_z$ films were deposited by reactive sputtering methods, with Hf content of ~5-6 at.% and ~18 at.% N. Suppression of crystallization observed in $HfSi_xO_yN_z$ films can be attributed to the incorporation of N and low Hf content in the films. $HfSi_xO_yN_z$ films with higher Hf content were also thermally stable after a "spike" anneal at 1050ºC for 1 sec, but crystallization was observed after 60 sec (see Figure 4) [5].

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[5] This research was supported by the SRC and the Texas Advanced Technology Program. The authors thank Drs. M. Visokay, L. Colombo and J.J. Chambers (TI) for the samples.

https://doi.org/10.1017/S1431927603442530 Published online by Cambridge University Press

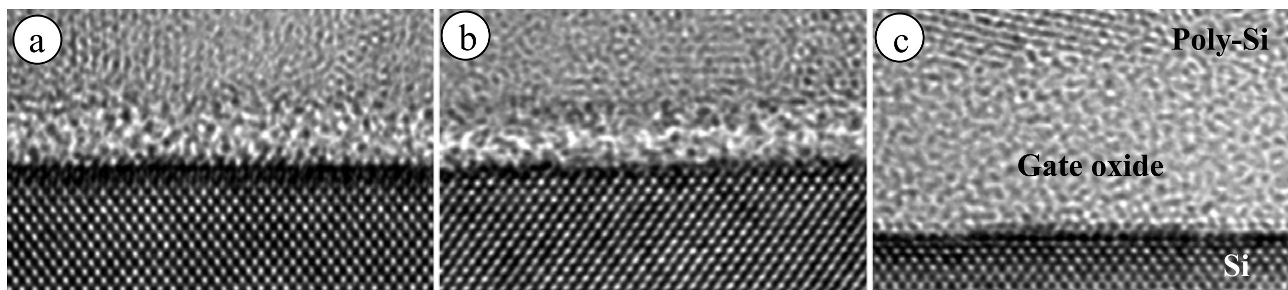

FIG. 1. Cross-sectional HREM images of poly-Si/SiO_2/Si interfaces: (a) as-deposited and (b) after rapid thermal annealing (RTA) at 1050ºC for 60 sec. (c) Thick gate oxide after RTA at 1050ºC for 60 sec. The observed amorphous SiO_2 gate oxides are thermally stable, as expected at this temperature (1050ºC). Z.A.=Si[110].

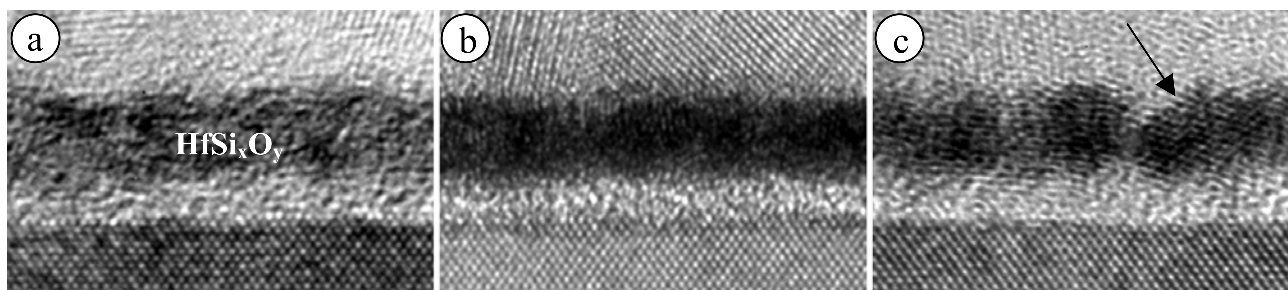

FIG. 2. HREM images of the poly-Si capped Hf-silicate thin films on Si(100): (a) as-deposited, and 60 sec RTA at (b) 950ºC and (c) 1050ºC. The as-deposited Hf-silicate film is amorphous. SiO_x interfacial layer is observed. Note nano-crystalline nature of the Hf-silicate film annealed at 1050ºC. The observed nano-crystals appear to be HfO_2, not Hf-silicate. Z.A.=Si[110].

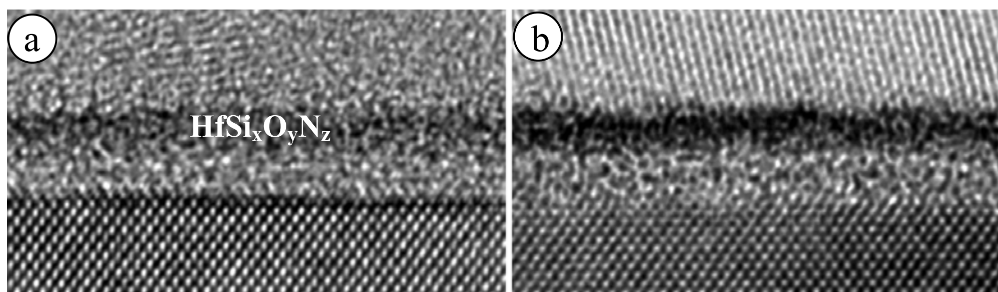

FIG. 3. Cross-sectional HREM images of the poly-Si capped $HfSi_xO_yN_z$ thin films on Si(100): (a) as-deposited and (b) 60 sec RTA at 1050ºC. No crystallization is observed in $HfSi_xO_yN_z$ films. Z.A.=Si[110].

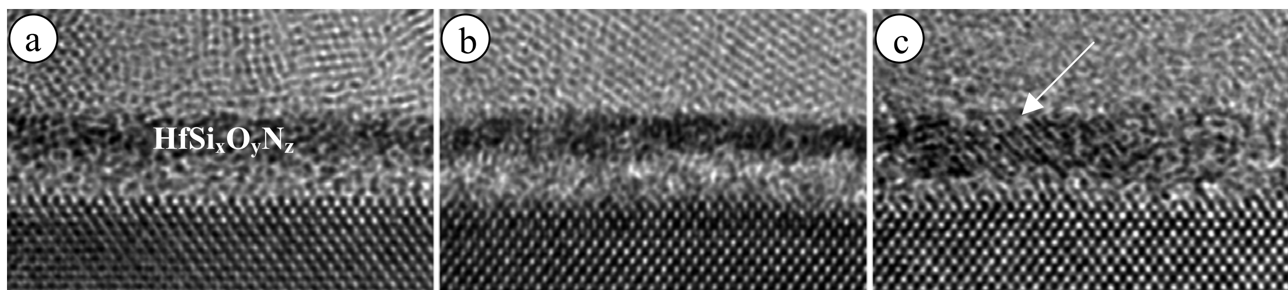

FIG. 4. Cross-sectional HREM images of the poly-Si capped $HfSi_xO_yN_z$ thin films with higher Hf content, compared with Fig. 3, on Si(100): (a) as-deposited, (b) 1 sec, and (c) 60 sec RTA at 1050ºC. $HfSi_xO_yN_z$ films are thermally stable after a “spike” anneal at 1050ºC for 1 sec, but crystallization was observed after 60 sec. Z.A.=Si[110].

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